Mechanisms of Nd(III) and Eu(III) Uptake by Cementitious Materials

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Publication Date:
2008

Permanent Link:
https://doi.org/10.3929/ethz-a-005807807

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Mechanisms of Nd(III) and Eu(III) uptake by cementitious materials

A dissertation submitted to the
Swiss Federal Institute of Technology Zürich

for the degree of
Doctor of Natural Sciences

presented by

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Zürich, 2008
TABLE OF CONTENTS

ABSTRACT .................................................................................................................. 1
ZUSAMMENFASSUNG .................................................................................................. 2

CHAPTER 1: Introduction
1. Introduction ............................................................................................................. 5
2. The chemistry of cement ....................................................................................... 8
3. The use of cement in waste management ............................................................ 9
4. Materials and methods ........................................................................................ 11
   4.1 The rietveld method ....................................................................................... 11
   4.2 X-ray absorption spectroscopy (XAS) .......................................................... 12
   4.3 Time resolved laser fluorescence spectroscopy (TRLFS) .............................. 14
5. Outline of the thesis ............................................................................................. 17

References ................................................................................................................. 21

CHAPTER 2: Structure of the hydrogen bonds and tetrahedral defects in the “dreierdoppelkette” of xonotlite
Abstract ..................................................................................................................... 27
1. Introduction .......................................................................................................... 28
2. Materials and methods ......................................................................................... 31
   2.1 Theoretical calculations .................................................................................. 31
   2.2 Materials and analytical methods ................................................................... 33
      2.2.1 Sample preparation ................................................................................. 33
      2.2.2 SEM/EDS analysis .................................................................................. 34
      2.2.3 Infrared spectroscopy ............................................................................. 34
      2.2.4 Thermogravimetric analysis (TG/DTA) .................................................. 34
      2.2.5 XRD analysis .......................................................................................... 35
3. Results .................................................................................................................... 35
   3.1 Ideal xonotlite structure ................................................................................. 35
   3.2 Calculations ..................................................................................................... 37
CHAPTER 3: Mechanism of Nd(III) uptake by 11 Å tobermorite and xonotlite

Abstract .................................................................................................................. 61

1. Introduction ........................................................................................................... 62
2. Materials and methods ....................................................................................... 66
   2.1 Materials ........................................................................................................... 66
   2.2 Nd sorption experiments .................................................................................. 67
   2.3 Re-crystallization experiments with $^{45}$Ca .................................................... 67
   2.4 Scanning electron microscopy (SEM) ............................................................. 68
   2.5 Sample preparation for EXAFS and X-ray diffraction measurements .......... 68
   2.6 EXAFS data collection and reduction ......................................................... 70
   2.7 X-ray diffraction measurements and Rietveld analysis ............................... 72
3. Results .................................................................................................................. 74
   3.1 Nd sorption isotherms .................................................................................... 74
   3.2 $^{45}$Ca recrystallization experiments ............................................................. 75
   3.3 SEM/EDS analysis .......................................................................................... 77
   3.4 EXAFS investigations ..................................................................................... 78
      3.4.1 EXAFS on Nd reference compounds ....................................................... 78
      3.4.2 EXAFS on Nd doped 11 Å tobermorite .................................................. 81
      3.4.3 EXAFS on Nd doped xonotlite ................................................................. 84
   3.5 Wavelet analysis of the EXAFS spectra ......................................................... 87

Supporting Information to Chapter 2 ..................................................................... 56
3.6 X-ray powder diffraction analysis of Nd doped 11 Å tobermorite and xonotlite...

3.6.1 Rietveld refinement of Nd doped 11 Å tobermorite...
3.6.2 Rietveld refinement of Nd doped xonotlite...

4. Discussion

4.1 Nd incorporation in the structure of 11 Å tobermorite...
4.2 Nd incorporation in the structure of xonotlite...
4.3 Charge compensation mechanism in 11 Å tobermorite and xonotlite...
4.4 Influence of Nd loadings on the Nd incorporation...
4.5 Influence of reaction time on the Nd incorporation...

5. Conclusions

6. References

Supporting Information to Chapter 3, Part A...
Supporting Information to Chapter 3, Part B...

CHAPTER 4: EXAFS study of Nd (III) uptake by amorphous calcium silicate hydrates (C-S-H)

Abstract...

1. Introduction...

2. Materials and methods...

2.1 Synthesis of calcium silicate hydrates (C-S-H)...
2.2 Preparation of the EXAFS samples...
2.3 EXAFS data collection and reduction...
2.4 Wavelet analysis...
2.5 Bond valence analysis...

3. Results and discussion...

3.1 EXAFS of Nd doped C-S-H...
3.2 Wavelet analysis of the EXAFS spectra...
3.3 Uptake mechanisms of Nd in C-S-H...

4. Summary...

5. References...
CHAPTER 5: Macro- and micro-spectroscopic study of Nd (III) uptake mechanisms in hardened cement paste

Abstract ........................................................................................................................................ 147
1. Introduction ......................................................................................................................... 148
2. Materials and methods ..................................................................................................... 150
   2.1 Cement sample preparation .......................................................................................... 150
   2.2 Scanning electron microscopic (SEM) investigations ................................................. 151
   2.3 μ-XRF, μ-XAS and bulk-XAS data collection and reduction ....................................... 152
3. Results and discussion ....................................................................................................... 154
   3.1 Distribution of Nd in the cement matrix ................................................................. 154
   3.2 Speciation of Nd on the micro-scale ......................................................................... 157
   3.3 Speciation of Nd on the macro-scale ......................................................................... 160
4. A mechanistic interpretation of the Nd immobilization in HCP ............................................ 162
5. Implication for radioactive waste management ................................................................. 165
6. References ........................................................................................................................ 167

CHAPTER 6: A TRLFS and EXAFS study on the Eu(III) uptake by 11 Å tobermorite

Abstract ......................................................................................................................................... 171
1. Introduction ......................................................................................................................... 172
2. Materials and methods ..................................................................................................... 174
   2.1 Sample preparation ........................................................................................................ 174
   2.2 TRLFS measurements ................................................................................................. 175
   2.3 EXAFS data collection and reduction ........................................................................... 176
3. Results and discussion ....................................................................................................... 177
   3.1 TRLFS measurements at high Eu(III) loadings ......................................................... 177
   3.2 TRLFS measurements at low Eu(III) loadings ......................................................... 181
   3.3 EXAFS measurements ................................................................................................. 183
4. A mechanistic interpretation of Eu(III) immobilization in 11 Å tobermorite ....................... 186
5. Conclusions ........................................................................................................................ 187
CHAPTER 7: A TRLFS and EXAFS study on the Eu(III) uptake by xonotlite

Abstract........................................................................................................... 193

1. Introduction.................................................................................................. 194

2. Materials and methods............................................................................... 197
   2.1 Sample preparation............................................................................... 197
   2.2 TRLFS measurements......................................................................... 198
   2.3 EXAFS data collection and reduction.................................................. 199

3. Results and discussion............................................................................... 200
   3.1 TRLFS measurements at high Eu(III) loadings................................. 200
   3.2 TRLFS measurements at low Eu(III) loadings................................... 204

4. EXAFS measurements............................................................................. 206

5. Structural model for Eu(III) retention by xonotlite.................................... 208

6. Conclusion.................................................................................................. 212

7. References.................................................................................................. 213

SUMMARY....................................................................................................... 217

OUTLOOK....................................................................................................... 225

ACKNOWLEDGMENTS.................................................................................. 229

CURRICULUM VITAE...................................................................................... 233
ABSTRACT

Cement is an important component of the multi-barrier system in repositories for low-level and intermediate level radioactive waste. The waste loading potential of cementitious materials is well established but their long-term ability to retard the release of radionuclides from waste repositories and the chemical mechanisms governing radionuclide immobilization are poorly understood at the molecular level. This knowledge, however, is essential for detailed long-term predictions of the environmental impact of cement-stabilized waste forms.

The present doctoral study aims at developing mechanistic models of the retention mechanism of lanthanides, in particular Nd(III) and Eu(III), in cementitious materials using synchrotron- and laser-light-based spectroscopic and laboratory-based X-ray diffraction techniques in combination with wet chemistry experiments. Macro- and micro-scale investigations on Nd(III) and Eu(III) doped crystalline and amorphous calcium silicate hydrates (C-S-H) provide fundamental information on uptake mechanisms at the atomic/molecular level. This information was used for the development of the retention model. Spectroscopic studies on Nd(III) doped cementitious matrices were performed to discern the coordination environment of these elements in cement matrices.

In the first phase of the doctoral study a mechanistic model was developed for two Nd(III) doped crystalline C-S-H phases, 11 Å tobermorite (Ca$_5$Si$_6$O$_{16}$(OH)$_2$·7H$_2$O) and xonotlite (Ca$_6$Si$_6$O$_{17}$(OH)$_2$). In the second phase the model was tested on Nd(III) doped amorphous C-S-H phases with calcium-to-silica molar ratios varying between 0.56 and 1.54 and in complex cement systems. In the last phase, studies on Eu(III) doped crystalline C-S-H phases were carried out to test whether or not the model developed for Nd(III) can be used to interpret the Eu(III) retention by cementitious materials at very low metal loadings. Trivalent lanthanides e.g., Nd(III) and Eu(III), were regarded as suitable chemical analogues for trivalent actinides based on their comparable ionic radii and similarities in the complexation behaviour. The proposed model could therefore be applied for interpreting the immobilization of trivalent actinides in cement-stabilized radioactive waste.
ZUSAMMENFASSUNG


In der ersten Phase der Dissertationsarbeit wurde ein mechanistisches Einbaumodel von Nd(III) in die beiden kristallinen C-S-H Phasen 11 Å Tobermorite (Ca₅Si₆O₁₆(OH)₂7H₂O) and Xonotlite (Ca₆Si₆O₁₇(OH)₂) entwickelt. Dieses Einbaumodel wurde in der zweiten Phase auf dessen Anwendung an amorphen C-S-H Phasen mit variablen, molaren Kalzium/Silizium Verhältnissen und hydratisiertem Zement getestet. In der letzten Phase wurden Untersuchungen an Eu(III)-dotierten, kristallinen C-S-H Phasen durchgeführt, um das Nd(III)-basierte Einbaumodel an Eu(III) bei sehr tiefen Metallbeladungen zu testen. Dreiwertige Lanthaniden wurden wegen Ähnlichkeiten in den Ioneneradien und im Komplexierungsverhalten als chemischen Analoge zu den dreiwertigen Aktiniden betrachtet. Dies erlaubt es uns, das mechanistische Einbaumodel, basierend auf den Untersuchungen mit Nd(III) und Eu(III), für die Interpretation der Rückhalteprozesse von dreiwertigen Aktiniden an Zement anzuwenden.
CHAPTER 1

Introduction

1. Introduction

The safe disposal of radioactive wastes in deep geological repositories is one of the challenging tasks in view of endorsing the sustainable development of modern civilizations. Although new technologies focusing on waste minimization will undoubtedly reduce waste arising in the future, strategies ensuring the safe disposal of intractable wastes are needed. The potential impact of radionuclides released from a deep geological repository can be controlled and reduced by a suitable choice of the engineered and geological barriers. Cement-based materials play an important role in multi-barrier concepts developed worldwide for the disposal of radioactive wastes.

Hardened cement paste (HCP) is a very heterogeneous material with discrete particles typically in the size range of about 2-200 micrometers. It consists of ~50 w.% calcium (aluminium) silicate hydrates (C-(A)-S-H: (CaO)x(SiO2)y(H2O)z), ~20 w.% portlandite, Ca(OH)2, and ~18 w.% calcium aluminates. HCP contains ~9 w.% minor phases (e.g., hydrotalcite, hydrogarnet, ferrite etc.). Among the different cement phases, C-S-H phases are considered to be the most important constituent of HCP with regards to their abundance and the diversity of structural sites exposed for cation and anion binding (Atkins and Glasser, 1992; Chen et al., 2004). Furthermore, C-S-H phases may control the long-term release of radionuclides due to their stability during the evolution of the cementitious near field.

In conjunction with the safe disposal of radioactive waste, the retention of radionuclides by the complex cement matrix and cement minerals, in particular C-S-H and calcium aluminates, has been studied in the past by combining wet chemical methods with synchrotron- and laser-light-based spectroscopic techniques e.g. Harfouche et al., 2006; Pointeau et al., 2001; Schlegel et al., 2004; Tits et al., 2003; Vespa et al., 2006a+b; Vespa et al., 2007. The laser-light-based spectroscopic studies showed that C-S-H could
play an important role in the immobilisation of lanthanides and trivalent actinides by cementitious materials (Stumpf et al., 2004). Nevertheless, the chemical mechanisms responsible for the immobilization of these elements by C-S-H phases and cementitious materials are still poorly understood.

The present study aims at filling this existing gap in our knowledge. For the present study wet chemistry experiments, X-ray absorption spectroscopy (XAS), time-resolved laser fluorescence spectroscopy (TRLFS) and laboratory- and synchrotron-based X-ray diffraction (XRD) in combination with Rietveld refinement were used to gain micro-scale information on the local chemical speciation and coordination environment of Nd and Nd taken up by crystalline and amorphous C-S-H phases and the complex cement matrix. The results obtained from the different experimental and theoretical approaches provide the basic information for the development of a mechanistic model of lanthanide retention by C-S-H phases and the complex cement matrix. These results were compared with sorption values for $^{152}$Eu on amorphous C-S-H phases reported earlier (Tits et al., 2003).

Wet chemistry studies were carried out in the first phase of the experimental work using crystalline C-S-H phases. These investigations include isotopic exchange experiments with $^{45}$Ca and Nd sorption experiments. The aim of these experiments was to determine the crystallization rate of the solid phases, as well as to measure the distribution of Nd between the solid and liquid phases.

XRD in combination with Rietveld analysis was used for solid phase characterization of Nd free and Nd doped crystalline C-S-H phases. This approach is suitable if sufficiently high Nd loadings on the solid phases can be achieved (>5 wt.%). Rietveld analysis allows detailed crystal information from the XRD data to be extracted. It does require models for the atomic coordinates of all phases present in the sample, which can be adopted from the literature or deduced theoretically (ab initio MD simulations; s. Chapter 2) or experimentally (XAS spectroscopy). The results from the XRD studies provide a first set of fundamental data for the development of the mechanistic uptake model.

The synchrotron-based spectroscopic investigations in the present work include the use of XAS on Nd and Eu(III) doped powder materials (bulk-XAS) and micro-scale
investigations on Nd doped solidified cementitious materials (micro-XRF/XAS). XAS was used for the determination of the local structure (i.e. within < 6 Å distance from the central atom) of elements sorbed onto or bound in the solid phases. Analysis of extended X-ray absorption fine structure (EXAFS) spectroscopy data yields molecular crystal-chemical information on the element of interest, such as the type of neighboring atoms, the co-ordination number and bond distances. Complementary bulk-XAS experiments were necessary to assess the information obtained on the micro-scale with respect to relevance for the bulk samples. Bulk-XAS measurements were carried out on Nd and Eu(III) doped cement minerals, in particular crystalline and amorphous C-S-H phases, and Nd doped HCP. The results from the bulk-XAS studies on the Nd doped cementitious materials were the second source of essential structural information (besides the X-ray diffraction data) used for the model development. The bulk-XAS studies were performed on suitable beam lines, such as BM26A (energy range 5 - 30 keV) at the ESRF, Grenoble, the XAS beam line (energy range 2.4 - 25 keV) at ANKA, Karlsruhe, in case of the Nd and Eu(III) samples. All the beam lines are highly tunable X-ray sources and are well equipped for measurements of dilute samples.

Spatially resolved micro-scale information on the spatial distribution, speciation, and phase association of Nd in the complex cement matrices was obtained by the synergistic use of micro-XAS and micro X-ray fluorescence (micro-XRF) (Scheidegger et al., 2006b; Vespa et al., 2006b). Micro-XRF maps are extremely useful for the identification of local hot spots/solid phases enriched in Nd and allow correlations between Nd and cement derived-element (e.g. Ca, Si etc.) to be established. Micro-XRF/XAS studies were carried out on thin sections prepared from Nd doped HCP. Micro-XRF/XAS measurements were collected on the microXAS beamline at the Swiss Light Source (SLS), Switzerland, and on beamline 10.3.2 at the Advanced Light Source (ALS), Berkeley, USA (Marcus et al., 2004). The synchrotron-based micro-spectroscopic investigations were complemented by microscopic characterization of the samples using scanning electron microscopy (SEM) with energy dispersive micro-analysis (EDS) and backscattered electron imaging (BSE). The latter techniques are suitable tools for a detailed characterization of the microstructure of Nd doped HCP. The results obtained from the micro-spectroscopic and microscopic studies enable us to assess whether or not
the proposed uptake model can be used for the interpretation of Nd binding mechanisms in the complex cement matrix.

TRLFS is the laser-light-based technique used in the present study. Pulsed laser light was employed for the excitation of fluorescing metal cations, such as Eu(III). TRLFS could not be applied to Nd because of their low fluorescing properties. The intensity and position of the emission peaks are good indicators of changes in the coordination sphere of the Eu(III) species. The emission lifetime yields information on the ligand exchange dynamics and the number of H₂O molecules bound in the first coordination sphere of Eu(III), thus allowing outer-sphere and inner-sphere surface complexes and Eu(III) species incorporated into crystal lattice of C-S-H phases to be distinguished from each other. The method is very sensitive and allows speciation studies to be conducted in very dilute systems (e.g. 0.4 μmol Eu / g solid phase) in contrast to EXAFS studies for which higher metal loadings are required. The resulting information on the nature of the Eu(III) species bound to crystalline C-S-H phases enables us to further assess the applicability of the proposed model for the interpretation of lanthanide uptake by cementitious materials. TRLFS studies were performed at the Institut für Nukleare Entsorgung (INE) at the Karlsruhe Institute of Technology (KTI), Germany.

2. The chemistry of cement

Portland cement is composed mainly of four types of minerals: alite (C₃S), belite (C₂S), aluminate (C₃A) and a ferrite phase (C₄AF) (Taylor, 1997). Also present are small amounts of clinker sulfates (sulfates of sodium, potassium and calcium) and also gypsum. The process by which cement reacts with water (termed “hydration”) to produce a range of hydration products, involves many different reactions, often occurring at the same time (Taylor, 1997).

Almost immediately after adding water to unhydrated cement, some of the clinker phases and gypsum dissolve, producing an alkaline, sulfate-rich solution. The C₃A phase, which is the most reactive of the clinker minerals, reacts with water to form an aluminium-rich gel. The gel reacts with sulfate in solution to form crystals of ettringite as shown elsewhere (Merlini et al., 2008). The alite and belite in the cement start to hydrate, giving rise to the formation of calcium silicate hydrate (C-S-H) and calcium hydroxide.
The C-S-H produced is the principal binding phase in Portland cements and is quantitatively the most significant hydration product (~50 wt.%).

**C-S-H phases.** C-S-H phases in cement are mostly amorphous. Several models have been proposed over the past years with the aim of explaining the structural properties of C-S-H phases (Grutzeck et al., 1999; Jennings, 2000; Nonat, 2004; Richardson, 2004; Taylor, 1986; Thomas et al., 2004). The structure of poorly ordered amorphous C-S-H phases can be envisaged as an imperfect tobermorite structure with many irregularities (Brunet et al., 2004; Nonat, 2004) or as tobermorite structure intermixed with jennite-like structural elements (Taylor, 1986). The structure of the minerals of the tobermorite group has been discussed in detail elsewhere (Bonaccorsi et al., 2005; Merlino et al., 1999; Merlino et al., 2001).

**Calcium hydroxide.** \( \text{Ca(OH)}_2 \) (or CH in cement chemist notation) is formed mainly from alite hydration. CH is crystalline, isostructural with the natural mineral portlandite (Zhao-Qi and Francis, 1984).

**Ettringite.** Ettringite \((\text{Ca}_6[\text{Al(OH)}_6]_2(\text{SO}_4)_3\cdot26\text{H}_2\text{O})\) is present as rod-like crystals in the early stages of cement hydration. The structural properties of ettringite were discussed in details by McConnell and Joseph (1962). Common to ettringite-type (A(\( \text{I'} \))t) phases is the formation of columnar type structure consisting of \((\text{Al,Fe})(\text{OH})_6\) octahedra alternating with groups of edge sharing \(\text{CaO}_8\) polyhedra. Inter-column regions contain loosely bound \(\text{SO}_4^{2-}\).

Monosulfate \((\text{Ca}_4[\text{Al(OH)}_6]_2(\text{SO}_4)_3\cdot6\text{H}_2\text{O})\) and monocarbonate \((\text{Ca}_4[\text{Al(OH)}_6]_2(\text{CO}_3)_3\cdot6\text{H}_2\text{O})\) occur in the later stages of cement hydration. Monosulfates gradually replace ettringite because the ratio of available alumina to sulfate increases with ongoing cement hydration. On mixing cement with water, most of the sulfate is readily available to dissolve, but much of the C\(_3\)A is contained inside cement grains with no initial access to water. Continued hydration gradually releases alumina and the proportion of ettringite decreases while that of monosulfate increases.

3. **The use of cement in radioactive waste management**

Cementitious materials are used as a containment matrix for nuclear waste immobilization, as well as for engineered structures of nuclear waste storage and disposal.
facilities (Chapman and McCombie, 2003). In Switzerland, for example, it is foreseen to dispose of cement-stabilized radioactive wastes arising from electricity production in nuclear power plants as well as medicine, industry and research (MIF wastes in Swiss terminology) in a deep geological repository. About 90 wt.% of the near-field material of the planned deep geological repository for low level waste (ILW) and long-lived intermediate-level (ILW) radioactive waste in Switzerland thus consists of cement and cementitious backfill materials. Cement will be used for waste conditioning and to construct the engineered barrier system (components of lining, backfill material). Wastes will be immobilized in cement within a steel container (Figure 1). The use of cement-based backfill constitutes an important barrier, which is designed to ensure that the groundwater will retain in the present alkaline condition (high pH) over long time scales. This is because the solubility of a great number of radionuclides, which are safety-relevant for long-term assessment of the safe disposal of radioactive waste, is very low under alkaline conditions.

**Figure 1**  Schematic representation of the multi-barrier containment of LLW and ILW
a) solidification in steel container; b) Emplacement in concrete containers; c) Near-field including container and backfill; d) Disposal site in deep geological formation.
4. Materials and methods

Crystalline and amorphous C-S-H phases with various C/S ratios were used in the present doctoral study as the prime host phases. The crystalline C-S-H phases tobermorite (Ca$_{4.5}$Si$_6$O$_{16}$(OH)$_{2.5}$H$_2$O) and xonotlite (Ca$_6$Si$_6$O$_{17}$(OH)$_2$) and amorphous C-S-H phases with C/S ratio typically in the range between 0.56 and 1.54 were prepared using standard procedures published in earlier studies (Cong and Kirkpatrick, 1996; Tits et al., 2003; Tits et al., 2006). The samples were characterized using chemical analysis, quantitative XRD, scanning electron microscopy coupled with microanalysis (SEM-EDX), thermogravimetric and differential thermo-analysis (TG/DTA).

A sulphate-resisting cement (Type CEM I, Lafarge, France), denoted as HTS (Haute Teneur en Silice) Portland cement, was used for the preparation of the cement samples in this study. The composition and the hydration process have been discussed in details elsewhere (Lothenbach and Wieland, 2006). The same type of cement is presently used for the conditioning of low- and intermediate-level and long-lived intermediate-level wastes in Switzerland. Both, crushed material prepared from HCP and compact cement cylinders prepared from HTS cement were treated with Nd at selected reaction conditions (initial radionuclide concentrations, different stages of cement degradation) and used for the different types of studies. Furthermore, thin sections were prepared for microspectroscopic investigations from this material.

4.1 The Rietveld Method

The Rietveld method is a tool for extracting detailed crystal structural information from X-ray (and neutron) powder diffraction data. The method originates from the refinement of crystal structures using neutron powder diffraction data (Rietveld, 1969). The Rietveld method fits point-to-point the difference between experimental intensities of the whole X-ray pattern and the calculated intensities based on a certain model of the crystalline structure, instrumental factors and characteristics of the sample. The Rietveld refinement minimizes the sum of the weighted, squared differences between observed and calculated intensities at every 20 step in a powder pattern:
\[ R = \sum_i w_i \left| y_i(\theta) - y_i(c) \right|^2 \]  

where \( y_i(\theta) \) and \( y_i(c) \) are the observed and the calculated intensities at point \( i \), and \( w_i \) is the weight assigned to each intensity. The calculated intensities at each point, \( y_i(c) \), are determined by summing up the contributions from the background and all Bragg reflections:

\[ y_i(c) = S \sum_j (p_k L_k |F_k| G(\Delta \theta_k) P_k) + y_{ib}(c) \]

where
- \( S \): the phase specific scale factor
- \( p_k \): the multiplicity factor
- \( L_k \): the Lorentz and polarization factor for the \( k \)th reflection
- \( F_k \): the structure factor for an individual reflection
- \( G(\Delta \theta_k) \): a reflection profile function
- \( \theta_{hk} \): the Bragg angle for the \( k \)th reflection
- \( P_k \): the preferred orientation function
- \( y_{ib}(c) \): the background contribution

The Rietveld method was successfully applied in this study to perform quantitative phase analysis and to extract detailed structural information, including the dimension of the unit cell, the content of the unit cell (e.g. atomic positions and occupancies), information about the crystallite sizes and strain in the structure. Detailed descriptions of the Rietveld method are given elsewhere (McCusker et al., 1999; Young, 1993).

4.2 X-ray absorption spectroscopy (XAS)

XAS spectra are produced typically over the range of 0.2 – 35 keV. The necessity to vary the photon energy implies the use of synchrotron radiation in XAS experiments. If the photon energy of the X-rays is gradually increased such that it traverses one of the absorption edges of the elements contained within the sample (e.g. Nd L\(_{\text{III}}\) edge ~ 6.208 keV; Eu L\(_{\text{III}}\) edge ~6.977 keV), a core electron is emitted by photoelectric processes and a large increase in absorption occurs. Below the absorption edge, the photons cannot excite the electrons of the relevant atomic level and thus absorption is low. Above the absorption edge the resulting photoelectrons have a low kinetic energy and can be
backscattered by the atoms surrounding the absorber atom (Fig. 2). This leads to an interference phenomenon, which depends on the distance between emitting and scattering atoms, and their atomic numbers. Constructive interference increase, while destructive interference decreases the absorption coefficient of the atom. The net result is a series of oscillations on the high photon energy side of the absorption edge. These oscillations can be used to determine the atomic number, distance and coordination number of the atoms surrounding the element whose absorption edge is being examined.

XAS can be divided into two regions: the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions. The first contains the fine structure from the absorption edge to about 50eV above the edge energy. XANES is mainly used to extract information on the oxidation state, based on the edge position, and for “fingerprinting” by comparing experimental spectra with those of reference compounds (Scheidegger et al., 2006a). The second region contains the fine structure from 50eV to about 1000 eV above the edge energy.

EXAFS spectroscopy provides structural information about a sample by way of the analysis of its X-ray absorption spectrum (Koningsberger and Prins, 1988). It allows the chemical environment of a single element to be determined in terms of the number and type of its neighbors, inter-atomic distances and structural disorders. EXAFS is a technique selective for a particular element and suitable to determine the short-range order (<6 Å).

Figure 2 Schematic representation of X-ray scattering in the EXAFS range. The photoelectron propagation from the absorber atom is represented by the solid circles. The scattering of the photoelectron by neighboring atom(s) is indicated by the dashed lines.
The EXAFS signal, \( \chi_i(k) \), for a photoelectron, which scatters from a single atom at distance \( r_i \), is given by:

\[
\chi_i(k) = \frac{N_i S_i^2 F_i(k)}{kr_i^2} e^{-\frac{kr_i}{\lambda}} \sin(2kr_i + \delta_i(k))
\]

with
- \( k \): the photoelectron wave vector
- \( N_i \): number of atoms in the \( i^{th} \) shell
- \( r_i \): the mean distance between the absorber and the \( i^{th} \) shell
- \( F_i(k) \): the magnitude of the backscattering amplitude of the \( j^{th} \) neighbor atom
- \( \delta_i(k) \): the phase shift due to the atomic potentials
- \( \lambda \): mean free path of the photoelectron
- \( \sigma_i^2 \): relative mean square displacement between the atoms pairs which define the path length \( r_i \)
- \( S_i^2 \): the amplitude reduction factor in coordination shell \( i \)

Fourier transformation (FT) of \( \chi(k) \) yields a spectrum in real space. This has the advantage that peaks in real space correspond to individual coordination shells, i.e. the real part of the FT gives a radial structure function (RSF). A more detailed description of the X-ray absorption theory is given by Koningsberger and Prins (1988).

**4.3 Time Resolved Laser Fluorescence Spectroscopy (TRLFS)**

Fluorescence is the emission of light that occurs after the absorption of light. The emission is a very fast process and occurs typically within nanoseconds (Figure 3). Molecules that are used in fluorescence spectroscopy due to their fluorescent properties are called fluorophores. When a fluorophore in its so-called “ground state” absorb photons, the absorbed energy moves an electron into a higher-energy orbital (“excited state”). The excited molecule uses several different pathways to return to the ground state, which are associated with a loss of the absorbed energy.

The photo-physical processes that occur from absorption to emission are often shown in a Jabłoński diagram (Figure 3).
Figure 3 Jabłoński diagram displaying the energy states of a molecule. Molecules not absorbing energy are mainly confined to the lowest vibrational states of the ground state $S_0$. The paths and the time intervals of the various steps in fluorescence excitation and emission and phosphorescence are given by arrows.

The Jabłoński diagram in Figure 3 shows the singlet states, in which nonbonding electrons exist as pairs with opposite spins and triplet states, where the nonbonding electrons exist in two separate orbitals with the electron spins parallel to each other. $S_0$ is the ground state and represents the energy of a molecule that is not being excited by light. $S_1$ and $S_2$ are excited singlet states. The energy of the $S_2$ state is higher than that of $S_1$ and the $S_1$ state has more energy than the ground state, $S_0$.

When an electron absorbs sufficient energy, it can be transmitted to a higher-energy orbital (“excited state”). Excited states are typically short-lived and the molecule returns to electronic states of lower energy by losing their excess energy. This energy loss may involve radiationless transitions (internal conversion, vibrational relaxation, or intersystem crossing) or radiative transitions (fluorescence and phosphorescence).

“Internal conversion” is a transition between electron orbital states (such as $S_2$ to $S_1$). In vibrational relaxation, the vibrational energy in the fluorophore is transferred to nearby molecules via direct interactions. Internal conversion and vibrational relaxation,
which take place within picoseconds, could bring the molecule to lower energy level $S_1$. Intersystem crossing is associated with a transition from the singlet state to the triplet state.

The excitation spectrum of a fluorophore can be determined by measuring the fluorescence yield at various wavelengths (measurements collected at small wavelength increment) and recording the produced fluorescence. The profile of the excitation spectrum reflects the energy levels in the molecule's Jablonski diagram.

The energy path back to the ground state is the release of a photon, with an energy, which covers the gap between the lowest vibrational state of $S_1$ and one of the vibrational or rotational states of $S_0$ (Figure 3). The emission spectrum of a fluorophore reflects the range of wavelengths that this emitted photon can have. This emission spectrum can be determined by exciting the fluorophore at different wavelengths and measuring the fluorescence spectrum.

The fluorescence lifetime, $\tau$, is determined by observing the decay in fluorescence intensity (decay profile) of a fluorophore after excitation. Immediately after a molecule is excited the fluorescence intensity will be at a maximum and then decrease exponentially:

$$N(t) = N_0 e^{-t/\tau}$$  \hspace{1cm} (4)

In this equation $N(t)$ is the number of molecules in the “exited state” after excitation at time $t$; $N_0$ is the number of molecules in the “exited state” immediately before the exiting process, at time 0; and $\tau$ is the lifetime of the "exited state". The fluorescence lifetime of a molecule is very sensitive to its molecular environment. Measurements of the fluorescence lifetime(s) provide information about the hydration state of the fluorophore and the kinetics of the relaxation process.

In TRLFS the fluorescence of a sample is monitored as a function of time after excitation by a laser light. More detailed description of the fluorescence spectroscopy theory can be found elsewhere (Lakowicz, 1999). The instrumentation is described in detail in Chapter 6.
5. **Outline of the thesis**

The Ph. D. thesis is composed of seven chapters, which are in different stages of the publication process.

**CHAPTER 2:**

*Structure of the hydrogen bonds and tetrahedral defects in the “dreierdoppelkette” of xonotlite*


This publication illustrates the use of a combined experimental/theoretical approach to investigate the structure and stability of the silicate “dreierdoppelkette” in xonotlite. The results show that defects in $Q^3$ sites are more abundant compared to $Q^2$ tetrahedra. The defect sites provide potential sites for the incorporation of metal cations in the xonotlite structure. The results obtained enable us to discuss the structure of silicate chains in tobermorite and amorphous C-S-H phases.

**CHAPTER 3:**

*Nd uptake mechanisms by 11 Å tobermorite and xonotlite (2009).*


In this chapter, the uptake of Nd by the crystalline C-S-H phases 11 Å tobermorite and xonotlite has been investigated by the combined use of wet chemistry techniques, scanning electron microscopy (SEM), extended X-ray absorption fine structure (EXAFS) spectroscopy and X-ray diffraction (XRD) in combination with Rietveld refinement. The X-ray diffraction data from the study show that Nd(III) can substitute for Ca(II) in the Ca sheets of 11 Å tobermorite and xonotlite, and in the interlayer of 11 Å tobermorite. The EXAFS data further reveal that the structural environment of Nd taken up by 11 Å tobermorite and xonotlite is dependent on equilibration time and Nd loading. The results
from this study suggest that long-term predictions of the immobilization of trivalent lanthanides and actinides by C-S-H phases should take into account uptake processes in the interlayer space and the Ca sheets.

CHAPTER 4:

_EXAFS study of Nd (III) uptake by amorphous calcium silicate hydrates (C-S-H)_
submitted to Journal of Colloid and Interface Science

This chapter presents the results of a study on Nd binding to amorphous calcium silicate hydrate (C-S-H) phases by using extended X-ray absorption fine structure (EXAFS) spectroscopy. The C-S-H phases used in the study had different calcium-to-silica ratio and had been aged up to 270 days. The EXAFS data show that, in the long term, amorphous C-S-H phases are capable of taking up Nd via exchange processes with Ca$^{2+}$ in the Ca sheets and the interlayer of the C-S-H structure. This finding is in line with conclusions drawn from the earlier study on Nd binding mechanisms to 11 Å tobermorite and xonotlite. Furthermore, the finding is essential for a detailed understanding of binding mechanisms of trivalent actinides in amorphous C-S-H phases due to chemical similarity of the latter elements with trivalent lanthanides.

CHAPTER 5:

_Macro- and micro-spectroscopic study of Nd(III) uptake mechanisms in hardened cement paste_
submitted to Environmental Science & Technology

The Nd uptake by hardened cement paste (HCP) has been investigated with aim of developing a mechanistic understanding of the immobilization processes of trivalent lanthanides in HCP on the molecular level. Information on the microstructure of HCP, the
Nd distribution in the cement matrix and the coordination environment of Nd in these matrices was gained from the combined use of scanning electron microscopy (SEM), synchrotron-based μ-X-ray fluorescence (μ-XRF), μ-X-ray (μ-XAS) and bulk-X-ray absorption spectroscopy (bulk-XAS) on Nd doped cement samples. Nd is predominantly bound to amorphous “inner”-C-S-H phases in the cement matrix. The Nd binding mechanisms proposed in this study support the option of long-term safe disposal of trivalent actinides in cement-based repositories for radioactive waste.

CHAPTER 6:

A TRLFS and EXAFS study on Eu(III) uptake by 11 Å tobermorite
submitted to Environmental Science & Technology

The results from Time-Resolved Laser Fluorescence Spectroscopy (TRLFS) and Extended X-ray Absorption Spectroscopy (EXAFS) studies on the Eu(III) uptake by 11 Å tobermorite are discussed. The results show that binding into the structure of 11 Å tobermorite is the dominant mode of Eu(III) immobilization. The latter finding, in combination with the results of previous studies on Nd uptake by crystalline and amorphous C-S-H phases and cement carried out at higher metal loadings, confirms that lanthanides can be incorporated into the structure of C-S-H phases in the long term.

CHAPTER 7:

A TRLFS and EXAFS study on Eu(III) uptake by xonotlite
submitted to Radiochimica Acta

This presents the results of TRLFS and EXAFS investigations on Eu(III) uptake by xonotlite. The results show that incorporation into the Ca layers of xonotlite is the dominant mode of Eu(III) immobilization after prolonged reaction time. Similar to 11
Å tobermorite, after short reaction time (≤ 1 day) Eu(III) forms several species on xonotlite. The results from the study shows that Eu(III) incorporation is facilitated with decreasing Eu(III) loading and increasing the reaction time. The complementary information obtained from TRLFS and EXAFS allowed developing of a chemical mechanistic model of the Eu retention by C-S-H.
6. References


CHAPTER 2

Structure of the hydrogen bonds and tetrahedral defects in the “dreierdoppelkette” of xonotlite

ABSTRACT

We use the combined experimental/theoretical approach to investigate the structure and stability of the silicate “dreierdoppelkette” in xonotlite. The M2a2bc polytype of xonotlite was found to be dominant in the synthetic samples. This polytype was used to predict the relative stability of different defects in the “dreierdoppelkette” of xonotlite. The defects in Q$^3$ sites were found to be substantially more abundant compared to Q$^2$ tetrahedra. Moreover, the paired substitutions in the silicate double chain at neighbouring Q$^3$ sites are energetically more stable than isolated Q$^3$ defects. The defects in the silicate chains of xonotlite offer structural channels accessible for diffusion of ions and water. The defect sites are potential candidates for incorporation of foreign ions in the xonotlite structure. The results obtained enable us to discuss the structure of silicate chains in tobermorite and C-S-H phases.
1. Introduction

Among various hydrous calcium silicate hydrates (C-S-H), xonotlite, \( \text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2 \), is formed as a by-product of the hardening Portland cement paste. Because of the high thermal stability, special xonotlite rich cements find an application as low density insulating materials (Kalousek et al., 1977). The basic structural element of the xonotlite is the layer of Ca-polyhedra made of three different Ca sites (Hejny and Armbruster, 2001). Two of them are seven-coordinated by oxygen while the third one is a distorted octahedron. The silicate tetrahedra form a double chain with \( 2/m \) symmetry, which is formed by condensation of two wollastonite chains (Figure 1A). The Si tetrahedra can be attached to the Ca layer in two structurally equivalent ways. This results in a number of xonotlite polytypes characterized by different relative arrangement of the silicate double chain in neighbouring Ca layers. The nomenclature of the xonotlite polytypes and their diffraction pattern have been discussed in a previous study (Hejny and Armbruster, 2001).

Despite the industrial importance and intensive experimental studies many aspects of xonotlite crystal chemistry are not fully resolved. According to the theoretical stoichiometry the calcium-to-silicon ratio (C/S) in xonotlite is equal to unity. The ideal xonotlite structure should contain only \( Q^2 \) and \( Q^3 \) type of the Si tetrahedral sites, where \( Q^2/Q^3=2 \) (in the \( Q^n \) notation “\( n \)” represents the number of bridging oxygen sites per tetrahedron \( Q \)) and only one type of OH groups attached to the Ca layer similar to the portlandite structure. High resolution MAS NMR \(^{29}\text{Si}\) and \(^1\text{H}\) spectra of xonotlite (Hansen et al., 2003; Noma et al., 1998) revealed a minor presence of the \( Q^1 \) tetrahedra. \(^1\text{H}\) MAS NMR spectra of both natural and synthetic samples indicate presence of three different types of proton environments, which can be attributed to Ca-OH, Si-OH linkage and molecular water. The spectral line assigned to Si-OH linkage is more pronounced in synthetic samples and seems to correlate with the amount of \( Q^1 \) tetrahedra (Cong and Kirkpatrick, 1996b). Another study (Cong and Kirkpatrick, 1996a) further revealed presence of \( Q^1 \) sites but absence of Si-OH linkage. The terminal \( Q^1 \) tetrahedra provide direct evidence for structural defects in \( Q^2 \) or \( Q^3 \) sites. The experimental spectra do not allow for unambiguous discrimination of defects between \( Q^2 \) or \( Q^3 \) tetrahedra. It is also not clear by which mechanism the local charge balance due to missing Si tetrahedra is
satisfied. Infrared and Raman spectra of natural xonotlite have a strong narrow band at 3620 cm\(^{-1}\) accompanied by a broad band in 3200-3500 cm\(^{-1}\) range, which is attributed to OH stretching. The commonly observed peak at 1640 cm\(^{-1}\) is characteristic for bending in molecular water (Garbev, 2004). Differential thermo-scanning calorimetry and thermo-gravimetric analysis show the main weight loss at 1040 K and 1150 K (Shaw et al., 2000) attributed to OH groups and dehydration of xonotlite into low-T-wollastonite. Minor weight loss observed at 350-370 K is presumably due to loss of molecular water.

![Fragment of the ideal xonotlite structure](image)

**Figure 1** Fragment of the ideal xonotlite structure (A). Gray octahedral polyhedral are Ca atoms. Silicate tetrahedra are purple. The oxygen atoms are shown as small red spheres. The oxygen sites of O(10)H groups are shown as big purple spheres. Possible tetrahedral defects “doppeldreierkette” of xonotlite are shown as white hatched polyhedra. Isolated Q\(^3\)(B) and Q\(^3\)(C) sites; coupled Q\(^2\)Q\(^3\)(D) and Q\(^2\)Q\(^3\)(E) defects.
The difficulties encountered in the experimental investigations of xonotlite can be overcome using the methods of computational chemistry which enable to simulate behaviour of the systems on the atomic scale. Such methods have been successfully applied to various problems of cement research including the mechanism of the water incorporation in the C-S-H phases (Kirkpatrick et al., 2005), isomorphous substitutions of the aluminium in the silicate chain (Faucon et al., 1997), sorption of water and cations on the surface of cement phases (Bell and Coveney, 1997; Coveney and Humphries, 1996; Kalinichev and Kirkpatrick, 2002; Kalinichev et al., 2007). The molecular modelling tools can be generally subdivided in two groups: the empirical force field methods and the ab initio quantum mechanic calculations which both have their weak and strong sides. In the ab initio methods the inter-atomic interaction are obtained solving electronic Schrödinger equation. Although the quantum mechanical calculations are formally exact and do not require any experimental information on the system, several numerical approximation are used to improve the computational efficiency and can, therefore, have an effect on accuracy of the results (Payne et al., 1992). Thus, the quality of the numerical scheme should be tested against known experimental data. In the empirical force field methods the inter-atomic interactions are described by model interaction potentials (usually coulomb and van der Waals forces or harmonic functions for strongly covalent bonds) fitted to reproduce some known experimental data or quantum mechanical results. Therefore, the structural information on the system of interest or a similar one should be available in advance. In contrast to computationally expensive ab initio methods that are limited to systems of relatively small size, the empirical force field methods benefit from computational simplicity that open up the possibility to simulate systems made by up to $10^6$ atoms for several micro seconds. Unfortunately the simple force field parameters are not capable to reproduce the bond breaking events which include electron transfer or unusual atomistic configurations like defects. In such area the quantum mechanical calculations have an inestimable advantage over the other methods.

In this work we use a coupled experimental–theoretical approach to shed light upon the unresolved problems of the xonotlite crystallography. Ab initio calculations based on the density functional theory were used to identify the structural positions of the OH groups, the mechanisms of defect formation in the double chain of the silicate
tetrahedra and possible incorporation of trace amounts of water in the structure of xonotlite. The theoretical calculations are compared with the results from X-ray diffraction technique (XRD) coupled with Rietveld quantitative phase analysis, scanning electron microscopy (SEM) with energy dispersive micro-analysis (EDS), infrared spectroscopy (IR) and thermogravimetric analysis on synthetic samples of xonotlite. Further, NMR data from the literature are used to discuss the structure of silicate chains in xonotlite.

2. Materials and methods

2.1 Theoretical calculations

All calculations in this work were performed using the density functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) implemented in the CPMD (Cpmd) simulation package. The exchange and correlation were taken into account by the generalized gradient approximation BLYP (Becke, 1988; Lee et al., 1988). Interaction of the valence electrons with the core states was described by the pseudopotential formalism. We used fully separable norm conserving pseudopotentials generated using the Troullier-Martin scheme (Troullier and Martin, 1991). Because of significant overlap of the valence charge density with the core states of the Ca atom, the 3s and 3p states were included in the valence. The wavefunctions of valence electrons were expanded into the plane wave basis set up to 70 Ry cut-off energy. The accuracy and transferability of the pseudopotentials as well as the convergence of the plane waves basis set expansion were tested against structure of the simple oxides and hydroxides of Ca and Si as well as their molecules in gas phase. The calculated lattice parameters of the solid phases agree with the experimental values within 1.0-1.5 %. The bond distances were reproduced within 1 %. The similar set of pseudopotentials for Si, O and H was already used in earlier simulations (Churakov et al., 2004). The ab initio Car-Parrinello molecular dynamics (MD) simulations in NVE ensemble (Car and Parrinello, 1985) were performed, with a time step of 0.12 fs and a fictitious electron mass of 700 au. In all calculations the supercell contained 2×2×2 unit cells of M2a2bc xonotlite polytype. The geometry of the supercell was fixed at the experimentally determined lattice parameters.
A single k=0 point in the origin of the Brillouin zone was used in the MD simulations and the geometry optimization. The hydrogen atoms were substituted with deuterium in order to take advantage of the longer integration time step for the equations of motion. Because of the minor influence of the isotopic substitution on the structural properties of solids the deuterium is referred as hydrogen in the discussion, unless the dynamic properties are of hydrogen bonds are addressed.

The IR absorption spectrum, $a(\omega)n(\omega)$, of xonotlite was calculated by the Fourier transform of the time correlation function $\langle M(t) \cdot M(0) \rangle$, of the total (ionic and electronic) dipole moment of the system according to (Silvestrelli et al., 1997):

$$a(\omega)n(\omega) = \frac{4\pi \omega \tanh(\beta \omega / 2)}{3hcV} \times \int_{-\infty}^{\infty} \langle M(t) \cdot M(0) \rangle e^{-i\omega t} dt,$$  \hspace{1cm} (1)

where $a(\omega)$ is the absorption coefficient, $n(\omega)$ the refractive index, $V$ the volume, $\beta = (k_B T)^{-1}$, $T$ the temperature, $k_B$ the Boltzmann constant, and $c$ the speed of light. In order to model the full spectrum from the Eq. (1) an infinitely long trajectory must be integrated. In practice, the simulations have a finite length that limits the accessible frequency range. The electronic contribution is calculated in the CPMD program using Berry phase scheme (Silvestrelli et al., 1997) and the spectrum was obtained using the maximum entropy method (Press et al., 1992). For characterisation of the IR-bands, we performed a finite difference vibration analyses and calculate the phonon density of state from the dynamics of individual atoms using Fourier transform of the velocity autocorrelation function. Due to the limited simulation time, only the high frequency part of spectra (above 1500 cm$^{-1}$) was analysed.

For a comparison of the calculated IR bands of deuterium substituted xonotlite with the experimental data, the frequency scale of the calculated spectra must be corrected for the isotope effect and influence of the fictitious electron dynamics on the high frequency vibrations (Blöchl and Parrinello, 1992).
In a harmonic approximation, the frequency shift due to substitution of hydrogen by deuterium can be expressed by Eq. (2):

\[ v_H = \frac{M_D}{M_H} v_D \approx 1.4 v_D , \]  

(2)

where \( v_H, M_H \) and \( v_D, M_D \) are frequencies and masses of hydrogen and deuterium, respectively. The correction factor (1.05) due to fictitious electron dynamics was obtained as the ratio of the frequencies calculated from the finite difference analysis of optimized structure of xonotlite at zero Kelvin and the vibrational modes obtained in MD simulations.

The structures of the defects in the double chain of Si tetrahedra were predicted by stepwise simulated annealing. The dangling oxygen sites in defects were terminated with OH groups to establish charge neutrality. To obtain optimal orientation of the OH groups short MD-simulation runs (~1ps) were performed at 400 K. Then the system was annealed to 300 K and equilibrated for ~ 1 ps. The far-IR spectra of xonotlite were derived from subsequent 1 ps trajectories using dipole dynamics technique. Such a short simulation time does not provide valuable record of the rearrangement dynamics of hydrogen bonds. Therefore, only vibrational dynamics of individual OH groups will be discussed, which is adiabatically decoupled from the other dynamical degree of freedom in the system. Once again the systems were annealed to 200 K and equilibrated for ~ 1 ps. Finally, the systems were cooled down to 0 K and refined using standard geometry optimization methods. The energies of optimized structures were calculated with k-point sampling on 16×16×16 Monkhorst-Pack mesh (Monkhorst and Pack, 1976) using the perturbation theory approach (Iannuzzi and Parrinello, 2001). The test calculations indicate that the uncertainties due to k-point mesh are below 0.1 kJ/mol. The energy differences are converged with respect to plane wave basis set within 3 kJ/mol.

2.2 Materials and analytical methods

2.2.1 Sample preparation

The sample of xonotlite was synthesized by mixing stoichiometric quantities of SiO\(_2\) and CaO powder materials (Ca/Si = 1.0) with 220 ml argon-purged Milli-Q water
(Kalousek et al., 1977). Milli-Q water generated by a Millipore water purification system was used for the preparation of the solutions (Millipore, USA). To prevent CO\textsubscript{2} contamination in the samples, all experiments and handling of the materials were carried out in a glovebox with controlled N\textsubscript{2} atmosphere (CO\textsubscript{2}, O\textsubscript{2} <2ppm, T = 290 K ±3 K). The suspension was placed in 250 ml Teflon Parr bombs and heated in a oven at 490 K for 30 days. The white paste obtained, was dried over saturated CaCl\textsubscript{2} solution in a closed container in the glovebox.

2.2.2 SEM/EDS analysis

Scanning electron microscopy (SEM) analysis was conducted at the Laboratory for Material Behaviour (LWV), Paul Scherrer Institut (PSI), using a Zeiss DSM 962 microscope, operated at an accelerating voltage of 20 kV. The microscope is equipped with a Si(Li)-detector for energy dispersive micro-analysis (EDS). The spot size was \( \sim 1\times1\ \mu\text{m}^2 \), and the penetration depth was \( \sim 6\ \mu\text{m} \) at the used incident beam energy.

2.2.3 Infrared spectroscopy

IR spectra were recorded at the Electrochemistry Laboratory (ECL), Paul Scherrer Institut (PSI), using a Perkin–Elmer System 2000 spectrophotometer. The measurements were conducted in the range 370 cm\textsuperscript{-1} – 5000 cm\textsuperscript{-1} at room temperature using KBr pellets, which were prepared by mixing appropriate amounts of KBr and xonotlite, dried at 520 K for 6 hours.

2.2.4 Thermogravimetric analysis (TG/DTA)

Thermogravimetric analysis (TG/DTA) was carried out at the Solar Technology Laboratory, Paul Scherrer Institut (PSI), on a Netzsch STA 409 oven Typ 6.225.6-83 in the range between 300 K and 1350 K. The measurements were conducted in open Al\textsubscript{2}O\textsubscript{3} vessels under a argon gas-flow (100ml/min) at a heating rate of 20 K/min using about 20 mg of powder material.
2.2.5 XRD analysis

The XRD measurements were performed at the Swiss Federal Laboratories for Materials Testing and Research (Empa, Dübendorf). The diffraction pattern used to identify the different xonotlite polytypes present in the synthetic sample was collected using a Philips Xpert diffractometer operating in Bragg–Brentano geometry (θ/2θ) and using an XCelerator detector module at a nominal pressure. The following conditions were employed: Power 40 kV, 40 mA, copper Kα1,2-radiation (ratio Kα1/ Kα2 0.50), divergence slit 0.25°, primary scatter slit 0.76 mm, receiving scatter slit 0.25°, two soller slits, flat-plate sample (round sample holder), specimen: 22 mm (radius) x 2 mm (thickness), particle size < 63 μm. The scans were taken between 2θ of 5.00° and 2θ of 80° at increments of 2θ 0.017°. The counting time was 60 seconds for each step. The crystal structure parameters of xonotlite polymorphs and their relative content in the synthetic products were obtained based on Rietveld refinement technique (see Appendix for details).

3. Results

3.1 Ideal xonotlite structure

The hydrothermal synthesis under the given conditions resulted in white fibrous crystals of xonotlite (Figure 2). The crystals had diameters from 50 nm to 200 nm and they are 2-8 μm in length. The results of SEM/EDS indicate that the best crystallized samples consisted of 17.8 % (±0.1) Ca and 17.5% (±0.1%) Si, which corresponds to a C/S ratio of nearly 1.0. For purely crystallized samples the C/S ratio can vary between 1.0 and 1.15. The XRD powder pattern did not indicate the presence of any other phases such as portlandite, calcite or 11.3 Å tobermorite (Figure 3). The absence of 11 Å tobermorite indicates the complete phase transition of 11 Å tobermorite to xonotlite. Nevertheless, the high background contribution is an indication for the presence of a small amount of amorphous material. The portion was estimated to be less than 3 %.
The excess of Ca can not be explained by the presence of additional phases, and therefore should be attributed to the crystal chemistry of xonotlite.

The refined lattice parameters and the relative contribution of the different xonotlite polytypes obtained by QPA using Rietveld refinement are given in Table 1. All four xonotlite polytypes were observed. The M2a2bc polytype is the dominant phase under the given reaction conditions. The results of the synthesis were different from the natural samples in which the M2a2b2c polytype is abundant. The difference is likely due to variation in the crystal growth conditions.

Table 1  Lattice parameter of xonotlite polytypes derived from the synthetic reaction product compared with published data for natural xonotlite samples.

<table>
<thead>
<tr>
<th>Cell parameters</th>
<th>Synthetic sample (this work)</th>
<th>Natural sample (Kalousek et al., 1977)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M2a2bc</td>
<td>Ma2bc</td>
</tr>
<tr>
<td>a [Å]</td>
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<td>8.70</td>
</tr>
<tr>
<td>b [Å]</td>
<td>7.367</td>
<td>7.35</td>
</tr>
<tr>
<td>c [Å]</td>
<td>7.033</td>
<td>13.99</td>
</tr>
<tr>
<td>α</td>
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<tr>
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<td>102.27</td>
</tr>
<tr>
<td>Space group</td>
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<td>P 2/a</td>
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<tr>
<td>Single polytypes fraction [%]</td>
<td>34.66</td>
<td>15.61</td>
</tr>
</tbody>
</table>
3.2 Calculations

The positions of atoms in the xonotlite structure were calculated as an average over ab initio MD trajectory on M2a2bc polytype which was found to be dominant in the synthetic samples. The results of the calculations and the experimental data are summarized in Table 2. The calculations are in agreement with the experimental data within 0.01 of the fractional coordinates.
3.3 Crystallographic position of hydrogen atoms and the structure of hydrogen bonds

Based on extended bond-valence sum calculations the protons in the structure of xonotlite were assigned to the O10 oxygen sites (Brown, 2002; Brown and Altermatt, 1985). The exact position of protons and the geometry of the hydrogen bonds have not been determined by analytical techniques. The positions of hydrogen atoms (the calculations were performed using mass of deuterium, see section 2.1 for details) averaged over molecular dynamic trajectory are given in Table 2.

Table 2  Average atomic position in xonotlite obtained by ab initio simulations and experimental XRD data (Hejny and Armbruster, 2001). D stands for deuterium.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Calculated (this work)</th>
<th>Hejny &amp; Armbruster (2001)</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>y</td>
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<tr>
<td>Ca1</td>
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<td>Ca2</td>
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</tr>
<tr>
<td>Ca3</td>
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</tr>
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<td>Ca4</td>
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<td>Si1</td>
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<td>0.22</td>
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<td>0.00</td>
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<td>O5</td>
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<td>O6</td>
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<td>0.75</td>
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<tr>
<td>O7</td>
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<td>O8</td>
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</tr>
<tr>
<td>O10</td>
<td>0.30</td>
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<tr>
<td>D</td>
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<td>0.45</td>
</tr>
</tbody>
</table>
The hydrogen-oxygen pair distribution function is shown in Figure 4 up to 3.5 Å. As expected the protons are bonded to the O10 sites and form hydrogen bond to the O2 sites. The O10-H and H…O2 contacts are 0.984 and 2.217 Å, respectively. The average interatomic distances indicate that only O2 site should have measurable influence on the vibrational dynamics of the O10H bond. The distances to O5 and O6 sites are, on average, too long to have any measurable effect on the O10H vibrations. This is consistent with a single sharp absorption line in the IR and Raman spectra generally reported for xonotlite (Garbev, 2004). The calculated IR spectrum (Eq. 1) was compared with the experimental measurements in Figure 5B. After correction for the isotopic shift, see Eq. (2), and the fictitious electronic dynamics (see section 2.1 for details) the calculated IR spectrum is consistent with the experimental data, as further discussed in the section 4.2.

3.4 Structure of defects in silicate double chain of xonotlite

The Ca/Si ratio of idealized xonotlite is exactly equal to 1.0. The natural and the synthetic samples differ from the ideal Ca/Si ratio (Kalousek et al., 1977). Increasing deviations from the ideal Ca/Si ratio indicates an increasing degree of disorder in the
xonotlite samples. The deficiency of Si in xonotlite can be explained by defects in the chain of Si tetrahedra. The structure of such defects and the mechanism of the charge balancing are still under debates. Presence of M\(^{3+}\) or M\(^{4+}\) cations in our samples, which could take the structural position of the Si atoms in the double chain, can be excluded by EDS analysis. It is also unlikely that Ca\(^{2+}\) atoms occupy Si\(^{4+}\) positions in an isolated tetrahedral site. Therefore, we assumed in the calculations that the charge compensation was fulfilled by the hydrogarnet substitution mechanism expressed in terms of the Kröger-Vink notation for point defects (Kröger, 1974) by:

\[
\{\text{Si}\}^-_{\text{Si}} + 2\text{H}_2\text{O} = \{\text{H}_4\}^-_{\text{Si}} + \text{SiO}_2
\]  

(3)

This assumption is consistent with the presence of the second type of OH groups commonly observed in NMR studies (Noma et al., 1998) and additional broad OH stretching band in IR spectra of xonotlite (Figure 5A). Ab initio crystal structure optimizations enabled us to predict the distribution of protons in the tetrahedral sites and the relative energies of defects formation. Although the composition of the defect was constrained by Eq. (3) the ab initio method allowed for bond breaking and bond forming, and in contrast to the empirical simulations, does not require a priori knowledge of the OH connectivity. The structural arrangement of protons in the defect was determined by the requirement of the global energy minimum.

At the upper limit of stability of C-S-H phases (500 K) the ratio was equal to 4.0×10\(^{-3}\). The volumetric and entropic contributions to the Gibbs free energy of defects formation were neglected in Eq. (4).

The silicate double chain is built by two “paired” Q\(^2\) tetrahedra (Si1, Si3) and one Q\(^3\) site (Si2) (Cong and Kirkpatrick, 1996b). Although the two different Q\(^2\) sites are present, the geometry of the Si1 and Si3 tetrahedra is very similar. The accuracy of the calculation was not sufficient to discriminate the energy difference between the defects in the Si1 and Si3 sites. Therefore, we arbitrary have chosen a Si3 tetrahedra to be representative for both Si1 and Si3 positions in Q\(^2\) site. Thus, two principally different isolated defects, \(\{\text{H}_4\}^+_{Q^2}\) and \(\{\text{H}_4\}^-_{Q^2}\) are possible as schematically shown in Figure 1B and Figure 1C, respectively.
Figure 5 Measured (A) and calculated IR absorption spectra of the ideal (B) and defected (C) deuterium-xonotlite structure. The upper axis in the calculated spectra shows the frequency scale corrected for the isotopic substitution of the hydrogen and the friction due to the fictitious dynamics of electrons (see text for details). The insert in Figure 5B shows the fragment of measured IR spectra in the range of frequencies corresponding to ab initio simulations.
According to the calculations, the static energy of the defect in \( \{H_4\}^{\times}_{Q^3} \) site was lower by 25.79 kJ/mol than in the \( \{H_4\}^{\times}_{Q^2} \) site. The \( \{H_4\}^{\times}_{Q^3} \) defects should therefore significantly prevail over \( \{H_4\}^{\times}_{Q^2} \) ones:

\[
\frac{\{H_4\}^{\times}_{Q^3}}{\{H_4\}^{\times}_{Q^2}} = \frac{N_{Q^3}}{N_{Q^2}} e^{-\frac{\Delta E}{RT}} = 2e^{-\frac{\Delta E}{RT}},
\]

where \( N_{Q^3} \) and \( N_{Q^2} \) are the total amount of \( Q^3 \) and \( Q^2 \) sites, \( T \) is the temperature, \( R \) is the gas constant and \( \Delta E \) is the energy difference between structures with \( \{H_4\}^{\times}_{Q^3} \) and \( \{H_4\}^{\times}_{Q^2} \) defects.

At room temperature (300 K), the ratio \( \frac{\{H_4\}^{\times}_{Q^3}}{\{H_4\}^{\times}_{Q^2}} \) is negligibly small (6.4x10^-5).

It should be noted that the thermal contribution to the free energy difference was small, i.e. order of 1 kJ/mol. The volumetric contribution is unknown but usually negligible at atmospheric pressure.

**Figure 6** Optimized structures of the defects in the tetrahedral silicate chain of xonotlite: \( \{H_4\}^{\times}_{Q^3}, (A), \{H_4\}^{\times}_{Q^2}, (B), \{H_8\}^{\times}_{Q^2, Q^3}, (C), \{H_8\}^{\times}_{Q^2, Q^3}, (D) \). See Figure 1 for the colour legend.

42
Figure 7  Hydrogen oxygen pair distribution function for the isolated defects in $Q^2$ and $Q^3$ sites.

Table 3  Structure of the hydrogen bonds in the tetrahedral defects of xonotlite.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>${H_4}_{Q^3}$</td>
<td></td>
<td></td>
<td></td>
<td>${H_8}_{Q^2,Q^3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O9H..O1</td>
<td>0.986</td>
<td>1.768</td>
<td>169.8</td>
<td>O9H..O1</td>
<td>0.986</td>
<td>1.768</td>
<td>169.8</td>
</tr>
<tr>
<td>O5H..O1</td>
<td>1.001</td>
<td>1.800</td>
<td>156.0</td>
<td>O6H..O1H2</td>
<td>0.994</td>
<td>1.910</td>
<td>154.1</td>
</tr>
<tr>
<td>O6H..O5</td>
<td>1.006</td>
<td>1.651</td>
<td>169.5</td>
<td>O3H..O1H4</td>
<td>0.982</td>
<td>1.861</td>
<td>165.0</td>
</tr>
<tr>
<td>O1H..O3</td>
<td>1.050</td>
<td>1.560</td>
<td>170.9</td>
<td>O9H..O1H2</td>
<td>0.982</td>
<td>1.861</td>
<td>165.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H'O1H''</td>
<td>110.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>${H_4}_{Q^2}$</td>
<td></td>
<td></td>
<td></td>
<td>${H_8}_{Q^2,Q^3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O4H..O8</td>
<td>1.018</td>
<td>1.703</td>
<td>162.9</td>
<td>O2H..O6</td>
<td>1.029</td>
<td>1.613</td>
<td>155.2</td>
</tr>
<tr>
<td>O4H..O5</td>
<td>1.014</td>
<td>1.702</td>
<td>151.8</td>
<td>O6H..O1</td>
<td>0.985</td>
<td>2.457</td>
<td>155.0</td>
</tr>
<tr>
<td>O8H..O5</td>
<td>0.990</td>
<td>2.051</td>
<td>159.9</td>
<td>O3H..O2</td>
<td>1.001</td>
<td>2.051</td>
<td>144.0</td>
</tr>
<tr>
<td>O2H..O5</td>
<td>1.008</td>
<td>1.612</td>
<td>162.9</td>
<td>O3H..O7</td>
<td>1.029</td>
<td>1.648</td>
<td>171.1</td>
</tr>
<tr>
<td>H'O4H''</td>
<td>96.7</td>
<td></td>
<td></td>
<td>H'O3H</td>
<td>98.4</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O5H..O6</td>
<td>1.021</td>
<td>1.685</td>
<td>172.9</td>
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<td>O9H..O1</td>
<td>0.990</td>
<td>1.724</td>
<td>172.2</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>O1H..O4</td>
<td>1.033</td>
<td>1.616</td>
<td>172.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O7H..O6</td>
<td>1.018</td>
<td>1.623</td>
<td>174.0</td>
</tr>
</tbody>
</table>
The structural arrangement of OH groups and hydrogen bonds in \{H_q\}_{Q'} and \{H_q\}_{Q''} defects is shown in Figure 6A and Figure 6B, respectively. The OH groups are shown as sticks terminated by small bright spheres. The parameters of hydrogen bonds are summarized in Table 3. The OH-pair distribution functions are presented in Figure 7.

In the energetically favourable \{H_q\}_{Q'}, defects the protons were found to be attached to the oxygen sites of the defect tetrahedra. Two chains of hydrogen bonds \(=O6H\ldots O5H\ldots O1H\ldots O3=\) and \(O9H\ldots O1\) were formed. The protonated O9 sites become structurally similar to \(\equiv Ca_3 – OH\) groups in portlandite. The other OH groups formed \(\equiv Si – OH\) linkage on the Q\(^1\) sites. The hydrogen bonds in the defects were significantly shorter than the common O10H…O bonds in xonotlite. We can therefore expect that the vibrational frequencies of the OH in the Si defects should be shifted.

In Figure 5C the calculated IR spectrum of xonotlite with defects in \{H_q\}_{Q'} tetrahedra is shown. The vibrational density of states of OD dipoles is given in Figure 8. The high frequency peak at (~2450 cm\(^{-1}\)) can be assigned to the O10D…O2 bond.

![Figure 8](image_url)  
**Figure 8**  
Vibrational density of states of the OH groups in \(Q^2\) and \(Q^4\) defects.
Several broad maxima at lower frequencies can be assigned to the O10D...O2 vibrations in defects based on the vibrational density of states shown in Figure 8. In $\{H_4\}_{Q}\}$ defects (Table 3) O5 sites remained de-protonated and acted as a strong hydrogen bond acceptor (O4H...O5, O2H...O5, O8H...O5). The O4 sites became doubly protonated and the configuration resembled that of a water molecule strongly sorbed on the Ca layer.

Considering the geometry of $\{H_4\}_{Q}\}$ defects as initial step for subsequent dissolution of the tetrahedral chain we calculated the static energy of coupled defects in the neighbouring silica tetrahedra. Two defect geometries were possible: a coupled substitution in adjacent $Q^3$ sites $\{H_4\}_{Q',Q}\}$ (Figure 1D) and that in neighbouring $Q^2$-$Q^3$ pair $\{H_4\}_{Q',Q}\}$ (Figure 1E). Optimal arrangement of OH groups and hydrogen bonds in $\{H_4\}_{Q',Q}\}$ and $\{H_4\}_{Q',Q}\}$ defects are shown in Figure 6D and Figure 6E, respectively. The parameters of hydrogen bonds are summarized in Table 3. The energy of the $\{H_4\}_{Q',Q}\}$ defect was found to be 40.06 kJ/mol lower than that of the $\{H_4\}_{Q',Q}\}$ substitution. The energy of the double defect $\{H_4\}_{Q',Q}\}$ was lower by 4.79 kJ/mol compared to two independent $\{H_4\}_{Q}\}$ substitutions (Table 4).

Because the $Q^2$ defects were very few it was reasonable to assume, for simplicity of the discussion, that defects were formed exclusively in the $Q^3$ sites. Such assumption should hold up to very high concentration of defects until almost all available $Q^3$ sites have been consumed. Although the obtained energy difference was close to the accuracy of calculations, the relative abundance of $\{H_4\}_{Q}\}$ and $\{H_4\}_{Q',Q}\}$, could still be calculated from the reaction:

\[
2 \{H_4\}_{Q}\} \{\text{Si}\}_{Q}\} = \{\text{Si}_2\}_{Q'}\} + \{H_4\}_{Q',Q}\}, \quad (5)
\]

\[
\frac{[\{\text{Si}_2\}_{Q'}\}][\{H_4\}_{Q',Q}\}]}{[\{H_4\}_{Q}\} \{\text{Si}\}_{Q}\}^2} = \exp\left[\frac{-\Delta E}{RT}\right], \quad (6)
\]
where \( \{\text{Si}_2\}^{x}_{Q^3,Q^3} \) is the concentration of undisturbed \( Q^3 \) pairs, \( \{H_4\}^{x}_{Q^3,Q^3} \) is the coupled defect in neighbouring \( Q^3 \) sites and \( \{H_4\}^{x}, \{\text{Si}_2\}^{x}_{Q^3} \) is the \( Q^3 \) pair with a single substitution.

Eq. (6) neglects the volume change upon defect formation. The volume contribution to the relative stability of defects in Eq. (5) is expected to shift equilibria to the right site, so that \( \Delta E \geq \Delta E + P \Delta V = \Delta H \).

**Figure 9** The equilibrium distribution of doubly substituted \( Q^3 \) sites \( \{H_8\}^{x}_{Q^3,Q^3} \), isolated defects \( \{H_4\}^{x}_{Q^3,Q^3} \), and undisturbed tetrahedral pairs \( \{\text{Si}_2\}^{x}_{Q^3,Q^3} \), as function of total concentration of \( Q^3 \) substitutions for 300, 400 and 500 K (solid lines). The dotted line shows ideal solution behaviour (\( \Delta E = 0 \) in Eq. (11)).
Table 4  The relative total energy ($E_{\text{Total}}$) of defect formation in the “dreierdoppelkette” of xonotlite for isolated and coupled defects. The defect formation in $Q^3$ sites is energetically favourable compared to $Q^2$ tetrahedra. Coupled substitution in the neighbouring sites is favourable compared to the two independent substitutions on $Q^3$ tetrahedra. To illustrate the accuracy of calculations, the single gamma point and k-point sampling contributions to the total energy are given as $E_\Gamma$ and $E_{\text{Pert}}$ respectively.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{Total}}$ [kJ mol$^{-1}$]</th>
<th>$E_\Gamma$ [kJ mol$^{-1}$]</th>
<th>$E_{\text{Pert}}$ [kJ mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E \left[ (H_4)_Q, (H_4)_Q \right]$</td>
<td>25.79</td>
<td>25.77</td>
<td>0.02</td>
</tr>
<tr>
<td>$\Delta E \left[ (H_8)_Q, (H_8)_Q \right]$</td>
<td>40.06</td>
<td>40.09</td>
<td>-0.03</td>
</tr>
<tr>
<td>$\Delta E \left[ 2(H_4)_Q, (H_8)_Q \right]$</td>
<td>4.97</td>
<td>4.84</td>
<td>0.13</td>
</tr>
</tbody>
</table>

The equilibrium distribution of coupled and isolated defects calculated with Eq. (6) is shown in Figure 9 as a function of the total fraction of $Q^3$ substitutions. The diagram clearly illustrates that due to small difference in the formation energy the double defect substitution became more abundant compared to isolated $Q^3$.

3.5 TG/DTA and IR measurements

The IR spectrum of the best crystallized sample of xonotlite is shown in Figure 5A. In the range of OH stretching frequencies, the spectrum revealed a sharp absorption peak at 3611 cm$^{-1}$ and a broad absorption band at ~3430 cm$^{-1}$. The pronounced absorption peak at 1640 cm$^{-1}$ corresponded to the bending frequency of molecular water. A number of overlapping bands in the range 500-1500 cm$^{-1}$ were attributed to the coupled stretching and bending of Si tetrahedra and Ca octahedra.

Main weight lost during TG/DTA measurements was observed at 1040-1150 K. At this temperature the OH hydrogens were released and the xonotlite transformed to low temperature wollastonite.
The small weight loss of about 0.8 wt % during TG/DTA measurements observed at 350-370 K can be also assigned to the loss of molecular water (Figure 10). Unexpectedly, the IR band of molecular water and TG/DTA loss at 370 K did not disappear completely after drying the samples at 520 K for several days.

Based on this, for the first glance contradictory observation, we argue that the larger portion of detected water should be classified as surface absorbed and rather then structurally incorporated. The drying of the probe at 520 K guarantees the release of molecular water from the samples. It is therefore most probably that the dried samples immediately absorb water from the air on the surface during sample preparation for IR and TG/DTA measurements. The kinetics of the water incorporation, on the other hand is slow enough to get the crystalline water during the time of TG/DTA and IR measurements. The C-S-H phases are known to have strongly hydrophilic surface characteristic (Nakshatra B. Singh et al., 2002; Thomas et al., 2004). Thus we may rule out significant presence of the structurally incorporated water in dried samples. The study
of Noma et al. (1998) suggest, that vacuum drying and additional measurement, presumably under vacuum, may allow water sorption on the surface of synthetic xonotlite to be excluded.

4. Discussion

4.1 Nature and formation of tetrahedral defects in xonotlite

Although the theoretical xonotlite structure contains only $Q^3$ and $Q^2$ tetrahedra, significant amount of $Q^1$ sites were detected using NMR, indicating the presence of tetrahedral defects in disordered samples. Our calculations suggest that such defects are formed almost exclusively in the $Q^3$ sites. Additionally, the coupled defects in $Q^3$ are dominant down to rather low total concentration of $Q^3$ defects (Figure 9). These results further support the two stage mechanism of xonotlite formation earlier proposed by Moorehead and Mccartney (1965) and later confirmed by Shaw et al. (2000), using in situ XRD technique. According to this concept, the crystalline phase domains with good periodicity parallel to the $ab$ plane and less ordered in the (001) direction are initially formed. In this step the reaction products are similar to C-S-H gel. In the second step, ordering on the structure in $c$-direction leads to the formation of xonotlite crystals. The ordering stage is likely to reflect inclusion of the missing silicate tetrahedra into the silicate chains.

Based on the defect formation energy, we can argue that in the first stage of xonotlite growth, the two dimensional domains of Ca layers contain only short chains of $Q^2$ silicate tetrahedra with numerous defects at $Q^3$ sites. Absence of $Q^1$ sites in the structure offer channels in the direction of $b$ axis (Figure 6C), which could facilitate the diffusive supply of silica and release water molecules in the proto-crystals of xonotlite. Figure 6C, for example, illustrates incorporation of water molecule in the coupled defects in $Q^3$ pair. In the second stage of xonotlite growth the defects in $Q^3$ sites of the tetrahedral chain are subsequently repaired while the relative concentration of the single and coupled defects is evolved according to the diagram in Figure 9. We believe that the degree of structural order and deviation from the ideal Ca/Si ratio in xonotlite could be directly related to the amount of defects in $Q^3$ tetrahedra.
According to the conditions of synthesis the system does not contain other cations than Ca and Si. Therefore, we assume that charge compensation in the defects is fulfilled through the incorporation of OH groups. In natural systems and industrial poly-phase cements the chemistry is more diverse and other cations can play a charge compensating role. The defects sites are therefore the primary candidates for incorporation of foreign ions into the xonotlite structure.

Similar to xonotlite, 11 Å tobermorite also contains bridging Q³ and “paired” Q² sites. On a speculative manner we can use the results obtained for xonotlite to discuss the structure of tetrahedral chains in tobermorite and C-S-H phases. We suggest that short silica chains, which consist of mainly “paired” Q² silica tetrahedra, are initially formed in C-S-H phases. The increase of the Si content in cement phases corresponds to “repairing” missing Q³-like sites, which give rise to extension of the silica chain. Indeed, a number of experimentally based models for C-S-H phases (Richardson, 1999, 2004; Taylor, 1986) assume omission of bridging tetrahedra and subsequent polymerisation of the silica chain. Depending on the Ca/Si ration the Ca ions play a charge compensating role bridging isolated Q² pairs. All these concepts are well in agreement with preferential stability of defects in Q³ sites of xonotlite chain observed in this work. It should be noted, however, that other factors like Al content for example play an important role in the formation of C-S-H phases and tobermorite (Sun et al., 2006). Further studies are necessary to reveal the relative importance of charge compensation mechanisms, the isomorphic substitutions and polymerisation of the silicate chain on the structure of C-S-H phases.

4.2 Interpretation of the IR spectra

Idealized xonotlite only contains hydrogen in the form of O10-H…O2 groups. The natural and synthetic samples indicate presence of at least two types of OH groups (Noma et al., 1998) and traces of molecular water. The IR spectral of the synthetic xonotlite contains a broad absorption band in the 3200-3500 cm⁻¹ range (Figure 5A). This band is most probably produced by stretching of the different OH groups forming strong hydrogen bonds in defects of the silicate double chain, the water molecules at the surface and possibly some traces of structurally incorporated molecular water. As described in the section 3.4, we were not able to produce the samples without surface absorbed water.
Therefore, an unambiguous identification of absorption bands, caused by the structurally incorporated OH groups in the measured spectra (apart from O10-H band) was not possible. The theoretical calculations also have limitations, which make the comparison of the experimental and the simulated IR spectra difficult. Unlike the measurements the calculated spectrum does not contain contributions from any kind of surface absorbed water, which allows identification of the OH bands in defects. Due to the small size of the simulated cell, however, the concentration of defects in the simulation is much higher than in the synthetic samples, which explains the high intensity of the defect associated OH vibrations compared to O10H band (Figure 5C). Additionally, the defects cause significant broadening of O10H band. One may expect that in larger simulation cell the absorption bands characteristic to OH groups in defects will be shifted toward the O10H frequency because of additional relaxation in the structure.

Based on the simulations the sharp absorption band at 3620 cm\(^{-1}\) can be unambiguously assigned to the O10H group. The calculated absorption bands for O9H, O5H and O6H groups in the Q\(^3\) defect tetrahedra coincide with the frequency range of the broad absorption band in the measured spectra at 3200-3500 cm\(^{-1}\), but can not be identified as single bands, due to above mentioned limitations of both the modelling and experimental data. At the present time, we are not able to distinguish between contributions from structurally incorporated OH groups and the surface absorbed water. Further theoretical and experimental investigations are necessary to distinguish the various contributions to the absorption band in the given range.
5. References


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6. Supporting Information to Chapter 2

According to the Rietveld method the crystal structure parameters are obtained by least-square fit of the powder diffraction pattern. The intensities $y_{ci}$ of each phase are determined from the structure factor, $|F_k|^2$, which is calculated from the structure model by summing up the calculated contributions from neighbouring Bragg reflections plus the background (Eq. S1):

$$y_{ci} = S_i \sum_k L_k |F_k|^2 \varphi (2\theta_i - 2\theta_k)P_k A + y_{bi},$$  \hspace{1cm} (S1)

where $S_i$ is the scaling factor of phase $i$, $k$ represents the Miller indices $(h k l)$ for a Bragg reflection, $L_k$ contains the Lorenz polarization and multiplicity factors, $\varphi$ is the reflection profile function, $P_k$ is the preferred orientation function, $A$ is the absorption factor, $F_k$ is the structure factor for the $k^{th}$ Bragg reflection and $y_{bi}$ is the background intensity. The factor minimized in the least-square refinement is the residual, $S_y$, calculated in the case of constant wavelength angle-dispersive data by Eq. (S2):

$$S_y = \sum_i w_i (y - y_{ci})^2,$$  \hspace{1cm} (S2)

where $w_i = 1/y_{ci}$, $y$ is the observed intensity and $y_{ci}$ is the calculated intensity (Young, 1993).

In the quantitative phase analysis (QPA) using the Rietveld method, the weight fraction $w_i$ of each crystalline component in the mixture is calculated from the corresponding scaling factor $S_i$ for that phase and the unit mass ($M_i$) and volume ($V_i$) by Eq. (S3):

$$w_i = \frac{S_i M_i V_i}{\sum_j S_j M_j V_j},$$  \hspace{1cm} (S3)

where

$$\sum_i w_i = 1.0,$$  \hspace{1cm} (S4)
In this work the Rietveld refinement was performed using the GSAS package (Larson and Von Dreele, 1994) and the graphical user interface (GUI) editor for GSAS experiment (Toby, 2001).

As starting models for the quantitative characterization of the samples, the four known xonotlite polytypes M2a2bc, Ma2bc, M2a2b2c and Ma2b2c (Gard, 1966), with the space groups $P-1$, $P 2/a$, $A-1$ and $A2/a$, respectively are used. The Ca, Si and O atoms are ordered into positions 1h, 1f and 2i (Ca), 1i (Si and O) of $P-1$, 2i of $A-1$, 2e of $P2/a$ as well 4c of $A 2/a$ (Hejny and Armbruster, 2001).

The whole powder diffraction pattern of synthetic xonotlite including the region from 5.008 - 79.978 ($2\theta^\circ$) was refined and yielded an agreement index $\chi^2$ of 1.479 for 15 variables. The background was fitted using the shifted Chebyshev function with 24 background coefficients. As the complexity of the pattern did not allow background subtraction, the background was refined as proposed by McCusker and co-workers (McCusker, 1999). The profiles were modelled using Simpson’s rule integration of a pseudo-Voigt function (function 2) (Howard, 1982; Thompson, 1987). The Rp, wRp, and $R(F^2)$ values were determined to be 3.01, 4.14, and 6.76, respectively. The weighted Durbin-Watson $d$ value (Durbin and Watson, 1950, 1951, 1971) was estimated to be 0.74.

Whenever amorphous phases exist in the system, the scattering contribution of the amorphous phase is part of the background and thus not included in Eq. (S4). The fraction of the amorphous phase can be calculated using the internal standard method, where a known fraction of standard powder (for instance: corundum or quartz) is added to the sample and treated as a component of the sample. After finishing the Rietveld refinement, the refined phase fractions are converted into weight fractions and rescaled by the ratio between refined ($x_{sc}$) and the known ($x_s$) amount of added standard. The percentage of the amorphous phase $x_a$ in the sample can be calculated directly from the weight of the internal standard according to Eq. (S5) (Gualtieri and Brignoli, 2004):

$$x_a = \frac{100}{(100-x_s)} \left(1 - \frac{x_s}{x_{sc}} \right)$$

(S5)

To estimate the amorphous content in xonotlite, a data set from a xonotlite sample with pure quartz added as internal standard (10%) was collected. The quartz intensities
were corrected for a preferred orientation effect along the [101] direction using the March-Dollase formalism (Dollase, 1986).
CHAPTER 3

Mechanism of Nd uptake by 11 Å tobermorite and xonotlite

ABSTRACT

The uptake of Nd(III) by the crystalline C-S-H phases 11 Å tobermorite and xonotlite has been investigated by the combined use of wet chemistry techniques, scanning electron microscopy (SEM), extended X-ray absorption fine structure (EXAFS) spectroscopy, and X-ray diffraction (XRD) in combination with Rietveld refinement. Wet chemistry and EXAFS data indicated that the formation of any Nd solid phase with fixed stoichiometry could be ruled out. Formation of a “metastable” precipitate (solid solution) intermixed with the crystalline C-S-H phases was observed at high Nd loadings (350 μmol Nd/g) by SEM but could not be detected at low Nd loadings (≤ 35 μmol Nd/g). The XRD data showed that Nd substitute for Ca in the Ca sheets of 11 Å tobermorite and xonotlite, and in the interlayer of 11 Å tobermorite. The incorporation of Nd was accompanied by the release of “zeolitic” water and bridging Si tetrahedra, which resulted in the formation of more disordered structures in both C-S-H phases. The EXAFS data revealed that the structural environment of Nd taken up by 11 Å tobermorite and xonotlite was dependent on equilibration time and Nd loading. After one day of reaction time the determined EXAFS parameters indicated predominant presence of inner-sphere coordinated Nd(III) on the surface of the C-S-H phases. The fitted distances between Nd and neighboring Si and Ca atoms in both structures increased by more than 0.1 Å (±0.02 Å) with increasing reaction time irrespective of Nd loadings. The longer distances coincide with increasing numbers of neighboring Si and Ca atoms, thus supporting the idea of Nd incorporation into the structures as revealed from Rietveld refinement. Long-term predictions of lanthanide and trivalent actinide immobilization by C-S-H phases should consider these uptake processes in the interlayer space and the Ca sheets.
1. Introduction

Minerals of the tobermorite and xonotlite family (11 Å tobermorite: \( \text{Ca}_4.5\text{Si}_6\text{O}_{16}(\text{OH})\cdot5\text{H}_2\text{O} \); xonotlite: \( \text{Ca}_6\text{Si}_6\text{O}_{17}(\text{OH})_2 \)) occur in nature as hydrothermal alteration products found in contact zones of Ca bearing rocks with basic igneous rocks (BONACCORSI et al., 2005; HENMI and KUSACHI, 1992; KUSACHI et al., 1984; MCCONNELL, 1954; TILLEY, 1951). Tobermorites and xonotlites are also expected to form as secondary solid phase at elevated temperature in the hyper-alkaline environments surrounding cement-based nuclear and toxic waste sites (ATKINSON et al., 1995; JANTZEN et al., 1984; MATZEN et al., 1999; VIANI, 1998). 11 Å tobermorite and xonotlite are two crystalline members among the large number of calcium silicate hydrates (C-S-H) for which the structure has been solved (HEJNY and ARMBRUSTER, 2001; MERLINO et al., 1999; MERLINO et al., 2001; PRODAN et al., 1983).

The structure and chemistry of the minerals of the tobermorite group are closely related to the structure of amorphous calcium silicate hydrates (C-S-H) phases which form upon reaction of water with the clinker minerals of cement, in particular alite and belite (RICHARDSON, 2004; TAYLOR, 1986). Furthermore, (semi-)crystalline and amorphous C-S-H phases may also precipitate as secondary minerals in the chemically disturbed zone of a repository for radioactive waste due to the interaction of hyper-alkaline fluids emerging from the cementitious near field with sedimentary host rock (DE WINDT et al., 2004; FERRAGE et al., 2005; MÄDER et al., 2006; PFINGSTEN et al., 2006; RABUNG et al., 2005).

Several models have been proposed over the past years to explain the structural properties of amorphous C-S-H phases (CHEN et al., 2004; GRUTZECK et al., 1999; JENNINGS, 2000; NONAT, 2004; RICHARDSON, 2004; TAYLOR, 1986; THOMAS et al., 2003). At low calcium-to-silicon (C:S) ratios the structure of poorly ordered amorphous C-S-H phases can be envisaged as an imperfect 14 Å tobermorite structure with many irregularities. The structural model is based on the silicate chains length, which is infinite in the case of 14 Å tobermorite (BRUNET et al., 2004; NONAT, 2004), while at high C:S ratios (C:S > 1) the C-S-H structure is closer to jennite (TAYLOR, 1986). Note that 11 Å tobermorite is the most common tobermorite form found in nature and the structure of 11 Å tobermorite is very similar to that of 14 Å tobermorite (BONACCORSI et al., 2005;
A review of the various models has been presented by Richardson (2004; 2008). Regardless of the structural viewpoint, the structural elements of tobermorite are considered to be essential for the development of mechanistic models of cation binding by C-S-H phases. The layered structure of 11 Å tobermorite is built up of sheets of seven coordinated Ca polyhedra, which are condensed by wollastonite-type silicate chains on both sides (Figure 1).

The distance between the neighboring Ca sheets is 11.3 Å. The silica chains are built up by Si$_2$O$_7$ groups (“paired” silica tetrahedra) connected to the central Ca sheet and (via “bridging” Si tetrahedra) to the adjacent layer. An important feature of the structure of 11 Å tobermorite is the cavity between two adjacent building layers stacked along c, the “interlayer space”, which may contain water and calcium cations. The structural arrangement in the interlayer of 11 Å tobermorite is still under debate. Hamid (1981) proposed a model in which Si-tetrahedra form a single wollastonite-like chain, while Merlino et al. (2001) recently developed a structural model suggesting formation of double-wollastonite chains. The latter model is in agreement with earlier $^{29}$Si magic angle spinning nuclear magnetic resonance investigations, which showed that freshly synthesized 11 Å tobermorite contains two main peaks corresponding to Q$^2$ and Q$^3$ Si sites (Cong and Kirkpatrick, 1996a). In the Q$^n$ notation, “Q” represents a Si tetrahedral site and “n” represents the number of neighbouring Si tetrahedra. In this study the 11 Å tobermorite structure proposed by Merlino et al. (2001) is taken as the basis for detailed structural interpretation of the experimental data.

![Figure 1](image.png)  
*Figure 1*  
The crystal structure of 11 Å tobermorite.
In the case of xonotlite four polytypes can be distinguished according to the different arrangements of building layers along c (GARD, 1966). Common to all polytypes is the basic structural element consisting of a layer of Ca polyhedra (HEJNY and ARMBRUSTER, 2001) (Figure 2).

Half of the Ca sites in the Ca layer are seven-coordinated by oxygen while the other half are distorted octahedron. The Si tetrahedra arrange in a double chain with 2/m symmetry, which is formed by condensation of two silicate chains (Figure 2). Importantly, xonotlite has no interlayer space in contrast to 11 Å tobermorite. The nomenclature of xonotlite polytypes and the mechanism of defects formation in the crystal structure of xonotlite have been discussed in detail elsewhere (CHURAKOV and MANDALIEV, 2008; HEJNY and ARMBRUSTER, 2001).

Significant work has been carried out on the retention of monovalent and bivalent cations by crystalline C-S-H phases considering the latter also as surrogate for amorphous C-S-H phases (KOMARNENI and ROY, 1983; MCCULLOCH et al., 1985). The studies demonstrated that crystalline C-S-H phases (e.g., tobermorite, xonotlite) are capable of taking up monovalent (e.g., Cs⁺) and bivalent cations (e.g., Co²⁺, Ni²⁺ etc.) via a cation exchange process with Ca²⁺. Nevertheless, only few studies have addressed the retention of trivalent metal cations, such as Eu(III), by C-S-H phases (POINTEAU et al., 2001). These authors investigated the interaction of Eu(III) with C-S-H phases with varying C:S ratios (C:S = 0.34 - 1.65) in the pH range 10.0 - 12.4 using time-resolved laser fluorescence spectroscopy (TRLFS). They observed fast sorption kinetics of Eu(III) and...
determined two types of Eu(III) species with different fluorescence lifetimes (390 and 990 μs). Shorter lifetimes of excited Eu(III) species are correlated with increasing number of OH/H₂O ligands in the first coordination shell. The partial hydration of one Eu(III) species was attributed to either formation of a surface precipitate or complexation to C-S-H surface sites. The long lifetime indicates the presence of a second, de-hydroxylated Eu(III) species, which was assumed to be Eu(III) bound in the Ca sheet of C-S-H by substituting for Ca²⁺. Uptake of Eu(III) and Cm(III) by amorphous C-S-H phases was further investigated by (Tits et al., 2003) using TRLFS. Fluorescing Cm(III) allowed three different species to be distinguished upon Cm(III) uptake by an amorphous C-S-H phase after a reaction time of 119 days. Based on crystallochemical considerations using the defect 11 Å tobermorite structure as model the authors concluded that two species were bound in the structure of amorphous C-S-H phase by substituting Ca²⁺ in the Ca sheets and in the interlayer. The third species detected by Tits and co-workers was attributed to the presence of Cm(OH)₃. Potential substitution of Ca²⁺ in the Ca sheets and interlayer Ca of amorphous C-S-H phases by Eu(III) was further substantiated with X-ray absorption fine structure (XAFS) investigations carried out by Schlegel et al.(2004), who proposed the precipitation of a Eu(III)-containing C-S-H-like solid phase from temporary oversaturation. The results from these previous spectroscopic studies do not allow for an unambiguous discrimination between incorporation into the structure of C-S-H phases and the formation of C-S-H-like solid phases (surface precipitate). So far, direct determination of the crystallographic positions occupied by lanthanides and actinides in the C-S-H structures was not possible because poorly crystalline C-S-H was used as host phase.

In the present study, the uptake of Nd(III) by the crystalline C-S-H phases 11 Å tobermorite and xonotlite has been investigated by the combined use of laboratory and synchrotron-based techniques, including macroscopic sorption and recrystallization experiments, scanning electron microscopy (SEM) with energy dispersive micro-analysis (EDS), X-ray diffraction (XRD) analysis coupled with Rietveld refinement, and EXAFS. The aim of this study is to develop a structural model for the uptake of Nd by 11 Å tobermorite and xonotlite. Nd(III) is regarded as a suitable chemical analogue for trivalent actinides, such as Am(III) and Cm(III), due to the comparable ionic radii and
similarities in the complexation behaviour. Because the ionic radius of Nd\(^{3+}\) (0.983Å in sixfold coordination) is comparable to that of Ca\(^{2+}\) (1.00 Å and 1.07 Å for six- and sevenfold coordination, respectively) (Shannon, 1976), Nd is expected to substitute for Ca in the structure of C-S-H phases. A molecular-level understanding of the binding mechanisms is the key to further improvements in the development of thermodynamically-based models of lanthanide and actinide retention by crystalline and amorphous C-S-H phases. Availability of such models is particularly important for long-term predictions of actinide immobilization in cement-based repositories for radioactive waste.

2. Materials and methods

2.1 Materials

Throughout this study Fluka (Sigma-Aldrich, Buchs, Switzerland) or Merck (Dietikon, Switzerland) “pro analysis” chemicals and high-purity de-ionised water generated by a Milli-Q Gradient A10 system (Millipore, Bedford, USA) were used. All experiments were carried out in a glovebox under N\(_2\) atmosphere and ambient temperature (CO\(_2\), O\(_2\) <2ppm, T = 23° ± 3° C). 11 Å tobermorite and xonotlite were synthesized by mixing stoichiometric quantities of SiO\(_2\) and CaO powder materials (C/S = 0.75 for tobermorite and C/S = 1.0 for xonotlite) with 220 mL Argon-purged Milli-Q water (Kalousek et al., 1977; Winkler and Wieker, 1979). The suspensions were placed in 250 mL Teflon Parr bombs and aged in an oven as follows: 11 Å tobermorite at 160°C for 7 days and xonotlite at 220°C for 30 days. The white pastes (wet paste) resulting from synthesis were dried over saturated CaCl\(_2\) solution in a closed container in the glovebox until the weight was constant. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) measurements of samples dried at 55°C (data not shown) revealed water contents of 15.6 weight (wt) % and 6.0 wt%, respectively, which agrees with the theoretical release of structural water in 11 Å tobermorite and OH groups in xonotlite. TG/DTG, infrared spectroscopy (IR) (data not shown) and X-ray diffraction further showed that the samples are free of Ca(OH)\(_2\), CaCO\(_3\) and quartz. The surface
areas were determined to be 7 m$^2$ g$^{-1}$ and 40 m$^2$ g$^{-1}$, for 11 Å tobermorite and xonotlite, respectively, based on N$_2$ sorption measurements (BET method).

2.2 Nd sorption experiments

Nd uptake by 11 Å tobermorite and xonotlite was investigated as a function of increasing initial Nd concentrations (sorption isotherm). The sorption samples were prepared as follows: 0.125 g tobermorite and 0.121 g xonotlite (based on the dry weight as described in section 2.1) were added to 1000 mL equilibrium solution to prepare suspensions with a solid-to-liquid ratio (S/L) of 0.1 g L$^{-1}$. 30 mL aliquots of the vigorously stirred stock suspensions were withdrawn and transferred into 40 mL polyallomere centrifuge tubes (Beckmann Instruments, Inc). The suspensions were aged on an end-over-end shaker for one week. Subsequently, appropriate volumes of Nd stock solutions (10$^{-3}$ M – 10$^{-7}$ M) were added to the suspensions to achieve initial Nd concentrations ranging from 10$^{-5}$ to 10$^{-9}$ M. The Nd stock solutions were prepared by dissolving Nd(NO$_3$)$_3$·6H$_2$O in HNO$_3$ (10$^{-3}$ M). The Nd doped suspensions were then aged by shaking continuously end-over-end in the glovebox for 60 days. The final pH was estimated to be 11.7 and 10.7 for 11 Å tobermorite and xonotlite and the pH was not modified during sorption. Solid and liquid phase were separated by centrifugation (60 min at 95000 g) using a L7-35 ultracentrifuge (Beckmann Instruments, Inc). The Nd concentration in the supernatant solutions was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS).

2.3 Re-crystallization experiments with $^{45}$Ca

Re-crystallization experiments using $^{45}$Ca (t$_{1/2}$ = 163 d) were carried out to assess the role of Ca exchange in connection with Nd binding. A $^{45}$Ca stock solution was obtained from Isotope Products Europe (Berlin, Germany). 11 Å tobermorite and xonotlite suspensions with S/L ratios of 5 g L$^{-1}$ were prepared by mixing adequate amounts of each material (wet paste) with 1000 mL equilibrium solution. The application of wet paste instead of dry powder was necessary in order to avoid partial collapse of the
interlayer of 11 Å tobermorite caused by the dehydration procedure (Shaw et al., 2000b). From acid digestion of the wet pastes and ICP-OES analysis of the solutions the free water content was determined as 76.3 % in the case of 11 Å tobermorite and 86.3 % in the case of xonotlite. Thus, the dry weight of 11Å tobermorite and xonotlite pastes used for the $^{45}$Ca experiments amounted to 23.7 % and 13.7 % (of the initial weight of the wet paste). 35 mL aliquots of the vigorously stirred stock suspensions were withdrawn, pipetted into 40 mL polyallomere centrifuge tubes and spiked with 0.1 mL of a $^{45}$Ca solution (1:5 diluted stock solution with Ca concentration = 2 $\mu$g mL$^{-1}$). Standards were prepared in the same manner using solutions preequilibrated with the solids instead of stock suspensions. All samples were shaken continuously end-over-end in the glovebox and sampled at regular time intervals over a time period of one year. The solid and liquid phase were separated by centrifugation (60 min at 95000 g), and 5 mL aliquots of the supernatant solution were withdrawn and mixed with 15 mL liquid scintillation cocktail (Ultima Gold-XR™). Radio assay of the samples and standards was carried out using a Canberra Packard Tricarb™ 2250CA liquid scintillation analyzer (LSA) with an energy window set between 6 and 500 keV. The background activity measured in this window was typically ~40 cpm. The count rate for the samples was ~14000 cpm after 1 day equilibration and decreased to ~4000 cpm after 360 days reaction time.

2.4 Scanning electron microscopy (SEM)

SEM investigations were carried out using a Zeiss DSM 962 microscope, operated at an accelerating voltage of 20 kV and a beam current of 76 $\mu$A. The microscope was equipped with a Si(Li)-detector for energy dispersive micro-analysis (EDS). The spot size was ~1x1 $\mu$m$^2$, and the penetration depth was ~6 $\mu$m at the used incident beam energy.

2.5 Sample preparation for EXAFS and X-ray diffraction measurements

EXAFS and X-ray diffraction investigations were carried out on Nd doped 11 Å tobermorite and xonotlite materials and Nd reference compounds. Sample abbreviations given in Table 1 indicate equilibration time and Nd loadings.
Table 1  Chemical conditions of the Nd sample preparation for EXAFS and X-ray diffraction measurements.

<table>
<thead>
<tr>
<th>Material</th>
<th>Abbreviation</th>
<th>Reaction time (days)</th>
<th>Nd loading (μmol Nd/g solid)</th>
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The samples had varying Nd loadings and were equilibrated for time periods up to 400 days. The samples were prepared as follows: 35 mL aliquots of the vigorously stirred stock suspensions (50 g L\(^{-1}\) solid materials in equilibrium solution) were pipetted into 40 mL polyallomere centrifuge tubes and aged for one week on an end-over-end shaker. Appropriate volumes of a Nd stock solution (10\(^{-2}\) M Nd) were then added to the
suspensions to achieve the required Nd loadings on the solid. Note that no changes in pH were observed after Nd addition. The samples were equilibrated on an end-over-end shaker in the glovebox and sampled at regular time intervals (Table 1). After phase separation by centrifugation (60 min at 95000 g) the Nd treated samples were packed as a wet paste into Plexiglas sample holders and sealed with Kapton tape for the EXAFS measurements. X-ray diffraction analysis was conducted on dry samples with the highest Nd loadings (~5 wt %).

In addition to the Nd doped tobermorite and xonotlite samples a hydrothermally synthesized Nd-doped C-S-H phase (Tsyn14-350) and a Nd precipitate (T-prec) synthesized in the tobermorite equilibrium solution were analyzed by EXAFS. Synthesis of lanthanide silicates with tobermorite-like structure was recently reported by Ferreira et al. (2003). The former phase is considered to be a potential model compound with regards to Nd binding to C-S-H phases in the long run, while the Nd precipitate is supposed to represent possible structural arrangements of Nd in short term experiments. The Tsyn14-350 sample was prepared by mixing SiO$_2$ and CaO powder materials (C/S = 0.75 according to the tobermorite stoichiometry) with a Nd solution to achieve a final Nd loading of 350 μmol Nd/g solid phase. The Nd solution was prepared by dissolving 1.09 mg Nd(NO$_3$)$_3$∙6H$_2$O in 25 mL HNO$_3$ (10$^{-2}$ M). The suspension was aged in the Teflon Parr bomb at 160°C for 14 days. The product was found to be a still unknown phase. X-ray diffraction analysis indicated similarities to 11 Å tobermorite. The Nd precipitate (T-prec) was prepared by adding 14 mL 0.1 M Nd solution to 30 mL tobermorite equilibrium solution. In addition, a Nd(OH)$_3$ reference compound was synthesized by adding 0.1 M Nd solution to 30 mL 2 M NaOH.

2.6 EXAFS data collection and reduction

EXAFS spectra at the Nd L$_{III}$ edge (6208 eV) were collected at beamline BM26A (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, operating under beam conditions of 6 GeV at 200 mA, and at the ANKA-XAS Beamline of the Angstroemquelle Karlsruhe, operating with a beam current between 80–140 mA at 2.5 GeV storage ring energy. Both beamlines are equipped with a Si (111) double-crystal monochromator. The monochromator angle was calibrated by assigning the energy of
5989 eV to the first inflection point of the K-absorption edge of Cr metal foil. The EXAFS measurements were conducted at room temperature in fluorescence mode using a 9 channel monolithic Ge-solid-state detector at DUBBLE/ESRF and a five element Ge-detector at the ANKA-XAS. For each compound, at least three spectra were collected to improve the signal-to-noise ratio.

Data reduction was performed by using the WinXAS 3.11 software package and following standard procedures (RESSLER, 1998). After background subtraction, the energy was converted to photoelectron wave vector units (Å⁻¹) by assigning the ionization energy of the Nd L₃-edge (6208 eV), E₀, to the first inflection point of the absorption edge. Radial structure functions (RSFs) were obtained by Fourier transforming k⁳-weighted χ (k) functions typically in the range 1.7-10.8 Å⁻¹ using a Bessel window function with a smoothing parameter of 4. Single-shell fits were performed in real space across the range of the first- and second- coordination shell (ΔR = 1.25 – 4 Å) to determine the mean coordination number, N, the bond length, R, and the Debye-Waller factor, σ, for each shell. Optimization of the parameters was achieved with the E₀ shift constrained and the amplitude reduction factor, S₀², fixed at 1.0. The interatomic distances, R, coordination numbers, N, Debye-Waller factors, σ, were allowed to vary in the single-shell analysis. In a subsequent step multi-shell fits were performed by using the estimated data from the single-shell analysis. The Debye-Waller factor of the first Nd-O shell was allowed to vary in the multi-shell analysis. The Debye-Waller parameter was fixed for the second shell using the data from the single-shell fits of the second shell. The latter was necessary due to strong correlation of the Si and Ca backscattering contributions for the second shell. All other fitting parameters were treated as in the single-shell fits. Theoretical scattering paths for the fits were calculated using the FEFF 8.20 code (ANKUDINOV and REHR, 2000; NEWVILLE, 2001). The structures of 11 Å tobermorite (MERLINO et al., 2001) and the xonotlite polytype M2a2bc (HEJNY and ARMBRUSTER, 2001) were used as model compounds.

The structural model for Eu(III) retention by amorphous C-S-H phases with varying Ca/Si molar ratios, which was proposed earlier by SCHLEEGEL et al. (2004), was adapted for an analysis of the EXAFS data for Nd doped tobermorite and xonotlite. This model, which is based on the assumption that trivalent lanthanides, e.g. Nd and Eu,
substitute for Ca in the C-S-H structure, includes backscattering contributions from Si atoms at $R \sim 3.2$ Å and $R \sim 3.7 - 3.75$ Å, and Ca atoms at $R \sim 3.79 - 3.84$ Å. In the present study Nd incorporation into the lattice of tobermorite and xonotlite by substitution for Ca was assumed based on similarities in the ionic radii of the two elements in sevenfold coordination (1.01 Å and 1.06 Å, respectively) (SHANNON, 1976). Note that the short Si distance at $R \sim 3.2$ Å, which was reported by SCHLEGEL et al. (2004), was not considered in this study. EXAFS fits with samples reacted for short time periods (i.e. <400 days) did not result in meaningful residual parameters if the short Si distance was considered. Short Nd-Si distances were only visible after 400 days reaction time. Thus, the model proposed for Nd retention only considers one Ca and one Si shell at similar distances, i.e.: $R_{\text{Nd-Si}} \sim 3.70 - 3.75$ Å; $R_{\text{Nd-Ca}} \sim 3.75 - 3.80$ Å. Note, however, that the spatial resolution, which is given by $\Delta R = \pi/2\Delta k$, where $\Delta k$ is the range of $k$-space being fit ($\Delta k = 1.70 - 10.80$ Å$^{-1}$), was estimated to be ~0.17 Å. This finding implies that the two shells can be hardly resolved. Statistical F-tests were performed in order to prove whether or not the proposed fitting model with backscattering contributions from Si and Ca at long distances can be justified (see Part A of the Supporting Information to this Chapter). Based the results from these tests and additional crystallographic considerations of the structure of non-doped tobermorite, we infer that a model, which includes O, two Si and Ca atoms at similar distances, can be applied to adequately reproduce the coordination environment of Nd in the tobermorite and xonotlite structures.

2.7 X-ray diffraction measurements and Rietveld analysis

X-ray powder diffraction measurements were performed on a Philips PANanalytical X’Pert PRO system with X’Celerator detector operating in Bragg–Brentano geometry (θ/2θ) and at a nominal pressure using Cu Kα (40 kV and 40 mA). The sample material (particle size <63 μm) was emplaced in a specimen holder of 16 mm diameter. The measurements were carried out in the 2θ range 5.00° - 50° with a step size of 0.017° using a counting time of 60 s per step.

X-ray diffraction measurements on the Nd doped tobermorite sample equilibrated for 90 days (T90-350) were performed on Beamline 10.3.2 at the Advanced Light Source (ALS), USA (MARCUS et al., 2004). Diffraction data were collected using a Bruker
SMART6000 CCD detector mounted on a three-axis (XZΘ) stage. The beam energy was 14 keV, which was high enough to provide access to reflections with \( d \)-spacings down to 1.5 Å. Patterns were calibrated and integrated using the Fit2d program (Hammersley et al., 1996) with calibration data from \( \text{Al}_2\text{O}_3 \) powder.

Rietveld refinements were carried out using the GSAS package (Larson and von Dreele, 1994) and the graphical user interface (GUI) editor for GSAS experiments (Toby, 2001). The model used in the Rietveld refinement was deduced from the structure of 11 Å tobermorite (Merlino et al., 2001) and xonotlite (Hejny and Armbruster, 2001). The background was fitted using the shifted Chebyshev function. The profiles were modeled using Simpson’s rule integration of a pseudo-Voigt function (Howard, 1982; Thompson et al., 1987). Quality of the fits was assessed based on the \( R_p \), \( wR_p \), \( R(F^2) \) residuals (Larson and von Dreele, 1994) and visual inspection.

A stepwise approach was used in the refinement. In the first step the scale factor, unit parameters, full-width parameters, sample displacement, peak asymmetry and asymmetric peak broadening were refined using fixed atomic positions and occupancies from the references. The latter included the four known xonotlite polytypes M2a2bc, Ma2bc, M2a2b2c and Ma2b2c with the space groups \( P-1 \), \( P 2/a \), \( A-1 \) and \( A2/a \) (Gard, 1966; Hejny and Armbruster, 2001), and the structure of 11 Å tobermorite (Merlino et al., 2001). In the second step difference-Fourier maps were calculated for the T90-350 and X90-350 samples based on the observed Bragg intensities, which were converted into the structure factors, to localize the positions of the Nd species in the structure of 11 Å tobermorite and xonotlite. The overall scale factor was refined, and three-dimensional difference Fourier maps with 0.3 \( e/\text{Å}^3 \) resolution were calculated. In the third step the occupancies and positions of all atoms in T90-350 (except hydrogen atoms) were refined. No refinements of the occupancies and positions of the atoms in the tobermorite structure after 1, 14, 30 and 60 days as well as the Nd doped xonotlite samples were performed due to the low amount of Nd incorporated. For these samples only the first and the second steps were performed (see above). The bond lengths and angles in the asymmetric unit of 11 Å tobermorite structure after 90 days were restrained using soft constraints selected based on the EXAFS results. The mean square parameters \( B \) were fixed to 0.025 Å². For the xonotlite sample reacted for 90 days only atomic occupancies of Nd and Ca were

73
refined. No refinement of the atomic positions for the xonotlite structure was carried out due to the strong overlap of the Bragg peaks of the different xonotlite polytypes. The goodness of the fit between the observed and calculated X-ray diffraction powder patterns was calculated as suggested by (LARSON and VON DREELE, 1994).

3. Results

3.1 Nd sorption isotherms

Figure 3 shows that Nd uptake by 11 Å tobermorite can be interpreted in terms of a Freundlich-type isotherm (slope = 0.7 ± 0.2) over the entire concentration range. The xonotlite data were found to be consistent with the proposed interpretation of the sorption isotherm although scatter in the data was significant.

Figure 3  Nd sorption isotherms on 11 Å tobermorite and xonotlite. Experimental conditions: S/L ratio = 0.125 g L⁻¹ and 0.121 g L⁻¹ for 11 Å tobermorite and xonotlite, respectively; equilibration time = 60 days Additional data at higher Nd loadings are included for comparison.
The large uncertainty in the experimental data presumably originated from Nd bearing colloidal matter which remained in solution or was partially resuspended after centrifugation.

The wet chemistry data show that the Nd concentration in the C-S-H systems was not controlled by the formation of a solubility-limiting phase with fixed stoichiometry. Thermodynamic data for the Nd hydrolysis species and Nd(OH)\textsubscript{3}(cr) were evaluated by BAES and MESMER (1976)). The solubility product of amorphous Nd(OH)\textsubscript{3}(am) was estimated based on chemical analogy with Eu(III) (HUMMEL et al., 2002). Figure 3 shows the solubility limits of crystalline and amorphous Nd(OH)\textsubscript{3} (T=25°C, I = 0.01 M), which were calculated using the Hydra-Medusa software (PUIGDOMENECH, 2004) and the set of solubility and hydrolysis constants reported by HUMMEL et al. (2002). The initial Nd concentrations added to the C-S-H systems well exceeded the solubility limits with respect to crystalline and amorphous Nd(OH)\textsubscript{3}.

3.2 \textsuperscript{45}Ca recrystallization experiments

Removal of \textsuperscript{45}Ca from solution is a measure of the amount of recrystallized C-S-H phases, which further accounts for the amount of potentially Nd bearing solid material at the given S/L ratio. The percentage of \textsuperscript{45}Ca tracer removed from solution was calculated based on the difference between total \textsuperscript{45}Ca added to the suspensions and the activity determined in solution as a function of equilibration time.

The partitioning of \textsuperscript{45}Ca between solid and liquid phases was described in terms of an isotopic dilution:

\[
\frac{[Ca]_{\text{solid}}}{[Ca]_{\text{solution}}} = \frac{[\textsuperscript{45}Ca]_{\text{solid}}}{[\textsuperscript{45}Ca]_{\text{solution}}} \tag{1}
\]

The amount of recrystallized C-S-H was calculated from the portion of Ca in the C-S-H that exchanged with \textsuperscript{45}Ca as a function of time.

The maximum uptake of \textsuperscript{45}Ca was estimated according to Eq. (1) using the Ca concentrations of the solid and in solution in the C-S-H systems. In the case of xonotlite the suspension concentration was 5 g L\textsuperscript{-1}, corresponding to 0.68 g L\textsuperscript{-1} dry xonotlite (MW: 714) or 5.8 mmol Ca L\textsuperscript{-1}, respectively.
The Ca concentration in solution at equilibrium was determined to be 3.96 mmol L$^{-1}$. The maximum $^{45}$Ca uptake resulted to ~60%, which corresponded to 100% recrystallization. In the case of tobermorite complete recrystallization corresponded to a maximum $^{45}$Ca uptake of ~67%. After one year, the percentage of $^{45}$Ca taken up by the two solids was ~35%, which indicated ~50 - 60% recrystallization.

The recrystallization rate continuously decreased with time. The fast $^{45}$Ca uptake within the first day (~5%) could be attributed to a reversible exchange process with surface-bound Ca (Shrivastava et al., 1991). The recrystallization rate slowed down between 1 day and about 150 days when $^{45}$Ca replaced stable Ca in the structure of C-S-H phases. After 150 days $^{45}$Ca exchange was negligibly small. The results from these $^{45}$Ca exchange experiments revealed that a significant portion of the structures of 11 Å tobermorite and xonotlite were accessible to Nd uptake due to recrystallization of C-S-H phases. The different recrystallization rates of the two C-S-H phases were possibly related to the specific surface areas, i.e., 7 m$^2$ g$^{-1}$ in the case of 11 Å tobermorite and 40 m$^2$ g$^{-1}$ in the case of xonotlite.
3.3 SEM/EDS analysis

SEM / EDS analyses were performed to investigate whether the doping process of C-S-H minerals produced differences in the particle morphology.

Figure 5  SEM images of a-d) 11 Å tobermorite and e-h) xonotlite: Nd loading = 350 μmol Nd/g solid phase, a) non-doped sample; b) one day reaction time, 350 μmol Nd/g solid phase; c) 90 days reaction time, 350 μmol Nd/g solid phase; d) one day reaction time, 35 μmol Nd/g solid phase); e) non-doped sample; f) one day reaction time, 350 μmol Nd/g solid phase; g) 90 days reaction time, 350 μmol Nd/g solid phase; h) one day reaction time, 35 μmol Nd/g solid phase.
EDS analysis carried out at selected regions on the highly loaded samples revealed the presence of Nd.

The average molar Nd/Ca ratio of the T1-350 sample was determined to be 0.17 and the Ca/Si ratio = 0.90. The uncertainty on all ratios is estimated as ± 0.1. The latter value is close to the initial Ca:Si stoichiometry in tobermorite. Increase in the Nd/Ca ratio and decrease in the Ca/Si ratio was observed in the T90-350 sample (Nd/Ca = 0.32; Ca/Si = 0.59) compared to the T1-350 sample.

In the case of Nd doped xonotlite (Figure 5E), however, SEM images revealed the formation of a newly formed phase in the X1-350 sample with high Nd loading (Figure 5F). EDS analysis carried out on the X1-350 sample indicated a Nd/Ca ratio = 0.16 and the Ca/Si ratio = 0.93. In a similar way as for 11 Å tobermorite an increase in the Nd/Ca ratio coinciding with a decrease in the Ca/Si ratio was observed with increasing reaction time (X90-350: Nd/Ca = 0.32; Ca/Si = 0.73). The penetration depth at the given incident beam energy was ~6μm, indicating that the stoichiometric ratios account for surface rather than bulk compositions. For both C-S-H phases and low Nd loading (35 μmol Nd/g solid phase), formation of the secondary phase was not observed. The appearance of the observed secondary phase seems to be very similar to that of non-doped tobermorite, and thus distinction of the two phases in the case of 11 Å tobermorite was impossible even at higher magnifications under the SEM.

3.4 EXAFS investigations

3.4.1 EXAFS of Nd reference compounds

EXAFS measurements on Nd(OH)$_3$ as well as the Tsyn14-350 and T-Prec samples (T-Prec-1, T-Prec-28) were carried out to determine the structural parameters of Nd in potential reference systems. From Tsyn14-350 and Nd(OH)$_3$ measurements structural information on Nd-O and Nd-Nd backscattering pairs was obtained. Tsyn14-350 and Nd(OH)$_3$ were chosen as reference compound to gain structural information on incorporated Nd species. The T-Prec samples were analysed to determine structural data for Nd bound in a solid phase, which was freshly prepared from Ca and Si containing equilibrium solution to simulate the early phase of Nd binding to the C-S-H phases. It
was expected that the different Nd species could be distinguished by comparing the EXAFS parameters deduced from the reference compounds with those determined for the Nd doped tobermorite and xonotlite samples.

Figures 6a/b/c show $k^3$-weighted, normalized, background subtracted EXAFS spectra, the corresponding RSFs and the Fourier-backtransform ($R = 1.5$-4.0 Å) spectra of Nd(OH)$_3$, as well as those of the Tsyn14-350 and T-Prec-1 samples. The EXAFS parameters obtained from the fits are listed in Table 2.

All spectra showed a pronounced peak at $R + \Delta R \sim 2.0$ Å in the Fourier transform (FT), corresponding to backscattering contributions from the nearest neighboring oxygen shell, which can be fitted by assuming the presence of a single oxygen shell. The number (N) of neighboring oxygen atoms in Nd(OH)$_3$ was determined as 8.7.

**Figure 6**  $k^3$-weighted spectra and b) the corresponding RSFs of experimental (solid line) and fitted (dashed and dotted lines for the imaginary and the real part, respectively) Nd L$_{III}$-EXAFS of Nd doped 11 Å tobermorite, Nd precipitate and Nd(OH)$_3$; c) $k^3$-weighted EXAFS function for the Fourier-backtransform spectra obtained from Figure 6b (range: $R \pm \Delta R = 1.7$-4.0). RSF positions are not corrected for phase shift.

79
The fitted distance $R_{\text{Nd-O}} = 2.50 \text{ Å}$ is in excellent agreement with reported Nd-O distances for Nd(OH)$_3$ ($R_{\text{Nd-O}} = 2.51 \text{ Å}$) (BEALL et al., 1976). The broad peak in the FTs at $R + \Delta R \sim 4.0 \text{ Å}$ was fitted by assuming Nd neighboring atoms. The number of Nd-Nd backscattering pairs was calculated as 1.7 and 6.2 at distances of $R_{\text{Nd-Nd}} = 3.74 \text{ Å}$ and $R_{\text{Nd-Nd}} = 4.16 \text{ Å}$ for the first and the second Nd shells, respectively. These values are in excellent agreement with those published by BEALL et al. (1976) ($N = 2$ and $R_{\text{Nd-Nd}} = 3.74 \text{ Å}; N = 6$ and $R_{\text{Nd-Nd}} = 4.15 \text{ Å}$), considering the experimental uncertainties on the EXAFS data. The Nd-O distances in the T-Prec (T-Prec-1, T-Prec-28) and Tsyn14-350 samples ($R_{\text{Nd-O}} = 2.45 - 2.47 \text{ Å}$) were shorter than those in Nd(OH)$_3$ ($R_{\text{Nd-O}} = 2.5 \text{ Å}$) (Table 2).

Note, however, that the measured distances in these samples compared well with average Nd-O distances of known neodymium-silicate compounds ($R_{\text{Nd-O}} = 2.42 - 2.48 \text{ Å}$) (CHICHAGOV and BELOV, 1968; SMOLIN and SHEPELEV, 1970).

The number of nearest neighbouring oxygen atoms ($N_0$) was determined to be about 6.7 in the T-Prec sample, which is lower than in Nd(OH)$_3$ ($N = 8.7$).

**Table 2** Structural information obtained from EXAFS Nd L$_{III}$-edge data analysis of reference compounds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eq. time (days)</th>
<th>Nd loading (μmol Nd/g)</th>
<th>$\Delta k^a$</th>
<th>$N_0^b$</th>
<th>$R_{\text{Nd-O}}$ (Å)</th>
<th>$\sigma^c$ (Å)</th>
<th>$N_{\text{Nd-Nd}}^b$</th>
<th>$R_{\text{Nd-Nd}}$ (Å)</th>
<th>$\sigma^c$ (Å)</th>
<th>$N_{\text{Nd-Nd}}^b$</th>
<th>$R_{\text{Nd-Nd}}$ (Å)</th>
<th>$\sigma^c$ (Å)</th>
<th>$\Delta E_0^e$</th>
<th>$R_f^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-Prec-1</td>
<td>1</td>
<td>-</td>
<td>1.7-10.8</td>
<td>6.7</td>
<td>2.46</td>
<td>0.009</td>
<td>4.6</td>
<td>3.81</td>
<td>0.012</td>
<td>5.5</td>
<td>3.84</td>
<td>0.007</td>
<td>6.8</td>
<td>6.3</td>
</tr>
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<td>Tsyn14-350</td>
<td>1, 350</td>
<td>1.7-10.8</td>
<td>8.1</td>
<td>2.45</td>
<td>0.011</td>
<td>5.1</td>
<td>3.87</td>
<td>0.005</td>
<td>6.7</td>
<td>3.91</td>
<td>0.01</td>
<td>8.21</td>
<td>12.9</td>
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</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eq. time (days)</th>
<th>Nd loading (μmol Nd/g)</th>
<th>$\Delta k^a$</th>
<th>$N_0^b$</th>
<th>$R_{\text{Nd-O}}$ (Å)</th>
<th>$\sigma^c$ (Å)</th>
<th>$N_{\text{Nd-Nd}}^b$</th>
<th>$R_{\text{Nd-Nd}}$ (Å)</th>
<th>$\sigma^c$ (Å)</th>
<th>$N_{\text{Nd-Nd}}^b$</th>
<th>$R_{\text{Nd-Nd}}$ (Å)</th>
<th>$\sigma^c$ (Å)</th>
<th>$\Delta E_0^e$</th>
<th>$R_f^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd(OH)$_3$</td>
<td>-</td>
<td>-</td>
<td>1.7-10.8</td>
<td>8.7</td>
<td>2.50</td>
<td>0.008</td>
<td>1.7</td>
<td>3.74</td>
<td>0.003</td>
<td>6.2</td>
<td>4.16</td>
<td>0.009</td>
<td>7.01</td>
<td>9.5</td>
</tr>
</tbody>
</table>

$^a$ Fourier-transformed $\chi(k)$ range, $^b$ Number of neighbor atoms, $^c$ Interatomic distance, $^d$ Debye-Waller factor, $^e$ Energy shift of the theoretical calculated spectrum to the energy grid of the measured spectrum, $^f$ The residual factor $R_f$.

\[
R_f = \frac{\sum (\chi_{\text{calc}} - \chi_{\text{obs}})^2}{\sum (\chi_{\text{obs}})^2} \times 100
\]

Estimated errors: ($R_{\text{Nd-O}}, R_{\text{Nd-Nd}}, \Delta E_0$) ±0.02 Å; ($N_0, N_{\text{Nd-Nd}}$) ±20% $\chi_{\text{calc}}$ and $\chi_{\text{calc}}$: experimental and theoretical data points.
In case of the Tsyn14-350 sample and Nd(OH)$_3$, however, the coordination numbers were comparable within the experimental uncertainties ($N_O = 8.1$ and $N_O = 8.7$).

To account for the additional neighboring atoms present in the T-Prec and Tsyn14-350 samples quantitative analysis was performed by considering Nd-Si and Nd-Ca backscattering contributions at ~ 3.3 Å. Note that inclusion of Nd-Nd backscattering pairs did not improve the quality of the fits and thus, these contributions were ignored in the final analysis. The Nd-Ca and Nd-Si distances determined for the two T-Prec samples and Tsyn14-350 sample are compared in Table 2 and indicate significantly longer Nd-Ca and Nd-Si distances in the hydrothermally synthesized tobermorite-like material than in the Nd-precipitate. Thus, we infer that prolonged reaction time or increasing temperature leads to structurally well ordered solid phases with longer Nd-Ca and Nd-Si distances.

### 3.4.2 EXAFS of Nd doped 11 Å tobermorite

Nd doped 11 Å tobermorite samples with varying reaction times (1, 90, 270 and 400 days) and different Nd loadings (2.3, 7 and 35 μmol/g) were analyzed by EXAFS (Figure 7). The RSFs of all Nd doped tobermorite samples showed a peak at $R + \Delta R \sim 2.0$ Å, which was fitted by assuming the presence of a single oxygen shell. The Nd-O distances were determined to be 2.44 – 2.45 Å and the coordination numbers, $N_O$, ranged in value between 6.7 (T1-35) and 8.4 (T90-2.3). No clear trend with regards to reaction time and loading was found. The Debye-Waller factor (DW), which accounts for the effects of thermal motion or structural disorder ranged in value between 0.010 Å$^2$ and 0.012 Å$^2$ in most cases. The DW factor was comparable (or slightly higher) than in the case of reference compounds but significantly higher than values reported for Nd-silicates (0.002 Å$^2$ – 0.008 Å$^2$ (Okudera et al., 2003).

The presence of further backscattering atoms was indicated by the broad peak in the FTs at $R + \Delta R \sim 3.0$ Å, which could be fitted by considering Nd-Si and Nd-Ca backscattering paths. The Nd-Si and Nd-Ca distances were found to increase with increasing reaction time and decreasing Nd loading.
Dependency on the metal loadings was well illustrated in the case of the T1-2.3, T1-7 and T1-35 samples: R$_{\text{Nd-Si}}$ was determined to be 3.84 Å, 3.75 Å and 3.73 Å and the corresponding R$_{\text{Nd-Ca}}$ distances amounted to 3.85 Å, 3.78 Å and 3.76 Å (Table 3). The same trend in bond distances was observed for the aged sample (compare structural data for the T90-2.3, T90-7 and T90-35 samples in Table 3). Longer Nd-Si and Nd-Ca distances were observed with increasing reaction time at the same Nd loadings.
Table 3  
Structural information obtained from EXAFS Nd L_{III}-edge data analysis of Nd doped 11 Å tobermorite.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (days)</th>
<th>Nd loading (μmol Nd/g)</th>
<th>Δk^2</th>
<th>N_{Nd}</th>
<th>R_{Nd-O} (Å)</th>
<th>σ_{Nd-O}^2 (Å^2)</th>
<th>N_{Si}</th>
<th>R_{Nd-Si} (Å)</th>
<th>σ_{Nd-Si}^2 (Å^2)</th>
<th>N_{Ca}</th>
<th>R_{Nd-Ca} (Å)</th>
<th>σ_{Nd-Ca}^2 (Å^2)</th>
<th>ΔE_f (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1-2.3</td>
<td>1</td>
<td>2.3</td>
<td>1.7-10.8</td>
<td>7.7</td>
<td>2.44</td>
<td>0.012</td>
<td>2.2</td>
<td>3.84</td>
<td>0.004</td>
<td>3.2</td>
<td>3.85</td>
<td>0.006</td>
<td>4.7</td>
</tr>
<tr>
<td>T1-7</td>
<td>1</td>
<td>7</td>
<td>1.7-10.8</td>
<td>8.1</td>
<td>2.44</td>
<td>0.011</td>
<td>1.7</td>
<td>3.75</td>
<td>0.01</td>
<td>2.0</td>
<td>3.78</td>
<td>0.006</td>
<td>6.0</td>
</tr>
<tr>
<td>T1-35</td>
<td>1</td>
<td>35</td>
<td>1.7-10.8</td>
<td>6.7</td>
<td>2.44</td>
<td>0.011</td>
<td>2.0</td>
<td>3.73</td>
<td>0.01</td>
<td>2.0</td>
<td>3.76</td>
<td>0.007</td>
<td>5.6</td>
</tr>
<tr>
<td>T90-2.3</td>
<td>90</td>
<td>2.3</td>
<td>1.7-10.8</td>
<td>8.4</td>
<td>2.44</td>
<td>0.010</td>
<td>4.8</td>
<td>3.86</td>
<td>0.01</td>
<td>4.5</td>
<td>3.91</td>
<td>0.007</td>
<td>5.8</td>
</tr>
<tr>
<td>T90-7</td>
<td>90</td>
<td>7</td>
<td>1.7-10.8</td>
<td>7.9</td>
<td>2.45</td>
<td>0.011</td>
<td>4.8</td>
<td>3.87</td>
<td>0.005</td>
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<td>3.91</td>
<td>0.01</td>
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<tr>
<td>T90-35</td>
<td>90</td>
<td>35</td>
<td>1.7-10.8</td>
<td>8.2</td>
<td>2.45</td>
<td>0.012</td>
<td>2.0</td>
<td>3.76</td>
<td>0.008</td>
<td>2.5</td>
<td>3.78</td>
<td>0.005</td>
<td>7.1</td>
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<tr>
<td>T270-7</td>
<td>270</td>
<td>7</td>
<td>1.7-10.8</td>
<td>8.1</td>
<td>2.45</td>
<td>0.011</td>
<td>5.6</td>
<td>3.89</td>
<td>0.005</td>
<td>4.8</td>
<td>3.95</td>
<td>0.01</td>
<td>7.3</td>
</tr>
<tr>
<td>T270-35</td>
<td>270</td>
<td>35</td>
<td>1.7-10.8</td>
<td>8.1</td>
<td>2.45</td>
<td>0.010</td>
<td>4.1</td>
<td>3.87</td>
<td>0.004</td>
<td>4.0</td>
<td>3.91</td>
<td>0.006</td>
<td>8.1</td>
</tr>
<tr>
<td>T400-35</td>
<td>400</td>
<td>35</td>
<td>1.7-10.8</td>
<td>7.2</td>
<td>2.44</td>
<td>0.007</td>
<td>3.8</td>
<td>3.87</td>
<td>0.01</td>
<td>3.5</td>
<td>3.95</td>
<td>0.01</td>
<td>5.0</td>
</tr>
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</table>

Additional interatomic distance determined after 400 days reaction time

| T400-35  | 400         | 35                     | 1.7-10.8 | - | - | - | 1.0 | 3.54 | 0.01 | - | - | - | 5.0 | 11.4 |

1 for a-f see Table 2

In the case of the T270-7 and T270-35 samples, for example, the Si and Ca distances were significantly longer than those of the T1-7 and T1-35 samples (e.g., T1-7: R_{Nd-Si} = 3.75 Å, R_{Nd-Ca} = 3.78 Å; T270-7: R_{Nd-Si} = 3.89 Å, R_{Nd-Ca} = 3.95 Å; T1-35: R_{Nd-Si} = 3.73 Å, R_{Nd-Ca} = 3.76 Å; T270-35: R_{Nd-Si} = 3.87 Å, R_{Nd-Ca} = 3.91 Å).

The distances between Nd and neighboring Si and Ca atoms increased with decreasing metal loading in the early stage of Nd binding to tobermorite, but they also increased with longer reaction time irrespective of the Nd loading. Hence, long Nd-Si and Nd-Ca distances were observed in all sample with low Nd loadings (T1-2.3, T90-2.3) and in the aged samples with higher loadings (T90-7, T270-7, T270-35 and T400-35). The Nd-Si and Nd-Ca distances in the aged samples were in the range of bond lengths of reference compounds T-Prec and T-syn14-350 (Table 3), indicating progressive Nd incorporation into the tobermorite structure.

A systematic dependency of the coordination numbers, N_{Si} and N_{Ca}, on Nd loading was less evident from the experimental data. A reduction in the coordination numbers was observed at the highest Nd loadings and prolonged reaction time (T90-7 and T90-35 versus T270-7 and T270-35 samples in Table 3). Nevertheless, no differences in the
coordination numbers was evident for the lower loadings, e.g., between T90-2.3 and T90-7 samples as well as between T270-2.3 and T270-7 samples (Table 3). Note, however, that $N_{Si}$ and $N_{Ca}$ were significantly lower in the samples after one day equilibration ($N_{Si} = 1.7 - 2.2$ and $N_{Ca} = 2.0 - 3.2$ in T1-2.3, T1-7 and T1-35) than in the samples equilibrated for 90 days or longer for which $N_{Si}$ and $N_{Ca}$ were typically $> 4$. The lower coordination numbers in the early stage of Nd binding to tobermorite could indicate predominant formation of Nd surface complexes, while increasing coordination numbers suggested structural binding of Nd in the Ca sheet and/or the interlayer. Overall, the observed coordination numbers of Nd compare well with those of Ca in the Ca sheet of 11 Å tobermorite ($N_{Si} = 5$ and $N_{Ca} = 5-6$).

### 3.4.3 EXAFS of Nd doped xonotlite

Nd doped xonotlite samples were analyzed in the same fashion as the tobermorite samples with the aim of assessing the influence of reaction time and Nd loading (Figure 8, Table 4).

The RSFs of all samples showed a peak at $R + \Delta R = 2.0 \text{ Å}$, corresponding to the contribution of the nearest oxygen shell (Figure 8b), which could be fitted by assuming the presence of a single oxygen shell. The coordination numbers and Nd-O distances for all samples were similar within the experimental uncertainties ($N_{O} = 6.7 - 7.9$; $R_{Nd-O} = 2.44 - 2.45 \text{ Å}$). The Nd-O distances of $\sim 2.41 - 2.43 \text{ Å}$ and coordination numbers of the first oxygen shell of about 6-7 agreed well with those of known Nd-containing silicates ($N_{O} = 6 - 7$; $R_{Nd-O} = 2.41 - 2.43 \text{ Å}$) (CHICHAGOV and BELOV, 1968; SMOLIN and SHEPELEV, 1970).

Presence of further backscattering atoms was indicated by the broad peak in the FTs at $R + \Delta R \sim 3.0 \text{ Å}$, which could be fitted by considering Nd-Si and Nd-Ca backscattering paths. Dependency of the bond distances on Nd loading was also observed for the Nd doped xonotlite as previously found in the Nd doped tobermorite samples. For example, the distances in the X60-7 and X270-7 samples ($R_{Nd-Si} = 3.75$ and 3.84 Å; $R_{Nd-Ca} = 3.81$ and 3.90 Å) were significantly longer than those for the X60-35 and X270-35 samples ($R_{Nd-Si} = 3.71$ and 3.75 Å; $R_{Nd-Ca} = 3.75$ and 3.82 Å).
The early stage of Nd binding was an exception of this trend (e.g., compare data for the X1-7 and X1-35 samples in Table 4).

The increase in bond distances, $R_{\text{Nd-Si}}$ and $R_{\text{Nd-Ca}}$, also coincided with a trend to larger coordination numbers, $N_{\text{Si}}$ and $N_{\text{Ca}}$, which was reflected in the data of the X60-7, X60-35, X270-7 and X270-35 samples (X60-1: $N_{\text{Si}} = 1.2$ and $N_{\text{Ca}} = 1.7$; X60-7/X60-35/X270-7/X270-35: $N_{\text{Si}} = 1.9 - 4.3$ and $N_{\text{Ca}} = 1.9 - 3.1$). Furthermore, as in the case of the tobermorite samples, bond distances increase with increasing reaction time.
Table 4  Structural information obtained from EXAFS Nd \textit{L}_{III}-edge data analysis of Nd doped xonotlite\(^1\).

<table>
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<tr>
<th>Sample</th>
<th>Time (days)</th>
<th>Nd loading (\textmu mol Nd/g)</th>
<th>(\Delta k^4)</th>
<th>(N_0^a)</th>
<th>(R_{\text{Nd-Si}}^c)</th>
<th>(\sigma^2 (\text{Å}^2))</th>
<th>(N_{\text{Si}}^b)</th>
<th>(R_{\text{Nd-Ca}}^c)</th>
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<td>7</td>
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<td>6.9</td>
<td>2.45</td>
<td>0.012</td>
<td>1.2</td>
<td>3.66</td>
<td>0.005</td>
<td>1.7</td>
<td>3.73</td>
<td>0.01</td>
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<td>2.44</td>
<td>0.012</td>
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<td>7</td>
<td>1.7-10.8</td>
<td>7.2</td>
<td>2.44</td>
<td>0.011</td>
<td>3.6</td>
<td>3.75</td>
<td>0.007</td>
<td>2.6</td>
<td>3.81</td>
<td>0.006</td>
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<td>2.44</td>
<td>0.011</td>
<td>1.9</td>
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<td>4.3</td>
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<td>3.1</td>
<td>3.90</td>
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<td>0.009</td>
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<td>3.1</td>
<td>3.82</td>
<td>0.007</td>
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<td>2.45</td>
<td>0.011</td>
<td>4.8</td>
<td>3.85</td>
<td>0.005</td>
<td>3.8</td>
<td>3.91</td>
<td>0.005</td>
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\(^1\)for a-f see Table 2

In the aged Nd doped xonotlite samples \(R_{\text{Nd-Si}} \sim 3.85\, \text{Å} \) and \(R_{\text{Nd-Ca}} \sim 3.91\, \text{Å}\), which was very close to the distances determined for the tobermorite samples and the crystalline Tsyn14-350 sample. \(R_{\text{Nd-Si}} \) and \(R_{\text{Nd-Ca}} \) in the early stage of Nd binding were even shorter than those determined for the tobermorite samples after one day equilibration (e.g., T1-7: \(R_{\text{Nd-Si}} = 3.75\, \text{Å}, R_{\text{Nd-Ca}} = 3.78\, \text{Å}; \) T1-35: \(R_{\text{Nd-Si}} = 3.73\, \text{Å}, R_{\text{Nd-Ca}} = 3.76\, \text{Å}; \) X1-7/X1-35: \(R_{\text{Nd-Si}} = 3.66\, \text{Å}, R_{\text{Nd-Ca}} = 3.73\, \text{Å}\)). As for the tobermorite samples, the coordination numbers were also lower in this phase than in the aged samples (\(N_{\text{Si}} = 1.2, N_{\text{Ca}} = 1.7\)). The early stage of Nd binding was an exception of this trend (e.g., compare data for the X1-7 and X1-35 samples in Table 4).

The increase in bond distances, \(R_{\text{Nd-Si}} \) and \(R_{\text{Nd-Ca}} \), also coincided with a trend to larger coordination numbers, \(N_{\text{Si}} \) and \(N_{\text{Ca}} \), which was reflected in the data of the X60-7, X60-35, X270-7 and X270-35 samples (X60-1: \(N_{\text{Si}} = 1.2 \) and \(N_{\text{Ca}} = 1.7\); X60-7/X60-35/X270-7/X270-35: \(N_{\text{Si}} = 1.9 - 4.3 \) and \(N_{\text{Ca}} = 1.9 - 3.1\)). Furthermore, as in the case of the tobermorite samples, bond distances increase with increasing reaction time. In the aged Nd doped xonotlite samples \(R_{\text{Nd-Si}} \sim 3.85\, \text{Å} \) and \(R_{\text{Nd-Ca}} \sim 3.91\, \text{Å}\), which was very close to the distances determined for the tobermorite samples and the crystalline Tsyn14-350 sample. \(R_{\text{Nd-Si}} \) and \(R_{\text{Nd-Ca}} \) in the early stage of Nd binding were even shorter than those determined for the tobermorite samples after one day equilibration (e.g., T1-7: \(R_{\text{Nd-Si}} = 3.75\, \text{Å}, R_{\text{Nd-Ca}} = 3.78\, \text{Å}; \) T1-35: \(R_{\text{Nd-Si}} = 3.73\, \text{Å}, R_{\text{Nd-Ca}} = 3.76\, \text{Å}; \) X1-7/X1-35: \(R_{\text{Nd-Si}} = 3.75\, \text{Å}, R_{\text{Nd-Ca}} = 3.78\, \text{Å}; \) X1-7/X1-35: \(R_{\text{Nd-Si}} = 3.75\, \text{Å}, R_{\text{Nd-Ca}} = 3.78\, \text{Å}; \) X1-7/X1-35: \(R_{\text{Nd-Si}} = 3.75\, \text{Å}, R_{\text{Nd-Ca}} = 3.78\, \text{Å}\).
= 3.66 Å, $R_{\text{Nd-Ca}} = 3.73$ Å). As for the tobermorite samples, the coordination numbers were also lower in this phase than in the aged samples ($N_{\text{Si}} = 1.2, N_{\text{Ca}} = 1.7$).

### 3.5 Wavelet analysis of the EXAFS spectra

Wavelet analysis of the EXAFS spectra can resolve the $k$ dependence of the absorption signal. A Wavelet diagram shows the ($k$,R) dependence of information derived from an EXAFS spectrum (Munoz et al., 2003). The Morlet Wavelet was used in this study, because of their similarity with the EXAFS signal and the possibility of adapting easily the measured and the calculated spectra using the Morlet parameters $\eta$ and $\sigma$ (Funke et al., 2005). Figure 9 illustrates the overview Wavelet of Nd(OH)$_3$ and the T270-35 sample using $\eta = 7$ and $\sigma = 1$, and a signal weighting of $k^3$.

**Figure 9** Overview Wavelet of selected samples using the Morlet parameters $\eta= 7$, $\sigma = 1$ and a signal weighting of $k^3$; A-B) Nd(OH)$_3$; C-D) T270-35 sample.
The peaks at $R + \Delta R = 2.0$ Å and $k \sim 4.8$ Å$^{-1}$ corresponded to the oxygen coordination shell as already indicated from the EXAFS. Nd(OH)$_3$ showed a well resolved broad peak at $R + \Delta R \sim 4.05$ Å and $k \sim 7.2 - 7.4$ Å$^{-1}$ (Figures 9a and b). The T270-35 sample (Figures 9c and d) exhibited a broad peak at about $R + \Delta R \sim 3.50$ Å and $k \sim 5.5 - 6.4$ Å$^{-1}$, containing scattering contributions from neighboring Ca and Si atoms. The peak at $R + \Delta R \sim 5.6$ Å and $k \sim 7.4$ Å$^{-1}$ in the T270-35 sample did not appear in the Nd doped 11 Å tobermorite sample equilibrated for one day (T35-1) and in the Nd doped xonotlite sample equilibrated for 270 days (X270-35) (figure not shown).

Based on the similarity with the $k$-space range of this contribution in Nd(OH)$_3$ ($k \sim 7.4$ Å$^{-1}$), the peak observed at $R + \Delta R \sim 5.6$ Å in the Nd doped C-S-H samples could be attributed to Nd-Nd backscattering contributions. Thus, Wavelet analysis showed the presence of Nd at $R + \Delta R \sim 5.6$ Å, corresponding to Nd bound in the interlayer of tobermorite, which was not visible from the EXAFS fits.

### 3.6 X-ray powder diffraction analysis of Nd doped 11 Å tobermorite and xonotlite

Powder diffraction allowed identifying possible impurities in the samples. Structural analysis of the Nd doped 11 Å tobermorite and xonotlite samples were completed by Rietveld refinement. X-ray diffraction did not indicate the presence of any other phases, e.g., portlandite or calcite, in the tobermorite and xonotlite samples (Figures 10a and b). The absence of 11 Å tobermorite in the sample of xonotlite indicated complete transition of the former phase during synthesis (SHAW et al., 2000a).

Four strong diffraction lines (002, 020, 022 and 200) dominated the X-ray diffraction pattern of Nd doped 11 Å tobermorite (Figure 10a). After 90 days reaction time the intensity of all reflections decreased and the half-width of the peaks was broadened, indicating that the crystallinity of Nd doped 11 Å tobermorite was reduced at longer reaction time. The first (002) reflection at $2\theta = 7.83$ was shifted towards higher $2\theta$ values after 90 days indicating a shorter $c$ period in the T90-350 sample. The (001) and (200) Bragg peaks are unique to xonotlite (SHAW et al., 2000a) (Figure 10b). Significant changes in the X-ray diffraction pattern of the Nd doped xonotlite were observed compared to the non-doped material.
The intensities of the (102) and (120) peaks at $2\theta = 27.5^\circ$ and $2\theta = 28.93^\circ$ decreased and their half-widths was broadened with time. In contrast, the Bragg peaks at $2\theta = 12.6^\circ$ (001), $2\theta = 31.65^\circ$ (121) and $2\theta = 35.88^\circ$ (220) remained unchanged. The XRD measurements suggested that the crystallinity of xonotlite was reduced and Nd-doped xonotlite turned into a more amorphous material over time.

### 3.6.1 Rietveld refinement of Nd doped 11 Å tobermorite

The 11 Å tobermorite structure is monoclinic (space group $B11m$) with the corresponding unit cell parameters of $a$ (Å) = 6.732, $b$ (Å) = 7.368, $c$ (Å) = 22.680, $\gamma$ (°) = 123.18 (MERLINO et al., 2001). After one day reaction Nd doped tobermorite had shorter $c$ period ($c$ (Å) = 22.513(3)) compared to a non-doped sample (Figure 11). Pattern profile fits revealed that in the samples equilibrated for 14, 30 and 60 days, only the length of the $c$-period slightly changed while $a$ and $b$ varied within the experimental error (pictures not shown).
Both conventional and synchrotron X-rays powder patterns revealed a shorter c-period after 90 days reaction time for Nd doped tobermorite, while a and b remained unchanged.

Difference-Fourier (ΔF) synthesis was applied to locate scattering density missing from the structure model, such as interlayer species or additional atoms in the structure (Figure 12). Strong ΔF peaks in the interlayer and the Ca layers of Nd doped tobermorite were observed in the analysis of the conventional X-rays powder pattern and was supported by the synchrotron data (not shown), indicating that the structure of the Nd doped samples could be analyzed successfully using a conventional X-ray source. Therefore, for the Rietveld refinement the data sets from the conventional X-ray source were used. The observed excess on electron density of 3.6 e⁻ / Å³ was attributed to an additional Nd placed into the interlayer of 11 Å tobermorite (partially occupied).

Figure 11 Pattern profile fits for the samples equilibrated for 1 day and 90 day from measurements with synchrotron and conventional X-rays (measured pattern (black line) and profile fit (red line). In the case of synchrotron data, the modelled pattern is dotted)
The next largest peak occurred in the vicinity of Nd located in the interlayer (2.6 e⁻/Å³) and was attributed to additional oxygen. ΔF of peaks in Ca layers on positions close to those of Ca were observed in Tob90-350 (not shown).

Tables 5 and 6 show the atomic coordinates and the bond distances for T90-350. XRD allows distinction of three different Nd positions. Two of them (Nd1 and Nd3) were located in the Ca sheet, while the third one (Nd2) was within the tobermorite interlayer. In T90-350 the Nd2 position differs from that of Ca in the interlayer (Ca2). The position of Nd in the Ca sheets of T90-350 was slightly shifted by ~0.15 Å - 0.27 Å compared to the initial position of Ca. In this position Nd was surrounded by 7 O atoms at 2.22 Å - 2.73 Å, 4-5 Si atoms at 3.6 Å - 4.1 Å and 5-6 Ca atoms at 3.6 Å - 4.1 Å. In the interlayer of T90-350 Nd was hexa-coordinated by oxygens in the range of 2.22 Å and 2.48 Å. Further, two Si atoms (bridging Si2) and two Ca atoms (interlayer Ca2) were found at short distances (2.67 Å and 2.59 Å) to Nd2. The averaged Nd-Ca distances for Nd from the Ca sheets amounted to $R_{Nd-Ca} = 3.86 - 3.91$ Å.

The refined structure of T90-350 was analyzed by the Bond-Valence (BV) method (BROWN and ALTERMATT, 1985) and supported the findings from the Rietveld refinement, showing that after 90 days reaction time Nd in the interlayer was surrounded

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**Figure 12** Difference-Fourier maps at $y = \frac{1}{2}$, superimposed onto projection of the structure of T90-350 along $a$ ($\alpha = 90^\circ$). The contour interval is 0.30 e⁻/Å³.
by six oxygens at distances between 2.22 Å and 2.48 Å (Table 6). The BV sum of Nd was equal to 3.05, which was very close to its nominal bond valence sum of 3. The calculated bond valence sums of the remaining cations and the anions in the structure of Nd doped tobermorite indicated stability of the structure obtained by our refinement.

*Table 5*  
Atomic coordinates for Nd doped 11 Å tobermorite (350 µmol Nd/g solid phase). Estimated standard deviations (e.s.d.), which refer to the least significant digit, are given in the parentheses.

**11 Å Tobermorite (T90-350)**  
(Structure data from measurements using conventional X-ray source).

\[
a (\text{Å}) = 6.722(3), ~ b (\text{Å}) = 7.365(3), ~ c (\text{Å}) = 22.504(3)
\]

\[\gamma (\text{°}) = 123.15(2), ~ \text{Spacegroup} ~ B \overline{1}m\]

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Table 6  Selected Bond Distances (Å) for T90-350

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<td>Ca1–O10</td>
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<td>Ca3–O4</td>
<td>2.414(15)</td>
<td>Nd2–O11</td>
<td>2.348(24)</td>
<td>Si1–O2</td>
<td>1.677(4)</td>
</tr>
<tr>
<td>Ca1–O4</td>
<td>2.404(11)</td>
<td>Ca3–O9</td>
<td>2.427(18)</td>
<td>Nd2–O5</td>
<td>2.352(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca2–O2</td>
<td>2.245(9)</td>
<td>Nd1–O9</td>
<td>2.226(12)</td>
<td>Nd3–O10</td>
<td>2.322(10)</td>
<td>Si2–O6</td>
<td>1.722(16)</td>
</tr>
<tr>
<td>Ca2–O13</td>
<td>2.383(11)</td>
<td>Nd1–O4</td>
<td>2.331(16)</td>
<td>Nd3–O9</td>
<td>2.364(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca2–O6</td>
<td>2.407(20)</td>
<td>Nd1–O3</td>
<td>2.384(19)</td>
<td>Nd3–O3</td>
<td>2.376(13)</td>
<td>Si3–O4</td>
<td>1.655(11)</td>
</tr>
<tr>
<td>Ca2–O11</td>
<td>2.684(8)</td>
<td>Nd1–O7</td>
<td>2.442(10)</td>
<td>Nd3–O6</td>
<td>2.393(11)</td>
<td>Si3–O3</td>
<td>1.663(5)</td>
</tr>
<tr>
<td>Ca2–O8</td>
<td>2.772(11)</td>
<td>Nd1–O10</td>
<td>2.495(16)</td>
<td>Nd3–O9</td>
<td>2.415(10)</td>
<td>Si3–O1</td>
<td>1.697(12)</td>
</tr>
<tr>
<td>Ca2–O1</td>
<td>2.917(12)</td>
<td>Nd1–O3</td>
<td>2.517(10)</td>
<td>Nd3–O4</td>
<td>2.426(14)</td>
<td>Si3–O2</td>
<td>1.725(14)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nd1–O4</td>
<td>2.733(12)</td>
<td>Nd3–O10</td>
<td>2.488(18)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The refinement of the atomic positions in the case of the Nd doped samples reacted between 1 and 60 days was not successful due to the low amount of Nd incorporated. For these samples only unit cell parameters were refined. Different Nd-O distances were observed if Nd is bound within the Ca layers or the interlayer of T90-350. The mean Nd-O distance in T90-350, which was estimated based on the different occupancies of Nd1, Nd2 and Nd3 was found to be 2.40 Å.

3.6.2 Rietveld refinement of Nd doped xonotlite

In Nd doped xonotlite the changes in the a, b and c periods, compared to values of the non-doped sample, were within the experimental errors. Synthetic xonotlite tends to form polytypes, resulting in varying a and c periodicity (HEJNY and ARMBRUSTER, 2001). This introduces high uncertainties in the experimental derived a and c periods of Nd doped xonotlite. The Rietveld refinement indicated that non-doped xonotlite contained a larger proportion of the basic polytype M2a2bc (CHURAKOV and MANDALIEV, 2008).
### Table 7

*Calculated percentage values for each xonotlite polytype in non-doped and Nd doped xonotlite.*

<table>
<thead>
<tr>
<th>Xonotlite</th>
<th>Cell parameters</th>
<th>Synthetic sample</th>
<th>Natural sample</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M2a2bc</td>
<td>Ma2bc</td>
<td>M2a2b2c</td>
</tr>
<tr>
<td>a [Å]</td>
<td>8.69</td>
<td>8.70</td>
<td>17.68</td>
</tr>
<tr>
<td>b [Å]</td>
<td>7.36</td>
<td>7.35</td>
<td>7.17</td>
</tr>
<tr>
<td>c [Å]</td>
<td>7.03</td>
<td>13.99</td>
<td>7.05</td>
</tr>
<tr>
<td>α</td>
<td>89.53</td>
<td>90.46</td>
<td>90.01</td>
</tr>
<tr>
<td>β</td>
<td>89.59</td>
<td>90.29</td>
<td>90.40</td>
</tr>
<tr>
<td>γ</td>
<td>102.20</td>
<td>102.26</td>
<td>102.27</td>
</tr>
<tr>
<td>Spacegroup</td>
<td>P-1</td>
<td>P2/a</td>
<td>A-1</td>
</tr>
<tr>
<td>non-doped</td>
<td>35%</td>
<td>15%</td>
<td>17%</td>
</tr>
<tr>
<td>1 day</td>
<td>56%</td>
<td>3.5%</td>
<td>16.5%</td>
</tr>
<tr>
<td>90 days</td>
<td>70%</td>
<td>2.9%</td>
<td>5.1%</td>
</tr>
</tbody>
</table>

1 data from this study
2 data from (KALOUSEK et al., 1977)

The data in the present study further suggested that Nd doped xonotlite had a variable polytype composition and the measured percentage values of the different xonotlite polytypes changed with longer reaction times (Table 7).

Such high variation in the polytype composition makes difficult the refinement of the atomic positions. Therefore, only the unit cell parameters and the occupancies of Ca and Nd were refined for sample X90-350, whilst atomic coordinates were adopted from the structure of non-doped xonotlite (HEJNY and ARMBRUSTER, 2001). The Refined unit cell parameters and occupancies for X90-350 are shown in Table B1 in the Supporting Information. The study of Hejny and Armbruster (2001) suggested that determination of the lattice periods and atomic positions in the xonotlite polytypes from strictly geometric principles or by the Order-Disorder (OD) theory may be more precise.

Four different Nd positions (Nd1, Nd2, Nd3 and Nd4) could be distinguished on the assumption that Nd substitutes for Ca in the Ca layers. Note that difference Fourier maps also reveal Nd incorporation in the Ca sheet in the case of Nd doped xonotlite
Nd was seven-fold coordinated to O atoms in the Nd1, Nd3 and Nd4 sites and six fold coordinated in the Nd2 position. Nd bound in the Ca sheet of X90-350 was surrounded by about 4 Si atoms (R_{Nd-Si} = 3.56 Å - 4.05 Å) and 5 Ca atoms (R_{Nd-Ca} = 3.69 Å - 3.82 Å). The mean values of the RNd-Ca distances determined for each Nd position was found to be between R_{Nd-Ca} = 3.77 Å and 3.82 Å.

4. Discussion

4.1 Nd incorporation in the structure of 11 Å tobermorite

A structural model of Nd uptake by 11 Å tobermorite and xonotlite can be proposed based on the XRD investigations on the T90-350 and X90-350 samples. After 90 days reaction time recrystallization, SEM and EXAFS experiments provide experimental evidence for the presence of Nd doped structures for both minerals. The averaged Nd-O and Nd-Ca distances from the Rietveld refinement for tobermorite samples reacted for 90 days (T90-350) agree with those deduced from EXAFS for the samples T90-2.3, T90-7 and T270-35 (Rietveld refinement: R_{Nd-O} ~ 2.40 Å and R_{Nd-Ca} ~ 3.86 – 3.91 Å; EXAFS: R_{Nd-O} ~ 2.44 Å and R_{Nd-Ca} ~ 3.91 Å). The above findings shows that after 90 days and low Nd loadings (2.3 - 7 µmol Nd / g solid phase) and after 270 days and high loading (35 µmol Nd / g solid phase) the large portion of Nd was incorporated in the Ca sheets of C-S-H.

From Rietveld refinement Nd-Nd distances between Nd bound in the interlayer and in the neighboring Ca sheets were determined to be 5.67 Å and 5.89 Å for the Nd1-Nd2 and Nd3-Nd2 pairs, respectively, which agrees well with the Nd-Nd backscattering contributions observed at longer distance (R_{Nd-Nd} ~ 5.6 Å - 5.7 Å) in the Wavelet (Figure 9). The position of Nd in the interlayer is shifted compared to the initial position of Ca (e.g. compare atomic coordinates for Ca2 and Nd2 in Table 5). In this position Nd has two bridging Si atoms (Si2) and two Ca atoms (Ca3) at short distances (2.67 Å and 2.59 Å, respectively), implying that only one site in such a pair could be occupied (either Nd2 or Ca3/Si2). The latter finding further implies that Nd incorporation into the interlayer of tobermorite causes changes in the Ca and Si contents of the interlayer with time. Nd-Nd backscattering contributions resulting from two neighboring Nd atoms located in the Ca
sheets, however, could not be detected by EXAFS as Nd is randomly distributed in the Ca sheets. Thus, the portion of Nd bound in the Ca sheets is not sufficient to give rise to an EXAFS signal above the noise level.

4.2 Nd incorporation in the structure of xonotlite.

In the case of Nd doped xonotlite, difference Fourier maps also revealed Nd incorporation in the Ca sheet (not shown). Nevertheless, the high variation in the polytype composition of Nd doped xonotlite did not allow the refinement of the atomic positions. Therefore, the atomic coordinates were adopted from the structure of non-doped xonotlite on the assumption that Nd was bound in the Ca layers. The average $R_{\text{Nd-Ca}}$ distances range in value between $R_{\text{Nd-Ca}} = 3.77$ Å and $3.82$ Å, which agrees with distances obtained from EXAFS in some Nd doped xonotlite samples (X60-7 and X270-35: $R_{\text{Nd-Ca}} = 3.81$ Å - 3.82 Å). The longer Nd-Ca distances observed in the samples X270-7 ($R_{\text{Nd-Ca}} = 3.90$ Å) and X400-35 ($R_{\text{Nd-Ca}} = 3.91$ Å) could not be reproduced. At the present time there is no conclusive explanation for this finding. Interestingly, the latter distances agree with those determined in Nd doped tobermorite samples equilibrated for 270 days and longer, suggesting similar coordination environments for Nd in both crystalline C-S-H phases after prolonged reaction time.

The distance of neighboring Nd atoms was estimated to be $R_{\text{Nd-Nd}} \sim 3.85$ Å on the assumption that Nd is not randomly distributed in the Ca sheets and all Ca positions can be occupied by Nd. Nevertheless, such short distances could not be observed by EXAFS, indicating that, as for tobermorite, Nd is randomly distributed in the Ca sheets of xonotlite. The absence of long Nd-Nd distances in the Wavelet analysis of Nd doped xonotlite is considered to be due to the absence of an interlayer. Nd-Nd backscattering contributions from Nd atoms bound in adjacent Ca sheets are not visible as the shortest Nd-Nd distance is 7.03 Å, which cannot be resolved by the Wavelet method (SAHNOUN et al., 2007).

4.3 Charge compensation mechanism in 11 Å tobermorite and xonotlite

The two mechanisms for Nd$^{3+}$ incorporation in tobermorite and xonotlite, namely incorporation in the interlayer space and substitution for Ca$^{2+}$ in the Ca-layer, requires
more detailed consideration of the charge balance in the structure. Due to similarities in the ionic radii, Nd$^{3+}$ is able to occupy Ca$^{2+}$ positions, which induces positive charge in the structure. In the interlayer of tobermorite Ca$^{2+}$ is coordinated to four water molecules. The de-protonation or hydroxylation of the Nd$^{3+}$ hydration shell could be the charge compensation mechanism in the early stage of Nd incorporation (after 1-60 days) in the interlayer of tobermorite. Nd-Ca replacement in the structure can be expressed in a simplified manner by Ca$^{2+}$ + H$_2$O ⇋ Nd$^{3+}$ + OH$^-$. As previously mentioned Nd uptake gives rise to the removal of bridging Si-tetrahedra (Q$^3$ sites), causing defect formation in both xonotlite and tobermorite. Continuous increase of the Si concentration in solution was observed in both cases (Table 8). After prolonged reaction time (90 days), the interlayer Nd in the tobermorite structure is preferentially located near dissolved Q$^3$ sites, as indicated from the XRD measurements. Preferential formation of Si defects in Q$^3$ sites of double tetrahedral chain of C-S-H phases and xonotlite was recently confirmed by ab initio density functional theory calculations and NMR observations (Churakov and Mandaliev, 2008; Cong and Kirkpatrick, 1996a; Cong and Kirkpatrick, 1996b). Furthermore, the Ca$^{2+}$ sites in the Ca-layer of xonotlite and tobermorite that are preferentially replaced by Nd$^{3+}$ are the ones adjacent to the bridging Si tetrahedra. Based on these observations the Ca-Nd exchange process can be expressed in a simplified manner as follows: Ca$^{2+}$ + Si$^{4+}$ ⇋ Nd$^{3+}$ + 3H$^+$. The protons involved in the reaction could protonate oxygen sites of the terminal Si tetrahedra, which are formed at positions of Q$^3$ defects. A small portion of Ca sites in the Ca-layer of xonotlite and tobermorite is coordinated by H$_2$O molecules or OH groups. A possible substitution mechanism for these sites is a Ca/H - Nd exchange process.

The earlier study of (Ronsbo, 1989) suggested a coupled substitution according to 2Ca$^{2+}$ ↔ Na$^+$ + Nd$^{3+}$ as a possible exchange mechanism for trivalent lanthanides in natural systems. As the concentration of alkalis, in particular Na$^+$, is negligible in the systems used in this study, it is very unlikely that the above mechanism takes place.

4.4 Influence of Nd loadings on Nd incorporation

The formation of any solid phase with fixed stoichiometry could be ruled out irrespective of Nd loading and reaction time. Wet chemistry data indicate that the Nd
concentration is not controlled by a solubility-limiting phase with fixed stoichiometry, in particular Nd(OH)₃(s). This would imply constant Nd concentrations in solution.

The absence of Nd(OH)₃(s) was further corroborated by the EXAFS data, which showed that the spectra of Nd doped 11 Å tobermorite and xonotlite and the resulting structural parameters are different from those of Nd(OH)₃ (compare Figures 6-8 and structural data in Tables 2-4). In particular, there is no evidence for Nd-Nd distances at 4.15 Å, which is typically observed in Nd(OH)₃ (BEALL et al., 1976). Thus, in agreement with the earlier studies of POINTEAU et al. (2001), TITS et al. (2003) and SCHLEGEL et al. (2004), the above findings provide no compelling evidence for precipitation of pure hydroxide phases or any other solid phase with fixed stoichiometry in alkaline C-S-H systems.

Formation of a precipitate intermixed with xonotlite was observed at high Nd loadings (~350 μmol Nd/g) in the SEM analysis (Figure 5). This phase seems to be metastable as it was found to be visibly absent in the SEM images after 90 days reaction time. SEM imaging did not indicate formation of an Nd-containing secondary precipitate on Nd doped tobermorite at high Nd loading.

Table 8  Composition of the supernatant solution of Nd doped 11Å tobermorite and xonotlite samples (Nd loading = 350 μmol Nd / g solid phase). Uncertainties on the measurements were estimated to be ~20%.

<table>
<thead>
<tr>
<th>Reaction time (days)</th>
<th>Tobermorite</th>
<th>Xonotlite</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca (μg/ml)</td>
<td>Si (μg/ml)</td>
</tr>
<tr>
<td>1 day</td>
<td>68</td>
<td>1.3</td>
</tr>
<tr>
<td>14 days</td>
<td>107</td>
<td>2.13</td>
</tr>
<tr>
<td>30 days</td>
<td>106</td>
<td>2.33</td>
</tr>
<tr>
<td>60 days</td>
<td>105</td>
<td>2.43</td>
</tr>
<tr>
<td>90 days</td>
<td>109</td>
<td>3.75</td>
</tr>
<tr>
<td>non-doped</td>
<td>125</td>
<td>1.49</td>
</tr>
</tbody>
</table>
Determination of the composition of the supernatant solutions of Nd doped tobermorite and xonotlite, however, indicate significant changes in the Nd, Ca and Si concentrations compared to the non-doped C-S-H systems (Table 8). After one day of reaction time Ca and Si concentrations were found to be strongly reduced in both systems. This finding suggests that an Nd-containing precipitate also formed in the tobermorite system. This phase, however, seems to be intermixed with the host phase and therefore, was not detectable by SEM imaging (Figure 5b-d). Increasing Ca and Si concentrations between one and 14 days in both systems, and decrease of the Nd concentration over the time period up to 90 days, could be interpreted in terms of progressive Nd incorporation in the C-S-H structures (Table 8). Ongoing Nd uptake could give rise to the formation of a solid phase with equilibrium solution activities different from that of non-doped tobermorite (solid solution). Formation of lanthanide-containing co-precipitates in C-S-H systems was previously reported by (SCHLEGER et al., 2004). These authors investigated Eu(III) binding to amorphous C-S-H phases at similar metal loadings (35 - 450 µmol Eu/g of C-S-H) and interpreted their observations in terms of co-precipitation of Eu with Ca and Si to form a C-S-H like solid phase. Though co-precipitation controls Nd binding to C-S-H phases at high Nd loadings SEM images provided no compelling evidence for the formation of a secondary precipitate at low Nd loadings. Nevertheless, lack of visible formation of a co-precipitate still discloses the possibility of solid solution formation.

4.5 Influence of reaction time on the Nd incorporation

Nd uptake experiments with 11 Å tobermorite and xonotlite were designed in a fashion to allow formation of different Nd species in the C-S-H systems. This was achieved by instantaneous addition of Nd. Due to the chosen experimental approach, the presence of the following Nd species can be envisaged: Nd bound in precipitates with fixed and variable (solid solution) stoichiometries, formation of Nd surface complexes (outer and inner sphere) and Nd incorporated in the C-S-H structure. Previous investigations showed only minor variations in the coordination environment of Eu in Eu doped C-S-H phases upon instantaneous (i.e., oversaturation with respect to Eu(OH)₃) or incremental (i.e., undersaturation with respect to Eu(OH)₃) lanthanide addition.
In this study the X-ray diffraction and EXAFS measurements allowed changes in the Nd speciation to be monitored as a function of reaction time and Nd loading.

Inner- and outer-sphere surface complex formation could dominate Nd binding to the crystalline C-S-H phases at short reaction times. Metal surface complexes show distinct coordination environments which are reflected in the structural parameters of the nearest neighboring atoms (Duff et al., 2004). Outer-sphere coordination implies that Nd binds to C-S-H phases with intact hydration shell and the Nd-O bond distances should compare well with those of the aqueous Nd species (Park et al., 2006). Nd-O bond distances in the latter species were reported to be about 2.49 - 2.50 Å (D'AngeLO et al., 2001), which is significantly larger than the first-shell Nd-O distances in Nd doped 11 Å tobermorite and xonotlite (R_{Nd-O} = 2.44 - 2.45 Å; Table 3). Furthermore, the coordination number of the first oxygen shell was determined to be 6.7 - 8.1, which is lower than that of the aqueous Nd species (N_O ~ 9.1; D'AngeLO et al., 2001). Thus, the observed structural parameters are not consistent with outer-sphere surface complexation but rather suggest inner-sphere coordination. Inner-sphere surface complexation is further supported in view of the structural parameters determined for the second and third shells of neighboring atoms (Tables 3 and 4). After one day of reaction time the number of neighboring Ca and Si atoms was low, i.e., N_{Ca} and N_{Si}, respectively, in the range between 1 and 3. This is indicative of predominant formation of surface bound Nd species in this early stage of Nd uptake by the C-S-H phases. Nevertheless, incorporation of small amounts of Nd into the interlayer of 11 Å tobermorite is supported by the partial collapse of the interlayer after one day reaction time. Therefore, at least two species (inner-sphere surface complex, Nd species in the interlayer) contribute to the EXAFS signal in the case of 11 Å tobermorite, whereby the main contribution originates from Nd binding via inner-sphere surface complexes.

X-ray diffraction analysis carried out on samples with high Nd loadings (e.g. 350 μmol Nd/g) and EXAFS measurements in combination with Wavelet analysis on samples with low Nd loadings (EXAFS: 2.3 -35 μmol Nd/g; Wavelet: 35 μmol Nd/g) provide clear evidence for Nd incorporation into the structures of 11 Å tobermorite and xonotlite after prolonged reaction time. This inference is in line with the earlier studies of...
POINTEAU et al. (2001), TITS et al. (2003) and SCHLEGEL et al. (2004), which suggested Eu-Ca substitution in the structure of amorphous C-S-H phases. Nd-Ca substitution is due to similarity of the ionic radii of the two elements in sixfold coordination (0.983 Å and 1.00 Å, respectively) (SHANNON, 1976). The number of neighbouring Si (N_{Si}) and Ca (N_{Ca}) atoms and bond distances reflected the extent of Nd incorporation, which depends on reaction time. In general, for reaction times longer than 60 days N_{Si} typically ranges in value between 3 and 6 in both crystalline C-S-H phases. Low coordination numbers (N_{Si} = 3-4) usually coincide with short Nd-Si distances (R_{Nd-Si} ~ 3.75 Å) while high coordination numbers (N_{Si} = 4-6) coincide with long Nd-Si distances (R_{Nd-Si} ~ 3.85 Å). In the case of neighboring Ca atoms, the situation is different for the two crystalline C-S-H phases and after long reaction times. In Nd doped 11 Å tobermorite typically between 3 and 5 nearest neighboring Ca atoms were observed at R_{Nd-Ca} ~ 3.90 - 3.95 Å. While distances are comparable in the Nd doped xonotlite the number of neighboring Ca atoms is significant lower (N_{Ca} = 3-4). The experimental EXAFS parameters can be assessed based on the 11 Å tobermorite structure proposed by (MERLINO et al., 2001). Ca from the central Ca sheet is surrounded by 7 oxygens at distances R_{Ca-O} = 2.3 - 2.6 Å, 3 - 4 Si at R_{Ca-Si} = 3.6 - 3.7 Å and ~5 Ca at R_{Ca-Ca} = 3.8 - 3.9 Å. Ca in the interlayer is surrounded by 6 - 7 oxygens (R_{Ca-O} = 2.4 - 2.8 Å), 2 - 3 Si (R_{Ca-Si} = 3.2 - 3.6 Å), about ~2 Si (R_{Ca-Si} = 4.2 - 4.3 Å), one Ca atom (R_{Ca-Ca} = 4.0 Å) and 3 Ca at long distance (R_{Ca-Ca} = 5.40 Å). Therefore, our observation of 3 to 5 nearest neighboring Ca atoms at R_{Nd-Ca} ~ 3.90 - 3.95 Å clearly indicates that Nd was predominantly bound in the Ca sheets (maximum 5 Ca at R_{Ca-Ca} = 3.80 - 3.96 Å) of tobermorite after prolonged reaction time. A hypothetical Nd incorporation solely in the interlayer in the long term could not explain the observed coordination number (N_{Ca} = 3 - 5).

In xonotlite Ca in the Ca sheets is surrounded by 6 - 7 oxygens (R_{Ca-O} = 2.38 - 2.46 Å), 3 - 4 Si (R_{Ca-Si} = 3.6 - 3.7 Å) and 5 - 6 Ca (R_{Ca-Ca} = 3.7 - 3.8 Å). Therefore, N_{Ca} = 3-4 as determined from EXAFS indicate that the large portion of Nd is bound in the Ca sheets of xonotlite. Nevertheless, a small but noticeable portion of Nd surface complexes seems to be still present after prolonged reaction time, which explains the lower number of nearest neighboring Ca atoms observed by EXAFS. Thus, the structural parameters of
neighbouring Ca seem to be more strongly influenced by changes in the Nd speciation compared to those of neighboring Si atoms. The coordination environment of Nd taken up by 11 Å tobermorite and xonotlite after long reaction times (> 60 days) can be compared with those determined for hydrothermally synthesized Nd doped tobermorite (Tsyn14-350) (see structural data in Tables 2, 3 and 4), which constitutes a structurally well ordered coordination environment of Nd in crystalline C-S-H phases. The numbers of nearest oxygen and Si atoms as well as Nd-O and Nd-Si distances of Tsyn14-350 compound and the Nd doped C-S-H phases are in excellent agreement. Nonetheless, the number of neighboring Ca atoms is higher in Tsyn14-350 than in Nd doped 11 Å tobermorite and xonotlite, thus implying that a higher portion of Nd is bound in the Ca sheets of Tsyn14-350 than in both Nd doped 11 Å tobermorite and xonotlite.

5. Conclusions

The Nd concentration in the Nd containing C-S-H systems is not controlled by a solubility-limiting phase with fixed stoichiometry although the total Nd concentration in these systems exceeded the solubility product with respect to Nd(OH)_3. Wet chemistry data indicate formation of a secondary precipitate in both crystalline C-S-H systems within the first day of equilibration. Formation of a secondary precipitate (“metastable” precipitate) was observed on xonotlite at high Nd loadings (350 μmol / g). However, this phase was not visible in the long-term experiments and at low Nd loadings. From SEM imaging, no evidence for solid phase formation was found on Nd doped 11 Å tobermorite. At low Nd loadings several Nd species formed on xonotlite and tobermorite. Changes in the relative fraction of Nd species could be assessed from variations in the EXAFS structural parameters. Nd was predominantly bound on the external surface of the crystalline C-S-H phases after one day of reaction time. Nd incorporation by recrystallization was the dominant process at decreasing Nd loading and over prolonged periods of time due to Nd-Ca replacement in the interlayer and Ca sheets. Nd uptake in the interlayer dominated in the short-term experiments. In the interlayer of 11 Å tobermorite Nd was incorporated on positions, which differ from those of the interlayer Ca. In the long-term experiments Nd binding in the Ca sheets of both crystalline C-S-H
phases dominated. Nd uptake. Nd incorporation caused the release of bridging Si tetrahedra and the formation of disordered structures. The binding mechanisms for Nd proposed in this study could provide the basis for a mechanistic interpretation of the immobilization of lanthanides and trivalent actinides in crystalline and amorphous C-S-H phases.
6. References


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Supporting Information to Chapter 3

Part A

Three different fitting models with the corresponding crystallographic R-factors as obtained from ATHENA/ARTEMIS were used for the F-tests. The R-factor measures the misfit between modeled and experimental Fourier transformed (FT) spectra. The square root of the calculated R-factor in ATHENA/ARTEMIS is given here as R as suggested elsewhere (DOWNWARD et al., 2007). In order to simplify the discussion, the crystallographic R-factors for the fits using models (1) and (2) were labeled as $R_i$ and the crystallographic R-factor for the fits using model (3) was labeled as $R_0$.

*Model (1)*: Fitting the EXAFS data using a oxygen shell at $R + \Delta R \sim 2.4 \text{ Å}$ and a Si shell at $R + \Delta R = 3.7 - 3.75 \text{ Å}$.

*Model (2)*: Fitting the EXAFS data using a oxygen shell at $R + \Delta R \sim 2.4 \text{ Å}$ and a Ca shell at $R + \Delta R = 3.75 - 3.8 \text{ Å}$

*Model (3)*: Fitting the EXAFS data using a oxygen shell at $R + \Delta R \sim 2.4 \text{ Å}$, a Si shell at $R + \Delta R = 3.7 - 3.75$ and a Ca shell at $R + \Delta R = 3.75 - 3.8 \text{ Å}$.

The confidence level, $\alpha$, that a fit that yields a crystallographic $R$-factor $R_0$ is a better fit than the fit that yields a residual $R_i$ can be calculated (BACCHI et al., 1996; DOWNWARD et al., 2007; HAMILTON, 1965) according to equation (1):

$$\alpha = P(F > F_{b,n-m,\alpha}) = 1 - I_x \left[ \frac{n-m}{2} \frac{b}{2} \right]$$

, where $P$ represents the probability (in %), $I_x \left[ \frac{n-m}{2} \frac{b}{2} \right]$ is the incomplete regularized beta function, the parameter $x$ is given by

$$x = \left( \frac{R_0}{R_i} \right)^2$$

, $b$ is the difference in the degrees of freedom between the fits, which were compared; $n$ is the number of independent data points as calculated by the Stern’s rule (STERN, 1993) and $m$ is the number of fit parameters. Model (3) has 8 independent parameters, that are coordination number, CN (3 parameters), and bond-distances (3 parameters) of the oxygen, Si and Ca shells, DW
factor of the oxygen shell (1 parameter) and the correlated $E_0$ (1 parameter). The models (1) and (2) have each 6 independent parameters, that are CN (2 parameters) and bond-distances (2 parameters) of the oxygen, Si or Ca shells, DW factor of the oxygen shell (1 parameter) and the correlated $E_0$ (1 parameter). The maximum number of free parameters describing the signal was estimated by applying the Stern’s rule in the chosen windows in the $k$- and $R$ spaces, $N_{\text{Ind.}} = 2\Delta k\Delta R/\pi + 2$, where $N_i$ is the number of relevant independent points, $\Delta k$ is the range of $k$-space being fit, and $\Delta R$ is the width of the characteristic frequency in the FT. For this study the fits were performed in the $k$-range of the Fourier transform of $\Delta k = 1.40 - 10.60$ Å$^{-1}$ and the $R$-range for the fit was $\Delta R = 1.25 - 4.0$. The maximal number of components (or free parameters) describing the EXAFS signal was estimated to be 16.1. In no case did the number of parameters that were varied during fitting procedure exceed the limit given by the Stern’s rule.

The significance of statistical F-tests can be illustrated on the basis of the Nd doped tobermorite sample equilibrated for 90 days (T90-350). When each data set is fit individually using WinXas 3.1 software package (i.e. fits assuming models (1), (2) and (3), respectively) the values for $R_0$ (model (3)) corresponded to 0.098 and the values for $R_1$ (models (1) and (2)) corresponded to 0.110 to 0.112 (Figure A1).

![Figure A1](image)

**Figure A1** Nd $L_{\text{III}}$-EXAFS of Nd doped tobermorite 90 days reaction time and 35 $\mu$mol/g Nd loading; RSFs of experimental (solid line) and fitted (dashed and dotted lines for the imaginary and the amplitude envelope, respectively) obtained from the fits using (a) oxygen, Ca and Si shells; (b) oxygen and Si shells; (c) oxygen and Ca shells.
The latter residual factors (or crystallographic R-factors) are very similar and optical evaluation of the fits is not possible, as there are very similar (Figure A1).

When each data set is fit individually with ATHENA/ARTEMIS, the values for $R_0$ (model (3)) corresponded to 0.03 and the values for $R_1$ (models (1) and (2)) corresponded to 0.04 to 0.06. Note that the crystallographic R-factor from ATHENA/ARTEMIS is appropriate for statistical tests, as the squared value of the experimental and theoretical data points is used (DOWNWARD et al., 2007). Thus, using $n - m = 8.1$, where n is the maximum number of free parameters as calculated by the Stern’s rule, m is the number of fit parameters used for the fit with crystallographic R-factor $R_0$ (fit assuming model (3)), and $b = 2$ (b is the difference in the number of free parameters of the fits being compared, i.e. fits resulting in crystallographic R-factors $R_0$ and $R_1$) in Eqn. (1) yielded confidences of 73 % and 99% that the fit using model (3) is a better fit than the fits with models (1) and (2), respectively. Using the EXAFS data for Nd doped tobermorite and xonotlite from this study, the fits using model (3) yielded confidences of 71 % to 91 %, and 83 % to 99 % that the fit using model (3) is a better fit than the fits with models (1) and (2), respectively. In most cases, the fits using model (3) yielded a better R-factors than those using model (2) and a high confidence level was calculated (up to 99 %), suggesting that the presence of Ca atoms at longer distances does improve the fitting. In the case of model (1) the confidence was below 95%, and we cannot definitively conclude from this data that the fit assuming neighbouring Ca and Si is better than that with only Si. Nevertheless, additional justification for the presence of Ca can be given from structural arguments. To this aim, the structure of non-doped 11 Å tobermorite was considered and assumed to be an suitable model for poorly ordered C-S-H (e.g. RICHARDSON, 2004; TAYLOR, 1986; Introduction in this Chapter and in Chapter 4).

The layered structure of tobermorite is built up of sheets of seven coordinated Ca polyhedra, which are condensed by wollastonite-type silicate chains on both sides (Figure 5). In the tobermorite structure each Ca position is surrounded by both Si and Ca atoms. Because the ionic radius of Nd$^{3+}$ (0.983Å in sixfold coordination) is comparable to that of Ca$^{2+}$ (1.00 Å and 1.07 Å for six- and sevenfold coordination, respectively) (SHANNON, 1976), Nd could substitute for Ca in the structure of C-S-H phases. Assuming Nd-Ca
replacement in the crystal structures of 11 Å tobermorite at Ca positions in the Ca sheets results in Nd - O, Nd - Si and Nd – Ca distances of $R_{\text{Nd-O}} \sim 2.37 - 2.46$ Å, $R_{\text{Nd-Si}} \sim 3.65 - 3.85$ Å and $R_{\text{Nd-Ca}} \sim 3.7 - 3.9$ Å. Note that lanthanides and trivalent actinides incorporation (e.g. Eu(III) and Cm(III)) into the Ca sheets of C-S-H was already suggested from previous studies (Tit et al., 2003, Schlegel et al., 2004). The latter finding is in agreement with the proposal that neighbouring Si atoms have to be included in the fitting and therefore supports EXAFS data fitting using model (3). Based on the crystallographic data on non-doped crystalline C-S-H and the results from the F-test, we assumed that a model, which includes three shells (i.e., O, Si and Ca atoms) as in model (3), is suitable to reproduce backscattering contributions from neighboring atoms in the structure of C-S-H phases. This model was also applied recently in EXAFS investigation of Eu(III) taken up by amorphous C-S-H phases (Schlegel et al., 2004).
Part B

*Table B1*  Refined unit cell parameters and occupancies for X90-350 (atomic coordinates were adopted from non-doped xonotlite).

**Xonotlite (X90-350)**

\[ a (\text{Å}) = 8.714(3), b (\text{Å}) = 7.34(2), c (\text{Å}) = 7.031(3) \]

\[ \alpha (^\circ) = 89.76 (2), \beta (^\circ) = 90.16(2), \gamma (^\circ) = 102.07(2), \text{ Spacegroup } P-1 \]

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CHAPTER 4

EXAFS study of Nd (III) uptake by amorphous calcium silicate hydrates (C-S-H)

ABSTRACT

Calcium silicate hydrate (C-S-H) phases control the immobilization of many metal cations in cementitious materials. In this study Nd binding to C-S-H phases, which have different C:S ratios, and which had been aged up to 270 days, has been investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy. The results from EXAFS were compared with a theoretical model, which was based on bond-valence calculations. The study revealed that Nd could form several species in contact with C-S-H phases. The EXAFS parameters determined in samples after one day of reaction indicated the formation of inner-sphere surface complexes. The EXAFS data further indicated increased numbers of neighboring Si and Ca atoms in the Nd treated C-S-H. Nd incorporation into the structures of C-S-H phases was proposed based on the observed bond-distances from EXAFS. After prolonged reaction times (≥ 45 days) Nd was predominantly incorporated into the Ca sheets of the C-S-H structure while small portions of Nd were also taken up by the interlayer. The results indicated that, in the long term, amorphous C-S-H phases were capable of taking up Nd via exchange processes with Ca\(^{2+}\) in the Ca sheets and the interlayer of the C-S-H structure. The results from this study were essential for a detailed understanding of the binding mechanisms of trivalent actinides in amorphous C-S-H phases due to chemical similarity of trivalent lanthanides and actinides.
1. Introduction

Cement stabilization of contaminated wastes is one of the most common solidification/stabilization (S/S) techniques prior to near-surface or underground disposal. Mixing toxic and radioactive waste products into a cementitious binder system improves the stabilization and the solidification of waste materials and significantly retards the release of metal cations and anions, which are bound in the waste matrix (CHAPMAN and McCOMBIE, 2003). Cement-stabilized radioactive waste is preferentially disposed in deep underground repositories. The latter waste form may contain significant inventories of trivalent actinides, such as $^{241/243}$Am(III). Trivalent actinides such as $^{241/243}$Am are safety relevant radionuclides and therefore, a detailed understanding of the binding mechanisms of trivalent actinides in hardened cement paste (HCP) is essential for long-term assessments of the safe disposal of radioactive waste. At present, however, these mechanisms are only poorly understood on the molecular level.

Trivalent lanthanides e.g., Eu(III) and Nd, are regarded as suitable chemical analogues for trivalent actinides based on their comparable ionic radii and similarities in the complexation behaviour (SHANNON, 1976). Calcium silicate hydrate (C-S-H) phases are considered to be particularly important in governing immobilization processes in cementitious materials, because they are the main constituent of fresh and degraded cement (~50 wt%) (ATKINS and GLASSER, 1992). Due to their stability during the evolution of the cementitious near field, C-S-H phases may control the long-term release of radionuclides (BERNER, 1992). The structure and chemistry of amorphous C-S-H phases, $x$CaO-SiO$_2$$\cdot$$y$H$_2$O ($x =$ calcium-to-silica (C:S) mol ratio), which is closely related to those of the minerals of the tobermorite group (e.g. 14 Å tobermorite: Ca$_5$Si$_6$O$_{16}$(OH)$\cdot$7H$_2$O and 11 Å tobermorite: Ca$_5$Si$_6$O$_{17}$$\cdot$5H$_2$O) (CHEN et al., 2004; MERLINO et al., 2001; RICHARDSON, 2004) consists of a layers of seven-coordinated Ca polyhedra bound to wollastonite-type silicate chains on both sides. An important feature of the structure of tobermorite is the cavity between two adjacent building layers, the “interlayer space”, which is more pronounced at low C:S ratios and may contain water and calcium cations (BONACCORSI et al., 2005; MERLINO et al., 1999; MERLINO et al., 2001). Thus, the structure of poorly ordered amorphous C-S-H phases can be envisaged as an imperfect tobermorite structure with many irregularities (BRUNET et al., 2004;
Calcium silicate hydrates exhibit a large number of structural sites available for cation and anion binding (Gougar et al., 1996). The study of Tits et al. (2006) showed that C-S-H phases are capable of taking up bivalent cations, e.g. Sr$^{2+}$ via exchange processes with Ca$^{2+}$. The influence of the C:S ratio on the uptake of trivalent lanthanides, such as Eu(III) and Nd, by C-S-H phases is poorly known. Only few studies have addressed their retention behavior on amorphous C-S-H phases (e.g. Pointeau et al., 2001; Schlegel et al., 2004). Eu(III) uptake by C-S-H phases with varying C:S ratios (0.34 - 1.65) was investigated using time-resolved laser fluorescence spectroscopy (TRLFS) (Pointeau et al., 2001). The authors determined two types of Eu(III) species with different fluorescence lifetimes (390 and 990 $\mu$s). The species with the short lifetime was believed to reflect either formation of a surface precipitate or complexation to C-S-H surface sites. The long lifetime indicates presence of a second, de-hydroxylated Eu(III) species, which was assumed to be Eu(III) bound in the Ca sheet of C-S-H. Schlegel et al. (2004) postulated that Eu(III) replaces Ca$^{2+}$ in the Ca sheets and interlayer of C-S-H phases using extended X-ray absorption fine structure (EXAFS) spectroscopy. The study further indicates possible precipitation of a Eu(III)-containing C-S-H-like phase (surface precipitate) on the basis of Eu(III) solubility limits determined from co-precipitation experiments. In a recently TRLFS study with Cm(III), three different species could be distinguished upon Cm(III) binding to a C-S-H phase (C:S ratio = 1.07) aged for 119 days. Based on crystallochemical considerations using the defect 11 Å tobermorite structure as model the authors concluded that two Cm(III) species were bound in the structure of amorphous C-S-H by substituting Ca$^{2+}$ in the Ca sheets and in the interlayer. The third species detected in the study was attributed to the presence of Cm(OH)$_3$.

In this study Nd binding to C-S-H phases, which had different C:S ratios and Nd loadings, and which had been aged up to 400 days, were investigated using EXAFS spectroscopy. Over the last years the latter technique has been successfully applied to investigate immobilization processes in C-S-H and cementitious systems on the molecular scale (e.g. Bonhoure et al., 2003; Harfouche et al., 2006).
2. Materials and Methods

2.1 Synthesis of Calcium Silicate hydrates (C-S-H)

Throughout this study Fluka (Sigma-Aldrich, Buchs, Switzerland) or Merck (Dietikon, Switzerland) “pro analysis” chemicals and high-purity de-ionised water generated by a Milli-Q Gradient A10 system (Millipore, Bedford, USA) were used. All experiments were carried out in a glovebox under N₂ atmosphere and ambient temperature (CO₂, O₂ <2ppm, T = 290 K ± 3 K). C-S-H phases with varying C:S ratios (C:S = 0.56, 0.87 and 1.54) were synthesized as described in detail elsewhere (Titte et al., 2006).

2.2 Preparation of the EXAFS samples

The Nd doped C-S-H samples used for the EXAFS study had different Nd loadings and were equilibrated over varying periods of time (1, 45 and 270 days). The samples were prepared as follows: 35 mL aliquots of the vigorously stirred stock suspensions (50 g L⁻¹ solid materials in equilibrium solution) were pipetted into 40 mL polyallomere centrifuge tubes and aged for one week on an end-over-end shaker. Appropriate volumes of the Nd stock solution (10⁻³ M) were added to the suspensions to achieve the required Nd loadings on the solids. The pH values of the equilibrium suspensions were measured with a Metrohm combination electrode. The pH values were estimated to be typically in the range 10.1(5) and 12.2(5) in all C-S-H samples. No changes in pH were observed after adding Nd solution. The samples were equilibrated on the end-over-end shaker in the glovebox and sampled after the time intervals indicated above.

In addition to the Nd doped C-S-H samples Nd doped Ca(OH)₂ and Nd doped SiO₂ (Aerosil) were prepared. Based on thermodynamic modeling presence of amorphous silica intermixed with tobermorite could be expected at C:S <0.6 while portlandite intermixed with tobermorite is expected at C:S >1.6 (Kulik and Kersten, 2001). The samples of Nd doped Aerosil and portlandite were prepared by mixing 1 g of SiO₂ and Ca(OH)₂ powder material with 35 mL Milli-Q water. Appropriate aliquots of the Nd
stock solution (10\(^{-3}\) M) were added to the suspensions to achieve the required Nd loadings on the solids. The samples were then equilibrated for one day.

After phase separation by centrifugation (60 min at 95000 \(g\)) all samples were packed as a wet paste into Plexiglas sample holders and sealed with Kapton tape for the EXAFS measurements.

### 2.3 EXAFS data collection and reduction

EXAFS spectra at the Nd L\(_{\text{III}}\) edge (6208 eV) were collected at beamline BM26A (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France and on the ANKA-XAS beamline of the Angstroemquelle Karlsruhe (ANKA), Germany. Both beamlines are equipped with a Si (111) double-crystal monochromator. The monochromator angle was calibrated by assigning the energy of 5989 eV to the first inflection point of the K-absorption edge of a Cr metal foil. The EXAFS measurements were conducted at room temperature in fluorescence mode using the nine-element Ge solid-state detector at DUBBLE/ESRF and the five-element Ge solid state detector at the ANKA-XAS. For each sample and dependent on the Nd loading, between three and seven spectra were collected to reach the required signal-to-noise ratio.

EXAFS data reduction was performed by using the WinXAS 3.11 software package and following standard procedures (Ressler, 1998). After background subtraction, the energy was converted to photoelectron wave vector units (Å\(^{-1}\)) by assigning the ionization energy of the Nd L\(_{\text{III}}\)-edge (6208 eV), \(E_0\), to the first inflection point of the absorption edge. Radial structure functions (RSFs) were obtained by Fourier transforming \(k^2\)-weighted \(\chi(k)\) functions typically in the range 1.4 - 10.6 Å\(^{-1}\) using the Kaiser-Bessel window function with a smoothing parameter of 4. Single-shell fits were performed in real space across the range of the first and second coordination shell (\(\Delta R = 1.25 \text{ - } 4.0\) Å) to determine the coordination number, \(N\), the bond length, \(R\), and the Debye-Waller (DW) factor, \(\sigma^2\), for each shell. The \(E_0\) shift was constraint, and the amplitude reduction factor, \(S_0^2\), was fixed at 1.0. The interatomic distances, coordination numbers, and Debye-Waller factors were allowed to vary in the single-shell analysis. In a subsequent step multi-shell fits were performed by using the estimated data from the single-shell analysis. The fitting parameters were treated as in the first shell fits except
that $\sigma^2$ was fixed for the second shell using the data from the single-shell fits. The latter was necessary due to strong correlation of the Si and Ca backscattering contributions for the second shell. Only $\sigma^2$ of the first Nd-O shell was allowed to vary in the multi-shell analysis. Theoretical scattering paths for the fits were calculated using FEFF 8.20 (Newville, 2001) and the structure of 11 Å tobermorite (Merlino et al., 2001).

For the EXAFS analysis of Nd doped C-S-H phases, a model proposed earlier by Schlegel et al. (Schlegel et al., 2004) for Eu(III) retention by amorphous C-S-H phases with varying C:S ratios was used. This model, which is based on the assumption that Eu(III) substitute for Ca in the C-S-H structure, includes backscattering contributions from Si atoms at ~R + ΔR = 3.2 Å and ~R + ΔR = 3.7 – 3.75 Å, and Ca atoms at ~R + ΔR = 3.79 – 3.84 Å. (Schlegel et al., 2004). In this study Nd(III) incorporation into the lattice of amorphous C-S-H phases by substitution for Ca was assumed based on similarities in the ionic radii of the two elements in sevenfold coordination (Nd$^{3+}$: 0.983Å in sixfold coordination; Ca$^{2+}$:1.00 Å and 1.07 Å for six- and sevenfold coordination) (Shannon, 1976). In no case did the EXAFS analysis result in meaningful results using short Si distances at ~ R + ΔR = 3.2 Å. The proposed EXAFS model for Nd(III) uptake by C-S-H contains also Nd-Si and Nd-Ca bond-distances which are closely spaced. e.g: R$_{Nd-Si}$ + ΔR ~ 3.70 - 3.75 Å; R$_{Nd-Ca}$ + ΔR ~ 3.75 - 3.8 Å) and could be difficult to be distinguished in EXAFS. Therefore, statistical F-tests (Bacchi et al., 1996; Downward et al., 2007; Hamilton, 1965) were performed using varying fitting models and the calculated crystallographic R-factors from the EXAFS fits to verify the plausibility of the EXAFS fitting model with backscattering contributions from Si and Ca within the second shell at R$_{Nd-Ca}$ + ΔR ~ 3.6 – 4.0 Å (see Supporting Information in Chapter 3).

Based on the crystallographic data of none-doped tobermorite, which is considered to be a good model for the structure of poorly ordered amorphous C-S-H, and the results from the F-test, we assume that the proposed EXAFS model with backscattering contributions from Si and Ca at 3.6 – 4.0 Å could correctly reproduce the long-range order in C-S-H phases. Note that the latter crystallographic model agrees well with those proposed by (Schlegel et al., 2004) for the Eu(III) retention by amorphous C-S-H phases with similar C:S ratios.
2.4 Wavelet analysis

Wavelet analysis of the measured EXAFS spectra was carried out to resolve the $k$ dependence of the absorption signal. Morlet wavelets were used for the wavelet transformation (WT) of the experimental $\chi(k)k^3$ signal and of the theoretical FEFF functions. The FORTRAN program HAMA (FUNKE et al., 2005) and IGOR Pro were used to calculate and to visualize the digitized waveforms. The theoretical contributions of the single Nd, Si and Ca scattering paths to the EXAFS spectrum was calculated using the structure of 11 Å tobermorite (MERLINO et al., 2001). All other cations except the target element (e.g. Nd, Si or Ca) were removed from the FEFF input file. For example, for the calculation of the single Nd scattering path, Ca and Si atoms were removed from the FEFF input file and the Ca atoms from the Ca sheets were exchanged by Nd. The FEFF input file was than used to generate the FEFF files using the FEFF 8.2 code. The correlated Debye model was used to calculate EXAFS Debye-Waller factors for the theoretical paths.

2.5 Bond valence approach

The bond valence (BV) approach was applied to evaluate potential structural sites for Nd binding on the surface of C-S-H phases. The calculations are based on the 11 Å tobermorite structure, which is considered to be a suitable model for C-S-H. The BV approach uses empirical correlations between the bond length and strength of chemical bonds in crystal structure based on the generalized Pauling’s electrostatic valence principle (PAULING, 1947). The decrease of the bond valence $s_{A-X}$ with bond length $R_{A-X}$ between a cation $A$ and an anion $X$ can be approximated by an inverse power relation in the form of Eq. 1:

$$s_{A-X} = \exp \left( \frac{R_{A-X}}{R_0} \right)^{-N_{AX}}$$

(1)

Here, $R_{A-X}$ is the distance between the two ions, $R_0$ is the length of a bond that would give the nominal valence, and $N$ determines the rate of decay of the bonding interaction.
between the $A^{th}$ and $X^{th}$ ions. In a crystal structure, each ion will account for bonding interactions in such a manner that the sum of all its bond-valences is equal to its nominal valence. Bond-valence sum calculations are used in crystal structure determinations for the localization of light atoms from X-ray data, to predict the surface reactivity in different crystallographic directions and to proof a proposed structure solution (ADAMS et al., 1993; SCHINDLER et al., 2004).

The FORTRAN program VALMAP 2.0 was used to calculate and to visualize the bond-valence sum of Nd in the C-S-H structure (GONZALEZ-PLATAS et al., 1999). For the calculations, the unit-cell parameters, the space-group and the atomic coordinates in the structure of 11 Å tobermorite were used. VALMAP 2.0 calculates the bond-valence sum $S_{A,X}$ of a Nd atom placed at any arbitrary point in the crystal. The bond valence $S_{A,X}$ of Nd is evaluated from Eq. 1 including the influence of the second, third and higher coordination shells. The positions of the Nd atom have been selected by moving it systematically along $a$, $b$ and $c$ axis of the surface Ca sheet ($z = 0$) of 11 Å tobermorite with a step size of 0.14 Å. The resulting bond valence sums were determined at each point of the selected grid and presented in contour lines with the same sum of bond valence (GONZALEZ-PLATAS et al., 1999). The maps show sharp peaks, which correspond to the position of atoms of the structure (empty circles), and smooth cavities with only few contour lines, which correspond to ideal atom positions, i.e., where the valence sum of Nd is at or close to its nominal valence +3 (GONZALEZ-PLATAS et al., 1999).

3. Results and discussion

3.1 EXAFS of Nd doped C-S-H

Figures 1 and 2 show the $k^3$-weighted, normalized, background subtracted EXAFS spectra, the corresponding RSFs and the Fourier-backtransform ($R + \Delta R = 1.5 - 4.0$ Å) spectra of Nd doped C-S-H samples. The structural parameters from multi-shell analysis ($R + \Delta R = 1.25 - 4.0$ Å) of the EXAFS spectra are in Table 1. The data allowed comparisons among the different samples with varying reaction times (1 day, 45 days and 270 days), different Nd loadings (35 µmol Nd / g solid phase (Figure 1) and (7 µmol Nd / g solid phase (Figure 2)) and different C:S ratios (0.56, 0.87 and 1.54) to be made.
All spectra showed a pronounced peak at $R + \Delta R \sim 2.0$ Å in the Fourier transform (FT), which corresponded to backscattering contributions from the nearest neighboring oxygen shell. The data showed no significant differences in the structural parameters for this shell in all samples.

**Figure 1** Nd $L_{III}$-EXAFS of Nd doped amorphous C-S-H phases with varying C/S ratios (0.56, 0.87 and 1.54), reaction times (1 day, 45 days and 270 days) and $35 \mu$mol/g Nd loading and Nd doped SiO$_2$ and Ca(OH)$_2$ (one day reaction; $35 \mu$mol Nd loading); a) $k^2$-weighted spectra, b) the corresponding RSFs of experimental (solid line) and fitted (dashed and dotted lines for the imaginary and the real part, respectively), and c) $k^2$-weighted EXAFS function for the Fourier-backtransform spectra obtained from Figure 1b.
The number (N) of neighboring oxygen atoms and the Nd-O bond distances were found to be similar within the experimental uncertainties, e.g. N_{O} = 6.5 - 7.9 and R_{Nd-O} = 2.43 - 2.45 Å. The DW factor was estimated to range in value between 0.008 Å² and 0.014 Å² in most cases. The observed numbers of next nearest oxygen, N_{O}, were similar to those of Ca in the Ca sheets of none-doped C-S-H phases with similar C:S ratios from EXAFS (e.g. C:S = 0.7 – 1.4: N_{O} ~6) (LEQUEUX et al., 1999).

**Figure 2** 
Nd L_{III}-EXAFS of Nd doped amorphous C-S-H phases with varying C/S Ratios (0.56, 0.87 and 1.54), reaction times (1 day, 45 days and 270 days) and 7 μmol/g Nd loading: a) $k^3$-weighted spectra, b) the corresponding RSFs of experimental (solid line) and fitted (dashed and doted lines for the imaginary and the real part, respectively), and c) $k^3$-weighted EXAFS function for the Fourier-backtransform spectra obtained from Figure 2b.
Table 1

Quantitative analysis of the first and higher EXAFS paths of Nd doped amorphous C-S-H with varying C/S ratio (0.56, 0.87 and 1.54), reaction time 1, 45 and 270 days and Nd concentration (7 and 35 μmol Nd / g solid phase)\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (days)</th>
<th>Nd (μmol Nd/g)</th>
<th>Nd\textsuperscript{*}</th>
<th>Nd\textsuperscript{c}</th>
<th>σ\textsuperscript{o} (Å)</th>
<th>Nd\textsuperscript{c}</th>
<th>σ\textsuperscript{c} (Å)</th>
<th>Nd\textsuperscript{c}</th>
<th>σ\textsuperscript{c} (Å)</th>
<th>ΔE\textsubscript{0} (eV)</th>
<th>Rf</th>
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<td>CSH154</td>
<td>1</td>
<td>7</td>
<td>7.1 2.44 0.01 1.9</td>
<td>3.73 0.006</td>
<td>2.8 3.77 0.007</td>
<td>7.53 0.82</td>
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<tr>
<td></td>
<td>45</td>
<td>7</td>
<td>6.8 2.43 0.008</td>
<td>3.88 0.009</td>
<td>2.8 3.80 0.002</td>
<td>6.3 0.85</td>
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<tr>
<td></td>
<td>270</td>
<td>7</td>
<td>6.8 2.44 0.008</td>
<td>3.80 0.007</td>
<td>2.8 3.77 0.007</td>
<td>7.97 0.89</td>
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<tr>
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<td>3.76 0.010</td>
<td>2.8 3.80 0.002</td>
<td>6.8 0.84</td>
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<td>7</td>
<td>7.7 2.44 0.010</td>
<td>2.6 3.76 0.010</td>
<td>2.5 3.79 0.008</td>
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<tr>
<td></td>
<td>270</td>
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<td>2.9 3.83 0.004</td>
<td>3.3 3.87 0.008</td>
<td>5.6 0.81</td>
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<tr>
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<td>7</td>
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<td>2.9 3.68 0.005</td>
<td>1.8 3.75 0.005</td>
<td>6.6 0.65</td>
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<td>6.5 2.44 0.010</td>
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<td>1.8 3.75 0.005</td>
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<tr>
<td></td>
<td>270</td>
<td>7</td>
<td>7.8 2.45 0.012</td>
<td>4.2 3.72 0.008</td>
<td>2.2 3.78 0.005</td>
<td>7.8 0.90</td>
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</table>

Nd on SiO\textsubscript{2} | 1 | 35 | 6.7 2.44 0.009 | 1.9 3.84 | - - - | - - - | 5.99 15.6 |

Nd on Ca (OH)\textsubscript{2} | 1 | 35 | 7.8 2.42 0.006 | - - - | 2.3 3.66 0.004 | 1.23 9.2 |

\textsuperscript{a} Fourier-transformed \(\chi(k)\) range \(\Delta k = 1.4 -10.6\), \textsuperscript{b} Number of neighbor atoms, \textsuperscript{c} Interatomic distance, \textsuperscript{d} Debye-Waller factor, \textsuperscript{e} Energy shift of the theoretical calculated spectrum to the energy grid of the measured spectrum, \textsuperscript{f} The residual factor \(R_f\)

\[
R_f = \frac{\sum_{i} (\chi_{\text{obs}}(k) - \chi_{\text{calc}}(k))^2}{\sum_{i} (\chi_{\text{obs}}(k))^2} \times 100
\]

Estimated errors: (\(R_{\text{Nd-Ca}}\), \(R_{\text{Nd-Si}}\), \(R_{\text{Nd-O}}\)) ~0.02\textsuperscript{a}; (\(N_{\text{obs}}\), \(N_{\text{calc}}\))~20%; \(\chi_{\text{obs}}\) and \(\chi_{\text{calc}}\): experimental and theoretical data points.

Presence of further backscattering atoms was indicated by the broad peak in the FTs at \(R+\Delta R \sim 3.0\) Å, which could be accurately fit by considering Nd-Si and Nd-Ca.
backscattering contributions. Fits did not improve by considering potential Nd-Nd backscattering contributions. The fit results showed that, in general, the Nd-Si and Nd-Ca distances increased with increasing reaction time in all Nd doped C-S-H samples. Nevertheless, the differences in bond distances between the short-term and long-term reacted samples were small and, as in the case of C-S-H samples with C:S ~0.56, within the estimated uncertainties (e.g. compare structural data for CSH056-7-1 and CSH056-7-270 in Table 1). At higher C:S ratios (e.g. C:S = 0.87 and 1.54) and low Nd loading (7 µmol Nd /g solid phase) the increase in the Nd-Si and Nd-Ca bond-distances was more pronounced (e.g. CSH154-7-1: R\textsubscript{Nd-Si} = 3.73 Å, R\textsubscript{Nd-Ca} = 3.77 Å; CSH154-7-270: R\textsubscript{Nd-Si} = 3.80 Å, R\textsubscript{Nd-Ca} = 3.86 Å; CSH087-7-1: R\textsubscript{Nd-Si} = 3.76 Å, R\textsubscript{Nd-Ca} = 3.83 Å; CSH087-7-270: R\textsubscript{Nd-Si} = 3.83 Å, R\textsubscript{Nd-Ca} = 3.87 Å).

The same trend in the bond-distances, i.e. longer Nd-Si and Nd-Ca bond-distances after longer reaction time was observed in the samples with higher C:S ratio (C:S = 0.87 - 1.54) and high Nd loading (35 µmol Nd /g solid phase), whereas changes in the bond-distances in the samples with C:S = 0.56 were within the uncertainties at higher metal loading (Table 1).

In addition to the observed prolonged Nd-Si and Nd-Ca bond-distances, increased coordination numbers, N\textsubscript{Si} and N\textsubscript{Ca}, after 270 days were observed. The latter appears to be depended on the C:S ratio. For example, in the samples with the highest C:S ratio (1.54) an increase in the number of next nearest Ca atoms, N\textsubscript{Ca}, was observed after 270 days, whereas changes in N\textsubscript{Si} were smaller (e.g. CSH154-7-1: N\textsubscript{Ca} = 2.8, N\textsubscript{Si} = 1.9; CSH154-7-270: N\textsubscript{Ca} = 5.3, N\textsubscript{Si} = 3.9). In contrast, at low C:S ratio and equal Nd loading, increased N\textsubscript{Si} was observed after 270 days, whereas changes in N\textsubscript{Ca} were small and within the uncertainties (e.g. CSH056-7-1: N\textsubscript{Ca} = 1.8, N\textsubscript{Si} = 2.9; CSH056-7-270: N\textsubscript{Ca} = 2.2, N\textsubscript{Si} = 4.2). Changes in N\textsubscript{Si} were again larger in the sample with the lowest C:S ratio (C:S = 0.54) at high Nd loading, i.e. CSH056-35-1, whereas the N\textsubscript{Ca} remain unchanged (Table 1). A trend to higher coordination numbers N\textsubscript{Ca} was also observed at the higher Nd loading (35 µmol Nd / g solid phase) and C:S = 1.54 (Table 1).

The above findings, i.e. changes in the bond-distances and the coordination numbers, suggested that the coordination environment of Nd in C-S-H phases determined after one day reaction was not representative for the aged samples. Both, Nd-Si and Nd-
Ca distances, and coordination numbers of the neighboring Si and Ca atoms increased with time. Thus, we assumed that the structural arrangement of Nd as determined in the samples, which were equilibrated for one day, only represented a “metastable” configuration.

3.2 Wavelet analysis of the EXAFS spectra

The wavelet diagrams presented in Figure 3 show the \((k,R)\) dependence of information derived from the EXAFS spectrum (Munoz et al., 2003). Wavelet analysis offers a direct way of distinguishing different atoms within one atomic shell. Figure 3 shows three different sets of data: The theoretical scattering functions of the Nd-Nd, Nd-Ca and Nd-Si paths, as described previously in section 2.4 (Fig. 3a-c), wavelet analysis of Nd reference compounds (Fig. 3d-f) and overview wavelet of Nd doped C-S-H phases after 270 days ageing (Fig. 3g-i). The EXAFS data for Figure 3d-f were taken from Chapter 3. Nd doped 11 Å tobermorite and Nd doped xonotlite were chosen as references based on their similarities with the structure of amorphous C-S-H phases (Churakov and Mandaliev, 2008; Merlino et al., 2001; Richardson, 2004).

The maxima of the first peak at \(R + \Delta R = 2.0 \text{ Å} \) and \(k \sim 4.8 \text{ Å}^{-1}\) in all samples in Figure 3 corresponded to the oxygen coordination shell as already indicated from the EXAFS data (Figs. 1 and 2). The intermediate peaks at about \(R + \Delta R = 3.5 - 4.0 \text{ Å} \) and \(k \sim 5.5 - 6.1 \text{ Å}^{-1}\) could contain scattering contributions from neighboring Ca and Si atoms. Nd backscattering contributions in C-S-H phases are expected to appear at similar distances to those of Ca on the assumption that Nd can replace Ca in the Ca sheets of C-S-H phases. Thus, although localized at similar distances, the Nd backscattering contributions were expected to appear at \(k \sim 7 \text{ Å}^{-1}\) (Fig. 3a) compared to \(k \sim 5.5 - 6.1 \text{ Å}^{-1}\) in the case of Ca and Si (Figs. 3b and c). The latter can be demonstrated based on WTs of reference compounds. For example, the WT of the Nd precipitate shows a strong peak at \(R + \Delta R \sim 3.7 \text{ Å} \) and \(k \sim 7.2 \text{ Å}^{-1}\) (Fig. 3d), which could be attributed to Nd backscattering contributions based on the similarity with the \(k\)-space range of the contribution in Nd(OH)\(_3\) (data not shown) and those of the theoretical Nd backscattering path (Fig. 3a). Small peaks at \(R + \Delta R \sim 3.2 - 3.5 \text{ Å} \) and \(k \sim 5 - 6 \text{ Å}^{-1}\) were indicative of Ca and Si backscattering contributions. In the WT of Nd doped 11 Å tobermorite a well resolved
peak at R + ΔR ∼ 5.6 Å and k ∼ 7.3 - 7.8 Å⁻¹ appears, which could be attributed to Nd backscattering (Fig. 3e) based on the similarity with the k-space range as described above. Additional maxima in the range R + ΔR ∼ 3.2 - 3.7 Å and k ∼ 5.3 - 7.1 Å⁻¹ could be attributed to Ca, Si and Nd backscattering paths.

**Figure 3** Overview wavelet of selected samples using the Morlet parameters η = 7, σ = 2 and a signal weighting of $k^3$: a) Nd-Nd theoretical scattering paths; b) Nd-Si Theoretical scattering paths; c) Nd-Ca theoretical scattering paths; d) Nd precipitate; e) Nd uptake by 11 Å tobermorite after 270 days reaction; f) Nd uptake by 11 Å tobermorite after 270 days reaction; g) CSH154-270-35; h) CSH087-270-35; i) CSH056-270-35. Blue and yellow colors correspond to high and low peak intensities, respectively.
Similar to 11 Å tobermorite, the WT of Nd doped xonotlite (Fig. 3f) showed intermediate peaks at about $R + \Delta R = 3.2 - 3.7 \ \text{Å}$ and $k \sim 5.3 - 7.1 \ \text{Å}^{-1}$, which contain backscattering contributions from neighboring Ca, Si and Nd atoms, based on the similarity with the $k$-space range in the theoretical scattering functions of the Nd-Ca and Nd-Si paths (Fig. 3b-c). The weak backscattering contributions at longer distances ($R + \Delta R \sim 7 \ \text{Å}$) could be attributed to backscattering contributions from the next neighboring Ca-layer.

In the CSH154-270-35 sample the diffuse peak at $k \sim 7.4 - 7.6$ covers the range between $R + \Delta R \sim 3.5 \ \text{Å}$ and $R + \Delta R \sim 4.6 \ \text{Å}$ (Fig. 3i). Based on structural considerations, the shorter distances in this range ($R + \Delta R \sim 3.8 - 3.9 \ \text{Å}$) could be attributed to Nd incorporated into the Ca sheets of C-S-H phases, while the longer distances ($R + \Delta R > 4 \ \text{Å}$) correspond to Nd-Nd distances between Nd bound in the Ca sheets and Nd bound in the interlayer of C-S-H phases. Nevertheless, Ca backscattering contributions in the Ca sheets could not be separated from Nd backscattering using the Morlet WT due to strong overlapping of these signals (SAHNOUN et al., 2007). Therefore only Nd-Nd backscattering contributions in absence of neighboring Ca backscatters were considered in the WA (e.g. Nd in the interlayer of C-S-H at $R + \Delta R \geq 4.6 \ \text{Å}$).

Fig. 3i showed that Nd-Nd distances in amorphous C-S-H are shorter than those determined in Nd doped 11 Å tobermorite ($R_{\text{Nd-Nd}} \sim 5.6 \ \text{Å}$), which could be attributed to the lower degree of crystallinity of these phases compared to 11 Å tobermorite (CONG and KIRKPATRICK, 1996). This further indicated shorter distances between the Ca atoms of the Ca sheets and those in the interlayer. Therefore, if Nd substitutes for Ca in the Ca sheets and the interlayer of amorphous C-S-H phases, shorter Nd-Nd distances could result compared to 11 Å tobermorite. An alternative possibility of Nd occupancy is close to the position of bridging Si tetrahedra. At high C:S ratios Ca atoms could replace a significant portion of the Si bridging tetrahedra in the C-S-H structure as reported elsewhere (RICHARDSON, 1999; RICHARDSON, 2004; TAYLOR, 1986). If Nd substitutes for Ca on positions of bridging Si tetrahedra, shorter Nd-Nd bond distances ($R_{\text{Nd-Nd}} \sim 4.6 \ \text{Å}$) resulted compared to those found in 11 Å tobermorite ($R_{\text{Nd-Nd}} \sim 5.6 \ \text{Å}$). Nevertheless, occupancy of the different Nd positions in the interlayer of amorphous C-S-H phases
could not be distinguished, and therefore, conclusive considerations regarding the Nd positions were impossible.

In the CSH087-270-35 sample the long Nd-Nd backscattering contributions at $R + \Delta R \sim 5.6 \, \text{Å}$ and $k \sim 7.5 \, \text{Å}^{-1}$ in Fig. 3h were rather weak compared to those observed in 11 Å tobermorite (Fig. 3e), which suggested lower portion of Nd incorporated in the interlayer of amorphous C-S-H phases. In CSH056-270-35 Nd was predominantly incorporated into the Ca sheets (Fig. 3i), while only a minor portion of Nd was bound in the interlayer. Note, however, that, in all samples, Nd backscattering contributions from Nd bound in Ca sheets were hardly visible as the Nd concentrations the Ca sheets was very low compared to Ca concentration.

### 3.3 Uptake mechanisms of Nd in C-S-H phases

A detailed understanding of metal binding to C-S-H phases requires that the different modes of Nd - solid phase interaction can be distinguished. Possible binding mechanisms are schematically illustrated in Figure 4. Inner- and outer-sphere surface complex formation may dominate the metal binding (DUFF et al., 2004). In the case of outer-sphere surface complexation the hydration sphere and the metal-oxygen bond distances of the surface complex should compare with those of the aqueous species as no direct binding to the surface is anticipated (Fig. 4a). By contrast, the metal complex is directly bonded to the surface via oxygen atoms in the case of inner-sphere surface complexation (Fig. 4b). In the latter case the number of water molecules in the hydration sphere is reduced and backscattering contributions from neighboring atoms of the solid phase appear in the EXAFS spectra. Metal incorporation into the C-S-H structure was found to be an important binding mode on crystalline C-S-H phases (Fig. 4c). In case of incorporation into the structure the coordination number of neighboring atoms and bond distances between the metal center and neighboring atoms should be consistent with the structure of the solid phase.

Finally, co-precipitation in solids with fixed and variable (solid solution) stoichiometries at higher metal loadings are a potential mode of metal cation immobilization under the highly alkaline conditions (Fig. 4d).
Figure 4 Schematic presentation of the mechanisms of Nd interaction with C-S-H phases: a) Outer-sphere surface complexation, b) Inner-sphere surface complexation, c) structural incorporation, and d) co-precipitation.

EXAFS spectra may include contributions from various Nd species which have different coordination environments: Nd adsorbed on the surface of C-S-H (formation of inner-sphere or outer-sphere complexes, respectively), Nd co-precipitation in solids with fixed and variable stoichiometries (e.g., solid solution), and Nd incorporation into the structure of C-S-H phases. Surface-bound species show distinct coordination environments, which are reflected in the structural parameters of the nearest neighboring atoms (e.g., DUFF et al., 2004). For example, outer-sphere coordination implies that metal ions binds to C-S-H phases with intact hydration shell (Fig. 4a) and therefore, the Nd-O bond distances should compare well with those of the aqueous species (DUFF et al., 2004). The Nd-O bond distances in the latter complex were reported to be about 2.49 - 2.50 Å (D'ANGELO et al., 2001), which is significantly larger than the first-shell Nd-O distances in Nd doped C-S-H ($R_{Nd-O} = 2.43 - 2.45$ Å). Furthermore, the coordination number of the first oxygen shell of the Nd doped samples was determined to be 6.3 – 7.6.
which is lower than that of the aqueous Nd species (\(N_O \sim 9 - 10\); (D'ANGELO et al., 2001)).

Nd adsorption by the potentially present amorphous silica and portlandite could not be supported from the EXAFS data. Note that amorphous silica could be present at C:S ratio \(~0.56\) as shown elsewhere (KULIK and KERSTEN, 2001) while Ca(OH)\(_2\) could be intermixed with C-S-H phases at higher C:S ratios. After one day reaction the number of neighbouring Ca and Si atoms was low, i.e., \(N_{Ca}\) and \(N_{Si}\), respectively, in the range between 1 and 3. The EXAFS results in Table 1 showed Nd sorbed onto amorphous silica was surrounded by \(~1.9\) Si atoms at distance \(R_{Nd-Si} = 3.84\ \text{Å}\) while Nd taken up by Ca(OH)\(_2\) was surrounded by \(~2.3\) Ca at \(R_{Nd-Ca} = 3.66\ \text{Å}\) (Table 1). The coordination numbers were similar, but the distance differs significantly from those observed in C-S-H with C:S = 0.56 (CSH056-7/35-1: \(N_{Si} \sim 2.6 - 2.9\) and \(R_{Nd-Si} = 3.67 - 3.68\ \text{Å}\)) and C:S = 1.54 (CSH154-7/35-1: \(N_{Ca} \sim 2.3 - 3.0\) and \(R_{Nd-Ca} = 3.76 - 3.77\ \text{Å}\)). Note that both Si and Ca backscattering contributions were always present in all samples, which could not be explained solely by adsorption onto amorphous silica or Ca(OH)\(_2\).

The above findings indicated that the structural parameters determined for Nd doped C-S-H phases after one day were not consistent with outer-sphere surface complexation or sorption onto the amorphous silica or Ca(OH)\(_2\) but rather suggested the formation of inner-sphere surface complexes. Inner-sphere surface complexation implies direct binding of the metal cation to the surface as schematically shown in Figure 4b.

Preferential positions for Nd bound on the surface of C-S-H phases could be estimated from BV-supported structural considerations. The bond valence map for Nd in the \(ab\) plane of 11 Å tobermorite at a high \(z = 0\) and the surface structure of the C-S-H phase in the same orientation were drawn (Figure 5). Minima in the contour lines indicated preferential positions for Nd binding on the C-S-H surface. The positions of Ca and Si atoms in the nearest surface layer of the 11 Å tobermorite structure were also localized.

Based on these best estimates for possible Nd positions the coordination environment of Nd adsorbed on the surface of 11 Å tobermorite was expected to have 7 neighboring oxygen atoms (or OH groups) at distances ranging between \(R_{Nd-O} = 2.26 - 2.56\ \text{Å}\), 2 - 3 Si atoms at \(R_{Nd-Si} = 3.73 - 3.87\ \text{Å}\) and ~2 Ca atoms at \(R_{Nd-Ca} = 3.67 - 3.75\ \text{Å}\).
Figure 5  

(a) Bond valence map for Nd in the ab-plane (parallel to Ca sheets) at z = 0 of 11 Å tobermorite, calculated with 50 contour levels and an bond valence interval of 0.3 vu. Contours are representative for areas with high bond valence deficiency. Positions of Ca and Si atom from the surface-nearest layers of 11 Å tobermorite are shown; (b) the structure of 11 Å tobermorite in the same orientation as the bond valence map. Ca from the Ca sheets and Si are labeled.

These structural parameters were consistent with the EXAFS parameters determined in the short-term experiments (Table 1). The latter finding supported the idea of predominant formation of inner-sphere surface complexes in the early stage of Nd interaction with amorphous C-S-H phases.

After prolonged ageing of the Nd doped C-S-H phases, however, the structural parameter determined from EXAFS were different from those in the early stage of the Nd - C-S-H interaction. After 270 days reaction, longer Nd-Si and Nd-Ca distances as well, in most cases, an increased number of nearest neighbouring Si and Ca, N_{Si} and N_{Ca}, were observed (Table 1). In general, higher coordination numbers coincided with longer bond distances (R_{Nd-Si} ~ 3.72 - 3.83 Å; R_{Nd-Ca} ~ 3.78 - 3.87 Å). The experimental EXAFS parameters determined after prolonged reaction time could further be assessed based on structural considerations as schematically shown in Figure 4c. In the 11 Å tobermorite
structure (MERLINO et al., 2001). Ca from the central Ca sheet is surrounded by 6 - 7 neighboring oxygen atoms \( (R_{Ca-O} = 2.46 \text{ Å}) \), 3 - 4 Si atoms \( (R_{Ca-Si} = 3.67 - 3.73 \text{ Å}) \) and 5 Ca atoms \( (R_{Ca-Ca} = 3.80 - 3.96 \text{ Å}) \). Therefore, our observation of 4 to 5 nearest neighboring Ca atoms at \( R_{Nd-Ca} \approx 3.78 - 3.87 \text{ Å} \) indicated presence of Nd in the Ca sheets of the C-S-H phases and we assume that the number of neighbouring Si and Ca atoms and bond distances reflected the extent of Nd incorporation.

Deviations from the theoretical \( N_{Si} \) and \( N_{Ca} \) in the samples with low and high C:S ratio could be explained with the differences in the crystal-structure of amorphous C-S-H phases. C–S–H have a layered structure that varies with their C:S ratio. Each layer is composed by a “pseudoctaedral” CaO plane between two tetrahedral silicate chains. The silicate chains form a dreierketten structure, where silicate dimers are connected by a bridging tetrahedron. At low Ca:Si ratios C-S-H systems could be seen as long polymerized (pentamers or longer) (RICHARDSON, 2004). When the Ca:Si ratio is raised, the polymerization degree is reduced and silica dimers replace the “dreierketten” structure. These dimmers are coordinated to the calcium ions of the layer and either the calcium ion or the proton of the interlayer, whereas missing Si chain links could be replaced by Ca atoms or OH groups (RICHARDSON, 2004). Our observation of high \( N_{Si} \) at low C:S ratios and high \( N_{Ca} \) at high C:S ratios could be explained with Nd incorporation into the Ca sheets of C-S-H. High polymerisation of the Si chains could lead to increased number of next nearest Si atoms, whereas replacement of Si chain links with Ca would explain the higher \( N_{Ca} \) in the case of C-S-H samples with C:S = 1.54.

4. Summary

This EXAFS study on the interaction of Nd with amorphous C-S-H phases revealed that Nd could form several species in contact with C-S-H phases. Changes in the relative portion of Nd species were visible from variations in the EXAFS parameters. Nd was predominantly bound on the external surface of amorphous C-S-H phases after one day reaction as an inner-sphere surface complex. After prolonged reaction times (≥ 45 days) Nd was predominantly incorporated into the Ca sheet of the C-S-H structure. The results from this study were essential for a detailed understanding of binding mechanisms of trivalent actinides in amorphous C-S-H phases due to chemical similarity of the latter
elements with trivalent lanthanides. A mechanistic understanding of the immobilization processes of trivalent actinides could significantly improve predictions of the safe disposal of radioactive waste in cement-based repositories.
5. References


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142

CHAPTER 5

Macro- and micro-spectroscopic study of Nd(III) uptake mechanisms in hardened cement paste

ABSTRACT

Cement is an important component in repositories for low-level and intermediate-level radioactive waste. In this study, Nd uptake by hardened cement paste (HCP) has been investigated with the aim of developing a mechanistic understanding of the immobilization processes of trivalent lanthanides and actinides in HCP on the molecular level. Information on the microstructure of HCP, the Nd distribution in the cement matrix and the coordination environment of Nd in these matrices was gained from the combined use of scanning electron microscopy (SEM), synchrotron-based μ-X-ray fluorescence (μ-XRF), μ-X-ray (μ-XAS) and bulk-X-ray absorption spectroscopy (bulk-XAS) on Nd(III)-doped cement samples. The samples reacted over periods of time between 15 min and 200 days. SEM and μ-XRF investigations show that Nd-containing phases form rims around “inner”-calcium silicate hydrates (C-S-H). The coordination environment of Nd taken up by HCP depends on reaction time. The fitted distances between Nd and neighboring Si and Ca atoms increase by about 0.1 Å over 200 days hydration. The longer distances coincide with higher numbers of neighboring Si atoms. Changes in these structural parameters support the idea of Nd incorporation into the structure of C-S-H phases. The Nd binding mechanisms proposed in this study support the option of long-term safe disposal of trivalent actinides in cement-based repositories for radioactive waste.
1. Introduction

Cement-based materials play an important role in multi-barrier concepts developed worldwide for the safe disposal of radioactive wastes in deep geological repositories (Chapman and McCombie, 2003). The potential impact of radionuclides released from the near field of a repository can be controlled and reduced by a suitable choice of engineered and geological barriers. In this context, knowledge of the long-term ability of the cement-based near field to retard the release of radionuclides into the far field and the chemical mechanism by which these radionuclides are bound to cement minerals are essential for safety analysis. Trivalent actinides such as $^{241/243}\text{Am}$ are safety relevant radionuclides and therefore, a detailed understanding of the binding mechanisms of trivalent actinides in hardened cement paste (HCP) is essential for long-term assessments of the safe disposal of radioactive waste. At present, however, these mechanisms are only poorly understood on the molecular level.

In this study Nd(III) was regarded as a suitable chemical analogue for other lanthanides and trivalent actinides (e.g., Am(III), Cm(III)) as their ionic radii are comparable (Shannon, 1976). HCP is a very heterogeneous material with discrete particles typically in the size range of about 2-200 μm, consisting of mainly calcium (aluminium) silicate hydrates (C-(A)-S-H), portlandite (calcium hydroxide) and calcium aluminates. Among the different cement phases, C-S-H phases are considered to be the most important constituent of HCP as they are abundant and expose a diversity of structural sites for cation and anion binding (e.g. ATKINS, 1992). In general, it was observed that immobilization processes in cement systems are highly specific with regards to the mineral components and mechanism involved (VESPA et al., 2006a).

Only few studies were focused on the uptake of trivalent lanthanides and actinides, such as Nd(III), Eu(III) and Cm(III), by cementitious materials and C-S-H phases has been investigated. STUMPF et al., (2004) investigated the interaction of Cm(III) with HCP under highly alkaline conditions using time-resolved laser fluorescence spectroscopy (TRLFS). The laser-based spectroscopic studies showed that Cm(III) uptake predominantly occurs in the C-S-H fraction of HCP after prolonged reaction time. TRLFS and X-ray absorption fine structure (XAFS) investigations suggested that Eu(III) and Cm(III) can substitute Ca$^{2+}$ in the Ca sheets and interlayer of
amorphous C-S-H phases (TITS ET AL. 2003; SCHLEGEL et al., 2004). This finding was further substantiated in X-ray diffraction (XRD) and XAFS studies on Nd(III)-doped crystalline C-S-H phases (SCHLEGEL et al., 2004). In particular, it was shown using XRD in combination with Rietveld refinement on Nd(III) doped 11 Å tobermorite and xonotlite samples that Nd is incorporated into the Ca sheets of xonotlite while it is bound in the Ca sheets and interlayer of 11 Å tobermorite (Chapter 3). The first step in Nd uptake by the latter phase is due to Nd binding in the interlayer, which coincides with the release of water and bridging Si tetrahedral and results in a disordered tobermorite structure. In the second step, Nd-Ca replacement in the Ca sheets occurs. The extent of Nd binding in the Ca sheets increased with time due to ongoing re-crystallization of the solid phase. Nd-Ca substitution in the Ca sheet was also observed in xonotlite, which has no interlayer space.

Nd incorporation into the structures of the crystalline C-S-H phases was further reflected in the XAFS parameters. In particular, it was observed that the number of neighboring Ca and Si atoms was typically > 4, and in addition, Nd-Ca and Nd-Si distances increased as the portion of Nd bound in the Ca sheets increased. These are important indications for Nd incorporation into the structure of C-S-H phases, which will be used as basis for data interpretation in the framework of this study.

The aim of this study was to investigate Nd uptake by HCP on the macro- and micro-scale in line with the approach developed earlier (VESPA et al., 2006b; VESPA et al., 2007). These authors combined scanning electron microscopy (SEM), µ-synchrotron X-ray fluorescence (µ-XRF), µ-X-ray absorption (µ-XAS) and bulk-X-ray absorption spectroscopy (bulk-XAS) to determine the binding mechanisms of Ni and Co in cement pastes. The combined approach provided spatially-resolved information on the elemental distribution in the compact cement matrix, including areas of metal accumulation and association with specific cement minerals. Furthermore, information on the speciation of the element of interest in selected regions of interest (ROI) of the cement matrix and in bulk material was obtained. Combining µ-XAS and bulk-XAS measurements allowed micro-scale information to be assessed with regards to their relevance for the bulk matrix. In this study Nd was used as absorber atom as the absorption of Fe (K-edge at 7112 eV), which is an important element in the cement matrix (~2.5 wt. % Fe in cement), does not interfere with the Nd LIII-edge (6208 eV) spectroscopic measurements.

149
2. Materials and methods

2.1 Cement sample preparation.

Cement samples were prepared using a commercial sulfate-resisting Portland cement (CEM I, Lafarge, France) and a procedure described in detail elsewhere (Vespa et al., 2006a). Briefly, metal-enriched hardened cement pastes were prepared by mixing a Nd(NO$_3$)$_2$ solution with unhydrated cement powder. The Nd stock solution (10$^{-3}$ M) was prepared by dissolving the metal salt (Nd(NO$_3$)$_3$.6H$_2$O, Merck “pro analysis”) in deionized water and adding an aliquot HNO$_3$ conc. for acidification. Aliquots of the acidified stock solution were mixed with the unhydrated cement powder at a water/cement (w/c) ratio of 0.4 according to a standard procedure (European Norm EN-196-3). The final metal concentration of the pastes was 26 µmol Nd/g HCP. The pastes were cast in Plexiglas moulds, which were tightly closed with polyethylene snap caps, and aged over appropriate periods of time up to 200 days. For this, the cylindrical samples (diameter of 4.1 cm, height of 1 cm) were stored in closed containers at room temperature at 100% relative humidity in a glove box under a N$_2$ atmosphere. Upon hydration, the samples were immersed in acetone for 24 h and dried in an oven at 40°. One portion of the HCP material was used for the preparation of polished thin sections for further use in the SEM-based analysis and synchrotron-based µ-XRF/XAS investigations. The other portion of the HCP material was crushed and sieved to obtain cement material (particle size <63 µm) for use in the bulk-XAS measurements. These samples were denoted as CHEMHYD (Table 1).

Nd sorption samples used for the bulk-XAS measurements were prepared according to a procedure described in Chapter 3. Briefly, 1 g of previously hydrated cement powder was mixed with 35 mL artificial cement pore water (pH = 13.3). The chemical composition of the latter is given elsewhere (Wieland et al., 2006). Appropriate volumes of an acidified Nd stock solution (10$^{-1}$ M) were added to the suspension to achieve final metal concentrations in the pastes of 26 µmol Nd/g HCP. These samples were denoted as CEMSORB (Table 1).
Table 1  Chemical conditions of the Nd-loaded cement-sample preparation for bulk and μ-XAS measurements. ROI = region of interest

<table>
<thead>
<tr>
<th>Material (hydrated cement)</th>
<th>Abbreviation</th>
<th>Nd loading (μmol Nd/g solid)</th>
<th>Hydration time (days)</th>
<th>Method</th>
</tr>
</thead>
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<tr>
<td>Crushed HCP</td>
<td>CEMHYD-15M-26</td>
<td>26</td>
<td>15 min.</td>
<td>bulk-EXAFS</td>
</tr>
<tr>
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<td>CEMHYD-1-26</td>
<td>26</td>
<td>1</td>
<td>bulk-EXAFS</td>
</tr>
<tr>
<td>Crushed HCP</td>
<td>CEMHYD-200-26</td>
<td>26</td>
<td>200</td>
<td>bulk-EXAFS</td>
</tr>
<tr>
<td>Crushed HCP</td>
<td>CEMHYD-700-26</td>
<td>26</td>
<td>700</td>
<td>bulk-EXAFS</td>
</tr>
<tr>
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<td>CEMSORB-1-26</td>
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<td>1</td>
<td>bulk-EXAFS</td>
</tr>
<tr>
<td>Crushed HCP</td>
<td>CEMSORB-28-26</td>
<td>26</td>
<td>28</td>
<td>bulk-EXAFS</td>
</tr>
<tr>
<td>Crushed HCP</td>
<td>PORTSORB-1-26</td>
<td>26</td>
<td>1</td>
<td>bulk-EXAFS</td>
</tr>
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<td>Intact HCP</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>28</td>
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<td>28</td>
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</tr>
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<td>28</td>
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</tr>
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<tr>
<td>Intact HCP</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>200</td>
<td>μ-EXAFS</td>
</tr>
<tr>
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<td>200</td>
<td></td>
</tr>
<tr>
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<td>CEMHYD-200-26-ROI-3</td>
<td>26</td>
<td>200</td>
<td></td>
</tr>
</tbody>
</table>

After phase separation by centrifugation (60 min at 95000 g) the Nd treated cement samples were packed as a wet paste into Plexiglas sample holders and sealed with Kapton tape. The list of samples including abbreviations, hydration time and Nd metal loadings is given in Table 1.

2.2 Scanning electron microscopic (SEM) investigations.

SEM analyses were conducted using a Zeiss DSM 962 microscope, operated at an accelerating voltage of 20 kV and a beam current of 76 μm. The microscope is equipped with a Si(Li)-detector for energy dispersive micro-analysis (EDS). The spot size was ~1x1 μm², and the penetration depth was ~6 μm at the used incident beam energy. The
Zeiss DSM 962 microscope is equipped with a multiplier for backscattered electron (BSE) imaging and mineral phase specification, which is based upon differences in the grey scale.

2.3 μ-XRF, μ-XAS and bulk-XAS data collection and reduction.

Overview μ-XRF maps were collected on the microXAS beamline at the Swiss Light Source (SLS), Switzerland, by scanning the samples under the monochromatic beam at the energy of 10000 eV (beam size ~10×10 μm²) and using the single-element Si-detector. Additional fine maps were collected with a beam size of ~2×3 μm². μ-XRF and μ-XAS Nd L_III edge data (6208 eV) were collected on beamline 10.3.2 at the Advanced Light Source (ALS), USA (Marcus et al., 2004). This beamline is equipped with a Si(111) crystal monochromator. The monochromator angle was calibrated by assigning the energy of 5989 eV to the first inflection point of the K-edge absorption spectrum of Cr metal foil. μ-XRF and μ-XAS measurements were collected at room temperature in fluorescence mode using a seven-element Ge solid state detector and a beam size ~5×5 μm².

Bulk-XAS spectra at the Nd L_III edge were collected on beamline BM26A (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The beamline is equipped with a Si (111) double-crystal monochromator. The monochromator angle was calibrated using a Cr metal foil. The measurements were conducted at room temperature in fluorescence mode using the nine-channel monolithic Ge solid state detector. For each sample, depending on the Nd loadings, between three and seven spectra were collected to achieve the required signal-to-noise ratio.

The μ-XRF maps were processed using the Labview software package of beamline 10.3.2 (Marcus et al., 2004) and MATLAB. μ-XAS and bulk-XAS data reduction was performed by using the IFFEFIT and the WinXAS 3.11 software packages.

EXAFS data reduction was performed by using the WinXAS 3.11 software package and following standard procedures (Ressler, 1998). After background subtraction, the energy was converted to photoelectron wave vector units (Å⁻¹) by assigning the ionization energy of the Nd L_III-edge (6208 eV), E₀, to the first inflection
point of the absorption edge. Radial structure functions (RSFs) were obtained by Fourier transforming $k^3$-weighted $\chi (k)$ functions typically in the range 1.6-10.3 Å$^{-1}$ with a Bessel window function with a smoothing parameter of 4. Single-shell fits were performed in real space across the range of the first- and second- coordination shell ($\Delta R = 1.25 – 4.0$ Å) to determine the mean coordination number, $N$, the bond length, $R$, and the Debye-Waller factor, $\sigma$, for each shell. Optimization of the parameters was achieved with the $E_0$ shift constrained and the amplitude reduction factor, $S_0^2$, fixed at 1.0. The interatomic distances, $R$, coordination numbers, $N$, Debye-Waller factors, $\sigma^2$, were allowed to vary in the single-shell analysis. In a subsequent step multi-shell fits were performed by using the estimated data from the single-shell analysis. The fitting parameters were treated as follows: $E_0$ shift was constraint, the amplitude reduction factor, $S_0^2$, fixed at 1.0, the interatomic distance, $R$, and the coordination number, $N$, varied, the Debye-Waller parameter, $\sigma^2$, was fixed for the second shell using the data from the single-shell fits of the second shell. Note that the Debye-Waller factor, $\sigma^2$, of the first Nd-O shell was allowed to vary in the multi-shell analysis. The latter approach was necessary due to strong correlation of the Si and Ca backscattering contributions for the second shell. Theoretical scattering paths for the fits were calculated using FEFF 8.2 (Newville, 2001) and the structure of 11 Å tobermorite (Merlino et al., 2001).

For the EXAFS analysis of Nd(III) doped cement phases, the model proposed earlier by Schlegel et al. (2004) for Eu(III) retention by amorphous C-S-H phases with varying Ca/Si molar ratios was adapted. This model, which is based on the assumption that trivalent lanthanides (e.g. Nd(III) and Eu(III)) substitute for Ca in the C-S-H structure, includes backscattering contributions from Si atoms at $R \sim 3.2$ Å and $R \sim 3.7 – 3.75$ Å, and Ca atoms at $R \sim 3.79 – 3.84$ Å. In this study Nd(III) incorporation into the lattice of “inner” - C-S-H by substitution for Ca was assumed based on similarities in the ionic radii of the two elements in sevenfold coordination (1.01 Å and 1.06 Å, respectively) (Shannon, 1976). Note that the short Si distances at $R \sim 3.2$ Å observed by Schlegel et al. (2004) were not considered in Nd doped C-S-H, as the EXAFS fits did not result in meaningful residual parameter using short Si distance. These distances were visible in Nd doped crystalline C-S-H phases only after 400 days of reaction time and not detected in Nd(III) doped amorphous C-S-H phases after reaction time up to 270 days.
(see Chapters 3 and 4). Probably, short Nd-Si distances are due to the higher crystallinity of tobermorite and xonotlite, compared to amorphous C-S-H phases and “inner”-C-S-H in cement and the higher degree of order close to Nd in the structure of crystalline C-S-H after long reaction time.

The proposed model for Nd(III) retention considers one Ca and one Si shell at similar distances, i.e.: $R_{\text{Nd-Si}} \sim 3.70 - 3.75 \, \text{Å}; R_{\text{Nd-Ca}} \sim 3.75 - 3.80 \, \text{Å}$. Two shells at similar distance, however, could be difficult to be distinguished in EXAFS as the spatial resolution, which was calculated from $\Delta R = \pi/2\Delta k$, where $\Delta k$ is the range of $k$-space being fit ($\Delta k = 1.60 - 10.30 \, \text{Å}^{-1}$), was estimated to be $\sim 0.18 \, \text{Å}$. Therefore, in order to verify the plausibility of the EXAFS fitting model with backscattering contributions from Si and Ca at similar distances, statistical F-tests were performed as described in the Supporting Information of Chapter 3. Based on the crystallographic data on non-doped tobermorite, which is considered as a good model for the structure of less crystalline C-S-H phases (see Chapter 4 for more details) and the results from the F-tests, it was assumed that a model, which includes O as well as one Si and one Ca shell can be applied to adequately reproduce the coordination environment of Nd in the C-S-H structure.

3. Results and discussion

3.1 Distribution of Nd in the cement matrix

BSE imaging allows identification of minerals of different compositions based on the gray-scale contrast (Scrivener, 2004). For example, “inner”- and “outer”-C-S-H phases, which form during hydration, could be distinguished based on their contrast caused by different densities. Figure 1a shows that Nd enriched rims formed around “inner”-C-S-H phases (white frame in Figure 1a). The “inner”-C-S-H fills up the space originally occupied by the alite grains. “Outer”-C-S-H (Figure 1a), which is less dense than inner-C-S-H and therefore has a darker grey tone, fills the porous space between the clinker minerals originally occupied by water. The Nd distribution map displayed in Figure 1b shows that Nd was preferentially accumulated in regions with “inner”-C-S-H. Nevertheless, some Nd spots also appeared to in regions where “outer”-C-S-H formed.
Figure 1  BSE image and elemental distribution maps of Nd, Ca and Si in 60 × 50 μm overview of a Nd enriched hydrated cement matrix with a water/cement ratio of 0.4, a hydration time of 200 days and a final metal concentration of 26 μmol Nd/g solid phase. The color bar represents relative Nd metal enrichments in the sample.

Metal accumulation around “inner”-C-S-H phases was already observed in a previous study on the immobilization of Ni in HCP (Vespa et al., 2006a). The authors proposed that the clinker mineral alite, which dissolves faster than belite, forms highly reactive zones of “inner”-C-S-H phases. These zones may exhibit a high surface area, which promotes Nd uptake and consequently, facilitates metal accumulation in these areas.

The regions studied by SEM were also investigated by μ-XRF. Figures 2a and b show the elemental distributions of Nd and Ca in an overview map (~1400×1400 μm²). The fine maps displayed in Figures 2 c - f were collected in the areas encircled in Figure 2a. All μ-XRF maps supported the heterogeneous distribution of Nd and Ca in the cement matrix previously observed with SEM-EDS. Further, Nd accumulation in the rims around clinker minerals was supported. The finding that μ-XRF maps also display Nd “spot-like” features in addition to rims could be attributed to the maximal depth of the
the existing X-ray fluorescence, which restricts vertical versus horizontal spatial resolution. The $\mu$-XRF maps revealed anti-correlation between Nd and Ca in the different regions.

![Figure 2](image)

**Figure 2** $\mu$-XRF elemental distribution maps of Nd and Ca for the Nd(III) doped HCP samples with a water/cement ratio of 0.4, a hydration time of 28 days and a final metal concentration of 26 $\mu$mol Nd/g solid phase (CEMHYD-28-26). Selected regions of interest for $\mu$-EXAFS measurement are labeled 1-4. The color bar represents relative metal enrichments in each sample.
The speciation of Nd was determined on several spots (referred to as regions of interest (ROI)) using $\mu$-extended X-ray absorption fine structure ($\mu$-EXAFS) spectroscopy.

### 3.2 Speciation of Nd on the micro-scale.

The $\mu$-EXAFS measurements were carried out on a total of 12 spots on the samples CHEMHYD 28-26 and CHEMHYD-200-26 (Table 2, Figures 3 and 4).

**Figure 3** Selected Nd $L_{III}$-$\mu$-EXAFS and bulk-EXAFS measurements for the Nd–doped HCP samples with a w/c ratio of 0.4, varying reaction time (1, 28, 120 and 200 days) and total metal concentrations of 26 $\mu$mol / g solid phase; a) $k^3$-weighted spectra and b) the corresponding RSFs of experimental (solid line) and fitted (dashed and doted lines for the imaginary and the real part, respectively); c) $k^3$-weighted EXAFS function for the Fourier-backtransform spectra obtained from Figure 3b (range: $R + \Delta R = 1.5 - 4.0$).
Table 2  Structural information obtained from μ-EXAFS Nd $L_{III}$-edge data analysis of Nd(III)-doped HCP samples$^a$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time</th>
<th>Nd loading (μmol/g)</th>
<th>ROI $N_{Nd}^o$ (Å)</th>
<th>$\sigma_{Nd-O}^o$ (Å)</th>
<th>$R_{Nd-O}$ (%)</th>
<th>$N_{Nd}^{\text{calc}}$ (Å)</th>
<th>$\sigma_{Nd-O}^{\text{calc}}$ (Å)</th>
<th>$\chi_{\text{calc}}$ (%)</th>
<th>$\Delta E_0^e$ (eV)</th>
<th>$R_f^f$ (%)</th>
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<td>1</td>
<td>7.1</td>
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$^a$ Fourier-transformed $\chi(k)$ range (for the samples in this table $\Delta k = 1.7 - 10.3^{-1}$), $^b$ Number of neighbor atoms $^c$ Interatomic distance $^d$ Debye-Waller factor $^e$ Energy shift of the theoretical calculated spectrum to the energy grid of the measured spectrum, $^f$ The residual factor $R_f$

The radial structural functions (RSFs) of all Nd(III) doped HCP samples showed a peak at $R + \Delta R \sim 2.0$ Å, which was fitted by assuming the presence of a single oxygen shell. The number (N) of neighboring oxygen atoms and the estimated Nd-O distances for all Nd(III)-doped HCP samples were found to be similar within the experimental uncertainties, e.g. $N_{O} = 6.9 - 8.5$ and $R_{Nd-O} = 2.43 - 2.46$ Å (Table 2).

The Debye-Waller factors (DW) were in the range 0.003 Å$^2$ to 0.010 Å$^2$ in most cases. Note that the DW factors were higher than those reported for Nd(III) doped crystalline C-S-H (compare structural data in Tables 3 and 4 in Chapter 3), which indicates a higher degree of disorder in the coordination environment of Nd in HCP samples.
Figure 4  a) $k^3$-weighted spectra and b) the corresponding RSFs of experimental (solid line) and fitted (dashed and dotted lines for the imaginary part and the amplitude envelope, respectively) Nd L$_{III}$-edge experimental spectra for $\mu$-EXAFS and bulk-EXAFS measurements of selected Nd - doped HCP samples with a water/cement ratio of 0.4, varying reaction time (15 min., 1 day and 28 days) and total metal concentrations of 26 $\mu$mol / g solid phase, and Nd doped portlandite; c) $k^3$-weighted EXAFS function for the Fourier-backtransform spectra obtained from Figure S1b (range: $R + \Delta R = 1.5 - 4.0$).

Presence of further backscattering atoms was indicated by the broad peak in the Fourier transforms (FTs) at $R + \Delta R \sim 3.0$ Å. This peak was fitted by considering Nd-Si and Nd-Ca backscattering contributions. The $\mu$-EXAFS measurements revealed significant variations in the EXAFS parameters of the neighboring Si and Ca atoms determined on the different ROIs in the CEMHYD-28-26 sample. For example, the coordination number
of Si varied between $N_\text{Si} = 2.8 - 5.6$ while the Nd-Si distances ranged between $R_{\text{Nd-Si}} = 3.78 \text{ Å} - 3.85 \text{ Å}$. The differences in both parameters were larger than the expected uncertainties, i.e. ± 20% for N and ± 0.02 Å for R. The corresponding variations in the μ-EXAFS parameters of the neighboring Ca atoms were comparable: $N_\text{Ca} = 2.8 - 4.9$ and $R_{\text{Nd-Ca}} = 3.83 \text{ Å} - 3.89 \text{ Å}$. The variability of the local coordination environment of Nd is due to structural disorder in C-S-H phases of hydrating cement. Interestingly, the coordination numbers $N_\text{Si}$ and $N_\text{Ca}$ were significantly larger than those expected for Nd sorbed on solid phases. For example, Nd sorption onto portlandite, which is one of the main secondary phases forming in hydrating cement, had $N_\text{Ca} = 2.3$ and a short Nd-Ca distance (3.66 Å) (Table 2). The structural parameters listed in Table 2 show that the number of neighboring second shell atoms in all samples was $> 2$, which suggests structural incorporation of Nd into solid phases.

In contrast to the variations in the structural parameters observed in the CEMHYD-28-26 sample the μ-EXAFS parameters determined on three ROIs in the CEMHYD-200-26 sample were similar in value. Although the number of spots probed was limited, consistency of the data was considerable. For example, the coordination numbers of neighboring Si and Ca atoms were in the range $N_\text{Si} = 5.5 - 6.6$ and $N_\text{Ca} = 4.4 - 5.8$ (Table 2). These variations were significantly less than in the CEMHYD-28-26 sample. Importantly, the Nd-Si and Nd-Ca distances were consistently longer than in the CEMHYD-28-26 sample, i.e., $R_{\text{Nd-Si}} = 3.85 \text{ Å} - 3.87 \text{ Å}$ and $R_{\text{Nd-Ca}} = 3.91 \text{ Å} - 3.92 \text{ Å}$ (Table 2), showing that Nd-Si and Nd-Ca distances in the Nd(III) doped HCP samples increased with time. Longer Nd-Ca and Nd-Si distances and increasing values for $N_\text{Si}$ and $N_\text{Ca}$ were previously observed on aged Nd(III) doped crystalline C-S-H phases (see Tables 3 and 4 in Chapter 3).

### 3.3 Speciation of Nd on the macro-scale.

Bulk-EXAFS measurements allowed the variability in the structural parameters observed on the micro-scale to be assessed with respect to their relevance for the respective cement sample. A comparison of the corresponding EXAFS parameters (Tables 2 and 3) for the CEMHYD-28-26 and CEMHYD-200-26 shows no significant differences in the structural parameters determined for the oxygen shell. However,
differences in the structural parameters of further coordination shells in the samples aged fro 28 days were observed. For example, in CEMHYD-28-26, the bulk-EXAFS data indicate long Nd-Si distances (R\textsubscript{Nd-Si} = 3.83 Å) and high coordination numbers (N = 4.6), while significantly shorter distances (R\textsubscript{Nd-Si} = 3.78 - 3.79 Å in ROIs 2, 5 and 9) and lower coordination numbers (N = 2.8 and 3.4 in ROIs 5 and 8) were found on the micro-scale.

This suggests that coordination environments with shorter Nd-Si distances and lower coordination numbers were not representative for the Nd(III) doped material aged for 28 days. This conclusion also holds for the Ca shell, i.e., Nd-Ca distances and the number of neighboring Ca atoms. By contrast, the structural parameters determined from micro-spectroscopic and bulk-EXAFS measurements for the CEMHYD-200-26 sample were similar, which indicates that micro-scale variability in the local coordination environment of Nd in HCP was significantly reduced with increasing hydration time.

The bulk-EXAFS data listed in Table 3 further show changes in the Nd-Si and Nd-Ca bond distances with time.

\textbf{Table 3} \hspace{1cm} \textit{Structural information obtained from bulk-EXAFS Nd L\textsubscript{III}-edge data analysis of Nd(III) doped HCP samples\textsuperscript{1}.}

| Sample (bulk-EXAFS) | Time (days) | Nd loading (μmol/g) | Δ\textsuperscript{k} (Å\textsuperscript{3}) | N\textsubscript{O} | R\textsubscript{Nd-O} (Å) | σ\textsuperscript{o} (Å) | N\textsubscript{Si} | R\textsubscript{Nd-Si} (Å) | σ\textsuperscript{o} (Å) | N\textsubscript{Ca} | R\textsubscript{Nd-Ca} (Å) | σ\textsuperscript{o} (Å) | ΔE\textsubscript{0} (eV) | R\textsubscript{f} |
|---------------------|------------|---------------------|---------------------|------------------|-------------------|----------------|------------------|-------------------|----------------|------------------|-------------------|----------------|----------------|
| CEMHYD 15 min.      | 26         | 1.5-10.6            | 7.6                 | 2.43             | 0.010             | 3.8            | 3.76             | 0.004             | 5.2             | 3.81             | 0.009             | 4.12             | 5.9             |
| CEMHYD 1            | 26         | 1.5-10.6            | 8.5                 | 2.46             | 0.011             | 4.8            | 3.78             | 0.003             | 4.6             | 3.84             | 0.004             | 6.83             | 8.2             |
| CEMHYD 28           | 26         | 1.5-10.6            | 7.8                 | 2.45             | 0.010             | 4.6            | 3.83             | 0.010             | 4.8             | 3.86             | 0.007             | 8.49             | 9.4             |
| CEMHYD 200          | 26         | 1.5-10.6            | 8.3                 | 2.45             | 0.011             | 6.3            | 3.85             | 0.004             | 4.7             | 3.91             | 0.003             | 5.82             | 7.3             |
| CEMSORB 1           | 26         | 1.5-10.6            | 6.9                 | 2.46             | 0.009             | 2.34           | 3.78             | 0.003             | 3.75             | 3.81             | 0.009             | 7.79             | 7.9             |
| CEMSORB 28          | 26         | 1.5-10.6            | 7.3                 | 2.46             | 0.009             | 2.61           | 3.77             | 0.003             | 4.3             | 3.83             | 0.009             | 7.39             | 4.8             |
| CH (Portlandite)    | 1          | 26                  | 7.8                 | 2.42             | 0.006             | -              | -                | -                 | 2.3             | 3.66             | 0.004             | 1.13             | 9.2             |

\textsuperscript{1} footnotes a-f are explained in Table 2
In the Nd(III) doped samples aged for 15 min and 1 h (CEMHYD-15M-26, CEMHYD-1-26), the Nd-Si and Nd-Ca distances were determined to be \( R_{\text{Nd-Si}} = 3.76 - 3.78 \, \text Å \) and \( R_{\text{Nd-Ca}} = 3.81 - 3.84 \, \text Å \). These shorter distances were similar to those determined on few ROIs in the CEMHYD-28-26 sample. Nevertheless, the distances were significantly shorter than those determined on the sample aged for 200 days for which Nd-Si and Nd-Ca distances were determined to be \( R_{\text{Nd-Si}} = 3.85 \, \text Å \) and \( R_{\text{Nd-Ca}} = 3.91 \, \text Å \). This finding corroborates the observed trend to longer Nd-Si and Nd-Ca distances with time, which was already indicated from the micro-spectroscopic data. The changes in \( R_{\text{Nd-Ca}} \) and \( R_{\text{Nd-Si}} \) distances with time reveal that the initial coordination environment of Nd determined after short reaction times (\( \leq 1 \) day) represented a “metastable” configuration.

In addition to the Nd-Si bond distances the coordination number of neighboring Si atoms changed with time (Table 3). In contrast, the number of neighboring Ca atoms showed no clear trend within the expected uncertainty range \( (N_{\text{Ca}} = 4.6 - 5.2) \). The number of neighboring Si atoms increased from \( N_{\text{Si}} = 3.8 \) and 4.8 in the CEMHYD-15M-26 and CEMHYD-1-26 samples, respectively, to \( N_{\text{Si}} = 6.3 \) in the aged CEMHYD-200-26 sample. This change in \( N_{\text{Si}} \) was above the expected uncertainty range (\( \pm 20 \% \)).

4. A mechanistic interpretation of Nd immobilization in HCP

Exposing unhydrated cement to water generates a chemically very reactive system. Detailed description of the hydration process of cement CEM I and the corresponding thermodynamic modeling were reported elsewhere (Lothenbach and Winnefeld, 2006). In contact with water the hydration process starts. In the first stage easily soluble solids such as the alkali sulphates and free lime dissolve, releasing Ca, Na, K, \( \text{SO}_4^{2-} \) and \( \text{OH}^- \) into solution. Less soluble solids such as gypsum (\( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \)) and calcite dissolve partially until equilibrium conditions are reached. In addition, the clinker phases (alite: \( \text{Ca}_3\text{SiO}_5 \); belite: \( \text{Ca}_2\text{SiO}_4 \); aluminate: \( \text{Ca}_3\text{Al}_2\text{O}_6 \); alumino-ferrite (\( \text{Ca}_4(\text{Fe}^{x-}_x \text{Al}_{1-x})_4\text{O}_{10} \) solid solution)) slowly dissolve and continuously release Ca, Si, Al, Fe(III), and \( \text{OH}^- \) to the solution. In the early stage of cement hydration (\( < 12 \) h) mainly portlandite, ettringite and C-S-H phases precipitate. In this stage the pore solution has a pH of about 12.7 - 13.1 with Na (\( \sim 35 - 40 \) mM) and K (\( \sim 34 - 53 \) mM) being the main counterions of
Other important constituents were Ca (~ 25 mM) and SO$_4^{2-}$ (~ 25 mM). After 24 hours, further evolution of the cement composition is controlled by the continuous formation of C-S-H phases and portlandite while the formation of ettringite is exhausted and formation of hydrotalcite and calcium monocarbonate starts (Lothenbach and Winnefeld, 2006). The later stage of cement hydration extends over years and is driven by slow dissolution of the clinker minerals alite and belite. In this stage the solution has a pH of about 13.3 (Na and K as the main counterions), while the concentrations of Ca and S are significantly lower than in the early stage (Ca ~ 2 mM; SO$_4^{2-}$ ~ 2 mM). Hence, the speciation of Nd in hydrating cement paste can be assessed with a view to the chemical conditions of the reacting cementitious system.

Upon adding Nd to the reacting cementitious systems several Nd species may appear: Nd bound on the surface of clinker and secondary minerals (outer- and inner-sphere surface complexes), Nd co-precipitated in solids with fixed and variable (solid solution) stoichiometries, and Nd incorporated in the structure of secondary minerals. As previously discussed, the speciation of Nd in hydrating cement is not dominated by the formation of Nd surface complexes (outer-sphere, inner-sphere) on single minerals, such as portlandite, due to the large number of neighboring Ca and Si atoms determined for Nd in HCP. Based on thermodynamic calculations, the formation of Nd(OH)$_3$(am) was anticipated under the highly alkaline conditions of a cementitious system (see Chapter 3). Neither micro- nor bulk-EXAFS spectra, however, showed the corresponding Nd-Nd backscattering contributions, which allows the formation of Nd(OH)$_3$(am) in these systems to be excluded. Rapid formation of a mixed Nd-Ca precipitate, however, could not be ruled out with a view to similarities in the EXAFS parameters of the CEMHYD-15M-26 and CEMHYD-1-26 samples, which were analyzed in this study with those of a mixed Nd/Ca precipitate detected after Nd addition to xonotlite suspensions (pH ~ 10.7) in a previous study (Chapter 3). The following structural parameters were determined for the precipitate: $R_{\text{Nd-Si}}$=3.81 Å and $R_{\text{Nd-Ca}}$=3.84 Å; $N_{\text{Si}}$=4.6 and $N_{\text{Ca}}$=5.5 (Table 2 in Chapter 3). The latter coordination numbers and bond-distances are comparable to those in the Nd(III) doped cement samples (CEMHYD-15M-26, CEMHYD-1-26) in the early stage of the hydration process: $R_{\text{Nd-Si}}$=3.76 - 3.78 Å and $R_{\text{Nd-Ca}}$=3.81 – 3.84 Å; $N_{\text{Si}}$=3.8 – 4.8 and $N_{\text{Ca}}$=4.6 - 5.2 (Table 3). Nevertheless, the shorter bond distances and lower
coordination numbers observed in the CEMHYD-15M-26 and CEMHYD-1-26 samples could indicate that, in addition to the formation of a Nd/Ca precipitate, a small portion of Nd is bound as surface complex in hydrating cement. Shorter distances and low coordination numbers were also observed in the case of sorption samples (CEMSORB-1-26 and CEMSORB-28-26). This indicates predominant formation of Nd surface complexes. Only a small fraction of Nd is incorporated within the 28 days reaction time.

The structural parameter determined for the aged CEM-200-26 samples can be compared with those determined earlier on Nd(II) doped, hydrothermally synthesized tobermorite (Chapter 3). The total inventory of Nd was found to be incorporated in the structure of the hydrothermally synthesized tobermorite. In the latter phase Nd has about 5 Si and 6.7 Ca neighbouring atoms at $R_{\text{Nd-Si}}=3.87$ Å and $R_{\text{Nd-Ca}}=3.91$ Å, respectively, indicating that Nd-Si and Nd-Ca bond distances are longer in well-ordered crystalline C-S-H phases than in the Nd/Ca precipitate and Nd surface complexes. Furthermore, Nd was found to preferentially replace Ca in the Ca sheets of 11 Å tobermorite (Chapter 3). The resulting bond distances were in agreement with those determined for Nd in the CEMHYD-200-26 samples ($R_{\text{Nd-Si}}=3.85$ Å and $R_{\text{Nd-Ca}}=3.91$ Å) (Table 3), indicating Nd incorporation into the structure of C-S-H phases in hydrating cement. Nd-Ca substitution in the Ca sheets of C-S-H phases due to similarities in the ionic radii of the two elements in sixfold coordination (0.983 Å and 1.00 Å, respectively). In the ideal tobermorite structure Ca from the central Ca sheet is surrounded by ~7 oxygens ($R_{\text{Ca-O}}=2.46$ Å), 3-4 Si ($R_{\text{Ca-Si}}=3.67-3.73$ Å) and about 5 Ca ($R_{\text{Ca-Ca}}=3.80-3.96$ Å) (Merlino et al., 2001). Therefore, our observation of about 5 nearest neighboring Ca atoms at $R_{\text{Nd-Ca}} \sim 3.85-3.91$ Å suggests that Nd was bound in the Ca sheets of the C-S-H phases present in HCP.

EXAFS investigations of the Nd uptake by amorphous C-S-H phases further corroborated the finding of longer Nd-Si and Nd-Ca distances upon ageing Nd(III) doped C-S-H phases for up to 270 days (Chapter 4). In particular, in the samples with the highest calcium-to-silica (C:S) ratio (C:S = 1.54), Nd-Si and Nd-Ca distances slightly increased from about $R_{\text{Nd-Si}}=3.75$ Å and $R_{\text{Nd-Ca}}=3.76$ Å, respectively, to about $R_{\text{Nd-Si}}=3.80$ Å and $R_{\text{Nd-Ca}}=3.84$ Å, respectively, over 270 days hydration time. C-S-H phases in HCP are expected to have a C:S ratio in the above range. The coordination numbers $N_{\text{Si}}$ and
were found to increase from \( N_{Si} \approx 1.5 \) and \( N_{Ca} \approx 2.3 \) to \( N_{Si} \approx 3.6 \) and \( N_{Ca} \approx 4 \) in the C-S-H systems. Thus, in Nd(III) doped amorphous C-S-H the coordination numbers, \( N_{Si} \) and \( N_{Ca} \), are lower and distances, \( R_{Nd-Si} \) and \( R_{Nd-Ca} \), are shorter after ageing for 270 days compared to those determined in the CEMHYD-200-26 sample. The reason for these differences in the structural parameters remains unclear. A tentative explanation can be given by taking into account differences in the crystallinity of “inner”-C-S-H formed in cement paste and the amorphous C-S-H phases prepared in the laboratory. In hydrated cement, Nd seems to preferentially accumulate in rims around “inner”-C-S-H phases. In situ formation of the latter phases may be much slower than precipitation of synthetic C-S-H phases allowing the formation of better crystallized C-S-H phases in HCP. This conclusion is consistent with observations made by BSE gray-scale contrast imaging (Scrivener, 2004). “Inner”-C-S-H phases have a higher density (in line with the lighter grey tone in BSE imaging) than “outer”-C-S-H phases, which suggests the presence of better crystallized material. Thus, one may conclude that the coordination environment of Nd in the denser “inner”-C-S-H and in synthetic C-S-H phases could be different. Furthermore, the coordination environment of Nd in well crystallized C-S-H phases may be representative for Nd bound in “inner”-C-S-H phases.

5. Implications for Radioactive Waste Management

The safe disposal and long-term storage of radioactive waste is worldwide a major concern and can be seen as a primary environmental task. The capability of near field materials to immobilize radionuclides is an important aspect of safety considerations. Efficiency of immobilization processes has direct consequences on the release of radionuclides from the near field into the far field surrounding a repository for radioactive waste. In this context, the present study provides substantial evidence for the long-term safe disposal of an important class of radionuclides, i.e., the trivalent actinides such as \(^{241/243}\text{Am}\). First, it is shown that trivalent lanthanides, and by analogy trivalent actinides, are preferentially accommodated by C-S-H phases in hydrated cement. This result confirms an earlier TRLFS study of Stumpf et al. (2004), which showed that Cm(III) preferentially sorbs to C-S-H phases in the cement matrix. This finding, in combination with the observed long-term persistence of C-S-H phases in an evolving cementitious
near field (e.g. Atkins, 1992), implies that the uptake-controlling cement phase for trivalent actinides (i.e., C-S-H phases) will be present in a cement-based repository over long time periods. Secondly, this study shows that binding into the structure of C-S-H phases is the dominant mode of Nd immobilization. Again, this finding supports the conclusions of an earlier study (Tits et al. 2003), which proposed Cm(III) incorporation into the Ca sheets and interlayer of C-S-H phases. Incorporation into the structure implies that trivalent actinides could be accommodated irreversibly in C-S-H phases. Thus, the binding mechanisms proposed in this study support the idea of long-term safe disposal of trivalent actinides in cement-based repositories for radioactive waste.
6. References


CHAPTER 6

A TRLFS and EXAFS study on Eu(III) uptake by 11 Å tobermorite

ABSTRACT

The uptake of Eu(III) by 11 Å tobermorite was investigated by the combined use of time-resolved laser fluorescence spectroscopy (TRLFS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Eu(III) doped tobermorite samples with varying metal loadings (0.4, 7 and 35 μmol Eu/g solid phase) and reaction time (1 - 570 days) were investigated. The structural environment of Eu(III) taken up by tobermorite was found to depend on both parameters.

At high Eu(III) loadings (7 μmol Eu/g solid phase) TRLFS indicate the presence of three Eu(III) species with different fluorescence lifetimes after one day reaction time. The emission lifetimes deduced for the different fluorescing Eu(III) species correspond to ~4.7, ~1 and zero H₂O/OH molecules in the coordination sphere, suggesting the presence of one surface species forming an inner-sphere surface complex and two species incorporated in the crystal lattice. After longer reaction time (90 days, 570 days), the surface species has disappeared.

At lower Eu(III) loadings (0.4 μmol Eu/g solid phase) and reaction time between 1 and 310 days only two Eu(III) species with ~1 - 2 and zero H₂O/OH molecules were detected, corresponding to Eu(III) being incorporated in the structure. The results from EXAFS carried out on samples with high Eu loadings (35 μmol Eu/g) reveal that the distances between Eu(III) and neighboring Ca and Si atoms increase after prolonged reaction time, coinciding with increasing numbers of neighboring Ca and Si atoms. The study shows that binding into the structure of 11 Å tobermorite is the dominant mode of Eu(III) immobilization after long reaction time. This finding is essential for assessment of the safe disposal of actinides in cement-based repositories for radioactive waste, because incorporation into the crystal structure could prevent radionuclide release into the environment.
1. Introduction

Cement-based materials play an important role in many multi-barrier concepts developed worldwide for the safe disposal of radioactive wastes in deep geological repositories (Chapman and McCombie, 2003). Cement stabilization of contaminated wastes is one of the most common solidification/stabilization (S/S) techniques prior to near-surface or underground disposal. The latter waste form may contain significant inventories of trivalent actinides, such as $^{241/243}$Am(III). Trivalent lanthanides, e.g. Nd(III) and Eu(III), are regarded as suitable chemical analogues for trivalent actinides based on their comparable ionic radii (Shannon, 1976) and similarities in the complexation behaviour. Further improvements in the molecular-level understanding of the binding mechanisms of trivalent lanthanides to cementitious materials are required because the chemical mechanisms governing radionuclide immobilization in these systems are poorly understood. This knowledge, however, is essential for detailed long-term predictions of the environmental impact of cement-stabilized waste forms.

Calcium silicate hydrates (C-S-H) are considered to be the most important constituent of hardened cement paste with regards to their abundance and the diversity of structural sites exposed for cation and anion binding (Atkins and Glasser, 1992). C-S-H phases may control the long term release of radionuclides due to their stability during the evolution of the cementitious near field. 11 Å tobermorite is a crystalline C-S-H phase for which the structure is well known (Hejny and Armbruster, 2001; Merlino et al., 2001) (details of the structure of 11 Å tobermorite are shown in the section “Introduction” in Chapter 3). In addition, 11 Å tobermorite is expected to form as secondary solid phase at elevated temperature in the hyper-alkaline environments surrounding cement-based nuclear and toxic waste sites (e.g. JANTZEN et al., 1984).

Several authors have investigated the interaction of lanthanides and trivalent actinides with C-S-H phases in the past decades (e.g. (Pointeau et al., 2001; Schlegel et al., 2004; Tits et al., 2003). POINTEAU et al., (2001) investigated the uptake of Eu(III) by amorphous C-S-H phases with varying calcium-to-silica (C/S) ratios (0.34-1.65) and 14 Å tobermorite in the pH range 10.0-12.4 using time-resolved laser fluorescence spectroscopy (TRLFS). The authors observed two Eu(III) species with different fluorescence lifetimes (390 and 990 μs) sorbed onto or incorporated in amorphous C-S-H
phases and tobermorite. The Eu(III) species with long lifetime was attributed to Eu(III) bound in the framework of C-S-H by replacing Ca. The second Eu(III) with shorter lifetime was proposed to be Eu(III) sorbed on the surface of C-S-H or in a surface layer. Tits et al. (2003) investigated the interaction of Eu(III) and Cm(III) with a C-S-H phase with C/S ratio of about 1.0 at pH 13.3 using batch-type sorption experiments and TRLFS. TRLFS allowed three different Cm(III) species with different lifetimes to be distinguished. The authors proposed different coordination environments and amounts of H₂O molecules in the first coordination sphere of the Cm(III) species based on the different fluorescence lifetimes. Using the defect 11 Å tobermorite structure as model for amorphous C-S-H phases these authors further concluded that Eu(III) and Cm(III) were incorporated into the structure of the C-S-H phase by substituting for Ca. SCHLEGEL et al. (2004) investigated the uptake of Eu(III) by amorphous C-S-H phases as function of the added Eu(III), the C/S ratio of the C-S-H phases and the reaction time using extended X-ray absorption fine structure (EXAFS) spectroscopy. The EXAFS data suggested incorporation of Eu(III) into the structure of C-S-H phases at the Ca structural sites.

Such spectroscopic investigations with Eu(III) do not allow for an unambiguous discrimination between the Eu(III) species formed in the early stages of the sorption process, i.e. inner- and outer-sphere surface complexation and Eu(III) incorporation into the C-S-H structure. Furthermore, the cited studies all involve the interaction of trivalent actinides and lanthanides with poorly-ordered amorphous C-S-H phases, which limits detailed characterization of the structural environment of incorporated species. This is the reason why minerals of the tobermorite family, which are considered to be good models for the structure of poorly ordered amorphous C-S-H (Nonat, 2004; Richardson, 2004; Taylor, 1986), have been used in the present study.

The aim of this study was to investigate Eu(III) uptake by 11 Å tobermorite by the combined use of TRLFS and EXAFS, thus allowing surface species and species incorporated into the lattice of C-S-H to be distinguished from each other. Eu(III) was chosen as a non-radioactive analogue for trivalent actinides due to its unique spectroscopic properties allowing speciation in the μ-mol range (STUMPF et al., 2007). The position of the main Eu(III) bands (⁵D₀ → ⁷Fᵢ,₄ transitions; J = 0, 1, 2, 3, 4) are almost independent of the chemical environment of the metal ion. However, the intensity
of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition changes significantly when Eu(III) forms complexes (Jorgensen and Judd, 1964). From the splitting of the fluorescence emission bands, in particular at low temperature, information on the ligand field and, hence, on the geometry of the coordination site of the Eu(III) ion can be deduced (Bünzli and Choppin, 1989). The ground state $^7\text{F}_0$ is non-degenerate. Hence, the number of peaks observed in the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ band corresponds to the number of Eu(III) species. TRLFS also allows the hydration state of the Eu(III)/tobermorite species to be studied using the linear correlation between the decay rate and the number of the H$_2$O molecules or OH groups in the first coordination sphere (Horrocks and Sudnick, 1979; Pointeau et al., 2001; Tits et al., 2003). Complementary information on atomic distances and coordination numbers of the Eu(III)/tobermorite species can be derived from EXAFS (STUMPF et al., 2007). Thus, the combined use of the two spectroscopic methods TRLFS and EXAFS is expected to provide complementary structural information essential for the development of a mechanistic picture of Eu(III) immobilization by 11 Å tobermorite.

2. Materials and methods

2.1 Sample preparation

Throughout this study Fluka (Sigma-Aldrich, Buchs, Switzerland) or Merck (Dietikon, Switzerland) “pro analysis” chemicals and high-purity de-ionised water generated by a Milli-Q Gradient A10 system (Millipore, Bedford, USA) were used. All experiments were carried out in a glovebox under N$_2$ atmosphere and ambient temperature (CO$_2$, O$_2$ < 2ppm, T = 290 K ± 3 K). 11 Å tobermorite samples were synthesized as described in Chapter 3. Eu(III) sorption samples used for the TRLFS measurements were prepared by adding appropriate volumes of a Eu(III) stock solution (10$^{-3}$ M) to tobermorite stock suspensions (5 g L$^{-1}$ (TRLFS) and 50 g L$^{-1}$ (EXAFS) solid materials suspended in their equilibrium solution) to achieve the required Eu(III) loadings (TRLFS: 0.4 and 7 µmol Eu/g solid phase; EXAFS: 7 and 35 µmol Eu/g solid phase). No changes in pH were determined after Eu(III) addition.
### Table 1  Chemical conditions of the Eu(III) sample preparation for EXAFS and TRLFS measurements

<table>
<thead>
<tr>
<th>Method</th>
<th>Sample</th>
<th>Reaction time (days)</th>
<th>Eu(III) loading (μmol Eu/g tobermorite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXAFS</td>
<td>Eu(III)/tobermorite-35-1</td>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/tobermorite-35-28</td>
<td>28</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/tobermorite-35-480</td>
<td>480</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/tobermorite-7-120</td>
<td>120</td>
<td>7</td>
</tr>
<tr>
<td>TRLFS</td>
<td>Eu(III)/tobermorite-7-1</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/tobermorite-7-90</td>
<td>90</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/tobermorite-7-570</td>
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<td>7</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/tobermorite-0.4-1</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/tobermorite-0.4-310</td>
<td>310</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The samples were equilibrated in the glove box and sampled after 1, 90 and 570 days (TRLFS) or 1 and 480 days (EXAFS), respectively. After phase separation by centrifugation (60 min at 95000 g) the Eu(III) treated samples were packed as a wet paste into Plexiglas sample holders and sealed with Kapton tape for the EXAFS measurements. TRLFS measurements were carried out on suspensions. Sample abbreviations are given in Table 1.

### 2.2 TRLFS measurements

TRLFS measurements were performed with an excimer pumped dye laser system (Lambda Physics, EMG, 308 nm, Scanmate 2). Direct excitation of the Eu(III) $^5D_0$-level was carried out using the dye Coumarin 153 (emission at 522–600 nm). The Eu(III) fluorescence emission was detected by an optical multichannel system consisting of a Czerny Turner polychromator (Jobin Yvon HR 320) with 300/600/1200 lines/mm gratings and a gated, intensified photodiode array (Spectroscopy Instruments, ST180, IRY 700G). The laser pulse energy was controlled by a pyroelectric detector on a pulse to pulse basis. A pulse generator (Spectroscopy Instruments, DG 535) was used to measure the time-dependent emission decay. TRLFS experiments were carried out at $T < 20$ K as
decreasing temperature increased the fluorescence intensity and allowed a better spectral resolution of the crystal-field splitting of the $^7F_J$ ($J = 1 - 4$) transitions, narrowing peak(s) in the excitation spectra. The cooling system (Cryodyne Cryocooler model 22C, compressor 8200, CTI Cryogenics, USA) used helium as refrigerant and allowed continuous closed cycle cooling of the copper sample holder at the cold head. The laser beam was focused on the copper sample holder, and the fluorescence emission signal was collected with a glass fibre and directed onto the polychromator. Site selective excitation of the $^5D_0 \rightarrow ^7F_0$ transition experiments were carried out (300 lines/mm grating) from 576.0 to 582.0 nm. For each sample, several excitation wavelengths were selected to record emission spectra at higher resolution, (600 lines/mm grating, resolution ~1 nm (Neon)), and to determine the emission lifetimes (300 lines/mm grating). The fluorescence lifetimes were determined by varying the delay time between laser pulse and camera gating with time intervals of 50 to 100 μs.

2.3 EXAFS data collection and reduction

EXAFS spectra at the Eu L$_{III}$ edge (6977 eV) were collected at beamline BM26A (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France and the ANKA-XAS Beamline of the Angstroemquelle Karlsruhe (ANKA). Both beamlines are equipped with a Si (111) double-crystal monochromator. Spectra were energy calibrated to the first inflection point of the K-absorption edge of a Fe foil (7112 eV). The EXAFS measurements were conducted at room temperature in fluorescence mode using a 9 channel monolithic Ge-solid-state detector at SNBL/ESRF and a five element Ge-detector at the ANKA-XAS. For each compound, depending on the metal loadings, between three and eight spectra were collected to achieve the required signal-to-noise ratio. Details on the EXAFS data reduction are given in Chapter 3 (EXAFS data collection and reduction).

For the EXAFS analysis of Eu(III) doped tobermorite, the structural model proposed earlier by Schlegel et al. (2004) for Eu(III) retention by amorphous C-S-H phases with varying Ca/Si molar ratios was used. This model includes backscattering contributions from Si atoms at $R \sim 3.2$ Å and $R \sim 3.7 - 3.75$ Å, and Ca atoms at $R \sim 3.79 - 3.84$ Å and is based on the assumption that Eu substitutes for Ca in the lattice of
amorphous C-S-H phases. This assumption is justified with a view to similarities in the ionic radii of the two elements in sevenfold coordination (1.01 Å and 1.06 Å, respectively) (Shannon, 1976). In this study the short Si distances at R ~ 3.2 Å proposed by Schlegel et al. (2004) was not considered, as the EXAFS fits did not result in meaningful residual parameter including Si at short distance. The proposed model for Eu(III) retention only considers one Ca and one Si shell at similar distances, i.e.: R_{Eu-Si} ~ 3.70 - 3.75 Å; R_{Eu-Ca} ~ 3.75 - 3.80 Å. Note, however, that the spatial resolution, which is given by \( \Delta R = \pi/2\Delta k \), where \( \Delta k \) is the range of k-space being fit (\( \Delta k = 1.70 - 10.80 \text{ Å}^{-1} \)), was estimated to be ~0.17 Å, implying that the two shells can be hardly resolved. Statistical F-tests were performed in order to prove whether or not the proposed fitting model with backscattering contributions from Si and Ca at long distances can be justified (see Supporting Information in Chapter 3). Based the results from these tests and additional crystallographic considerations of the structure of non-doped tobermorite, it was concluded that a model, which includes O, and Si and Ca atoms at similar distances, can be applied to adequately reproduce the coordination environment of Eu in the tobermorite structure.

3. Results and discussion

3.1 TRLFS measurements at high Eu(III) loadings

Spectroscopic information on the Eu(III)/tobermorite species was derived from the excitation spectra of the \( ^{5}D_0 \rightarrow ^{7}F_0 \) transmission (Figure 1), fluorescence emission spectra of the \( ^{5}D_0 \rightarrow ^{7}F_J \) \( (J = 0, 1, 2) \) transitions (Figure 2-4) and the fluorescence emission lifetime (Figure 5). In all samples the \( ^{5}D_0 \rightarrow ^{7}F_0 \) transitions were very large with a FWHM (full-width at half-maximum) larger than 1.5 nm (Figure 1). Further, all bands showed a clear shoulder on the left side of the peak. These observations strongly suggest the presence of multiple Eu(III) species (Marques Fernandes et al., 2008).

The emission spectra at various excitation wavelengths in the range of the \( ^{5}D_0 \rightarrow ^{7}F_0 \) transition (578.47 nm – 580.13 nm) were normalized to the peak area of the \( ^{5}D_0 \rightarrow ^{7}F_1 \) transition, which is known to be largely independent of the environment of the Eu ion (Marques Fernandes et al., 2008). The \( ^{5}D_0 \rightarrow ^{7}F_1 \) and \( ^{5}D_0 \rightarrow ^{7}F_2 \) emission bands
were split into at least three crystal field (CF) levels, which indicates low site symmetry around Eu(III) (Figure 2 and 4). The emission spectra clearly varied with varying excitation wavelengths (Figure 3). The $^5D_0 \rightarrow F_0$ transitions showed a strong red shift with increasing excitation wavelength.

The $^5D_0 \rightarrow F_1$ and $^5D_0 \rightarrow F_2$ emission bands excitation at $\lambda = 579.5$ nm were each split at least threefold (Figure 4), indicating low site symmetry around the Eu(III) ion. The spectra further showed that in all transitions the size and shape of the peak varied with the reaction time, suggesting again the presence of multiple Eu(III) sorbed species with varying, time-dependent relative portions.

**Figure 1** Eu(III) excitation spectra of Eu(III) taken by 11 Å tobermorite (7 μmol Eu/g solid phase) after 1, 90 and 570 days, measured at 18 K.

**Figure 2** Fluorescence emission spectra of the $^7D_0 \rightarrow F_{0,1,2}$ transitions in Eu(III) taken by 11 Å tobermorite (7 μmol Eu/g solid phase) after 1 day reaction time measured at 18 K and various excitation wavelengths.
The decay curve of the fluorescence emission after one day reaction time was fitted with a tri-exponential function, suggesting the presence of 3 Eu(III) species with different lifetimes (τ₁ = 200 μs, τ₂ = 647 μs and τ₃ = 2019 μs). After prolonged reaction time (90 and 570 days), however, only two Eu(III) species with different lifetimes were detected (90 days: τ₁ = 494 μs and τ₂ = 2570 μs; 570 days: τ₁ = 598 μs and τ₂ = 2199 μs). According to the empirical method developed by Horrocks and Sudnick (1979) the number of \( \text{H}_2\text{O}/\text{OH} \) molecules in the first coordination sphere of Eu(III) species is related to the emission lifetime by:
\[ N_{\text{H}_2\text{O}/\text{OH}} = 1.05 \; k_{\text{obs}} - 0.70 \]  

where \( k_{\text{obs}} \) is the observed decay rate of the excited state [ms\(^{-1}\)], which is related to the mean lifetime of Eu(III)/tobermorite species (\( k_{\text{obs}} = 1/\tau \)).

After one day equilibration about 4.7, 1.8 and zero \( \text{H}_2\text{O}/\text{OH} \) groups, respectively, were calculated to be bound in the first coordination sphere of the Eu(III) species. The uncertainties are ± 0.5 \( \text{H}_2\text{O}/\text{OH}^- \) as suggested elsewhere (Horrocks and Sudnick, 1979).

About 5 water molecules in the first Eu(III) coordination sphere were observed for Eu(III) inner-sphere complexes (Stumpf et al., 2007). The presence of two Eu(III)/tobermorite species with zero and ~2 water molecules is consistent with Eu(III) bound in the structure of tobermorite as Ca from the central Ca sheet and the interlayer is surrounded by zero and ~2 water molecules in the structure of non-doped 11 Å tobermorite (Merlino et al., 2001). Thus, assuming that no other quench processes (e.g. metal to ligand transfer) occurred in the vicinity of Eu(III), our observation of 4.7, ~2 and zero nearest neighboring water molecules suggests that three Eu(III) species, i.e. a Eu(III) surface-bound inner-sphere complex and two Eu(III) species bound in the structure of 11 Å tobermorite, existed in the early stage of Eu(III) interaction with tobermorite.

**Figure 5** Time dependency of Eu(III) emission decay by selective excitation of Eu(III) taken by 11 Å tobermorite (7 \( \mu \text{mol Eu/g solid phase} \)) after 1, 90 and 570 days, measured at 18 K (dotted and solid lines represent experimental data and the fit curves of the experimental data, respectively).
Based on the observed lifetimes it was estimated that 1.1 - 1.4 and zero H$_2$O/OH molecules were bound in the first coordination sphere of the Eu(III) species after reaction time $\geq$ 90 days. The estimated number of H$_2$O/OH groups for the Eu(III)/tobermorite species with the shorter (1.1 - 1.4 H$_2$O/OH) and longer lifetime (zero H$_2$O/OH) were very similar for the different reaction times, indicating similar coordination environments of Eu(III) in the Eu(III)/tobermorite-7-90 and Eu(III)/tobermorite-7-570 samples. The absence of the species with the shortest lifetime (4.7 H$_2$O/OH) after prolonged reaction time indicates incorporation into the tobermorite structure.

3.2 TRLFS measurements at low Eu(III) loadings

The Eu(III) $^5$D$_0$$\rightarrow$$^7$F$_0$ excitation spectra at low loadings exhibited slightly narrower excitation bands compared to those determined at high Eu(III) loading (compare Figures 1 and 6). Similar to the highly loaded samples the $^5$D$_0$$\rightarrow$$^7$F$_0$ transitions were very large with a FWHM (full-width at half-maximum) larger than 1.5 nm at the lower loading, thus suggesting the presence of more than one Eu(III) species.

The $^5$D$_0$$\rightarrow$$^7$F$_1$ and $^5$D$_0$$\rightarrow$$^7$F$_2$ emission bands recorded after excitation at 579.5 nm were at least threefold split (Figure 7). Splitting into three crystal field levels of the $^5$D$_0$$\rightarrow$$^7$F$_2$ emission band was more pronounced after 310 days reaction time than in the one day sample, indicating even lower site symmetry around the Eu(III) ion after prolonged reaction time.

The decay curves of the Eu(III) doped samples after 1 and 310 days reaction time could be fitted with a bi-exponential function, suggesting the presence of two Eu(III) species with two different lifetimes (Figure 8). The lifetimes after one day reaction time were determined to be $\tau_1 = 580$ $\mu$s and $\tau_2 = 1567$ $\mu$s. Based on these lifetimes the number of H$_2$O/OH molecules was estimated to be 1.1 and zero in the first coordination sphere of the Eu(III) species, indicating Eu(III) incorporation in the structure of tobermorite. After 310 days the fluorescence lifetimes of the Eu(III) species were estimated at $\tau_1 = 540$ $\mu$s and $\tau_2 = 2036$ $\mu$s, corresponding to 1.3 and zero H$_2$O/OH molecules. Thus, the number of H$_2$O/OH molecules in the first coordination sphere of the Eu(III) species were very similar in the Eu(III)/tobermorite-0.4-1 and Eu(III)/tobermorite-0.4-310 samples, indicating that the coordination environment of Eu(III) did not change significantly after
310 days reaction time. Similar to the tobermorite samples with high Eu(III) loadings, the low number of H$_2$O/OH molecules in the first coordination sphere of Eu(III) species suggests incorporation into the interlayer and the Ca layers of 11 Å tobermorite. The absence of the Eu(III) species with the shortest lifetime, corresponding to 4.7 H$_2$O/OH molecules, which was observed at high Eu(III) loading, reveals faster incorporation into the lattice of 11 Å tobermorite in the less concentrated samples. This suggests that Eu-Ca replacement in the Ca layers is the thermodynamically favorable process of Eu(III) immobilization by tobermorite.

**Figure 6** Eu(III) excitation spectra of Eu(III) taken by 11 Å tobermorite (0.4 µmol Eu/g solid phase) after 1 and 310 days, measured at 20 K.

**Figure 7** Fluorescence emission spectra of Eu(III) taken by 11 Å tobermorite (0.4 µmol Eu/g solid phase) after 1 and 310 days, measured at 18 K (excitation at 579.5 nm).
Figure 8 Time dependency of Eu(III) emission decay by selective excitation of Eu(III) taken by 11 Å tobermorite (0.4 µmol Eu/g solid phase) after 1 and 310 days, measured at 20 K (dotted and solid lines represent experimental data and the fit curves of the experimental data, respectively).

TRLFS is a surface sensitive method which provided insight into the different modes of Eu(III) binding to tobermorite. Nevertheless, structural information about incorporated Eu(III) species such as bond lengths and coordination numbers could not be derived from TRLFS measurements. Therefore, an EXAFS study on Eu(III) uptake by 11 Å tobermorite was carried out.

3.3 EXAFS measurements

The radial structural functions (RSFs) of all Eu(III) doped tobermorite samples showed a peak at \( R + \Delta R \sim 2.0 \, \text{Å} \), which was fitted by assuming the presence of a single oxygen shell (Figure 9). The number of neighboring oxygen atoms, \( N_O \), and the estimated Eu-O distances, \( R_{\text{Eu-O}} \), were found to be similar within the experimental uncertainties for all samples, e.g. \( N_O = 6.9 - 7.4 \) and \( R_{\text{Eu-O}} = 2.39 - 2.40 \, \text{Å} \) (Table 2).

Presence of further backscattering atoms was indicated by the broad peak in the Fourier transforms (FTs) at \( R + \Delta R \sim 3.0 \, \text{Å} \). This peak was fitted by considering Eu-Si and Eu-Ca backscattering paths. The EXAFS measurements revealed significant differences in the EXAFS parameters of the neighboring Si and Ca atoms after short (between 1 and 28 days) and long reaction time (480 days). For example, between 1 and 480 days the Si coordination number, \( N_{\text{Si}} \), increased from 3.9 to 5.1, whilst the Eu-Si distances increased by 0.07 Å (Table 2). The differences in both parameters were larger than the estimated
uncertainties, i.e. ± 20% for N and ± 0.02 Å for R from WinXAS 3.1. The corresponding variations in the EXAFS parameters of the neighboring Ca atoms were comparable to changes in the structural parameters of neighboring Si (1 day: N\textsubscript{Ca} = 2.7, R\textsubscript{Eu-Ca} = 3.75 Å; 480 days: N\textsubscript{Ca} = 4.2, R\textsubscript{Eu-Ca} = 3.82 Å). Note that changes in the structural parameters between 1 and 28 days as revealed from EXAFS were less evident and within the uncertainties of the method (Table 2).

\[ \text{Figure 9} \]

a) \( k^2 \)-weighted spectra and b) the corresponding RSFs of experimental (solid line) and fitted (dashed and dotted lines for the imaginary and the real part, respectively) Eu L\textsubscript{III}-EXAFS of Eu(III) doped 11 Å tobermorite with 7 and 35 \( \mu \)mol Eu/g solid phase loadings and reaction time 1, 28, 120 and 480 days; c) \( k^2 \)-weighted EXAFS function for the Fourier-backtransform spectra obtained from Figure 9b (range: R +\( \Delta R \)=1.25 - 4.0; \( k = 1.4 – 10.6 \text{ Å}^{-1} \)).
Table 2  
Structural information obtained from EXAFS spectra of Eu(III) doped 11 Å tobermorite$^a$.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Eu loading (μmol/g)</th>
<th>$N_{\text{O}}$ $^b$</th>
<th>$R_{\text{Eu-O}}$ $^c$ (Å)</th>
<th>$\sigma_{\text{O}}^d$</th>
<th>$N_{\text{Si}}$ $^b$</th>
<th>$R_{\text{Eu-Si}}$ $^c$ (Å)</th>
<th>$\sigma_{\text{Si}}^d$</th>
<th>$N_{\text{Ca}}$ $^b$</th>
<th>$R_{\text{Eu-Ca}}$ $^c$ (Å)</th>
<th>$\sigma_{\text{Ca}}^d$</th>
<th>$\Delta E_0$ $^e$ (eV)</th>
<th>$R_f$ $^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>6.9</td>
<td>2.39</td>
<td>0.009</td>
<td>3.9</td>
<td>3.69</td>
<td>0.003</td>
<td>2.7</td>
<td>3.75</td>
<td>0.006</td>
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<td>2.40</td>
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<td>4.4</td>
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<td>0.004</td>
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<tr>
<td>480</td>
<td>35</td>
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<td>2.40</td>
<td>0.009</td>
<td>5.1</td>
<td>3.76</td>
<td>0.007</td>
<td>4.2</td>
<td>3.82</td>
<td>0.010</td>
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</tr>
<tr>
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<td>7</td>
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<td>4.2</td>
<td>3.73</td>
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<td>3.7</td>
<td>3.82</td>
<td>0.004</td>
<td>4.9</td>
<td>8.9</td>
</tr>
</tbody>
</table>

$^a$ Fourier-transformed $\chi(k)$ range, $^b$ Number of neighbor atoms, $^c$ Interatomic distance, $^d$ Debye-Waller factor, $^e$ Energy shift of the theoretical calculated spectrum to the energy grid of the measured spectrum, $^f$ Residual factor $R_f$:

$$R_f = \sqrt{\frac{\sum (\chi_{\text{obs}}(k) - \chi_{\text{calc}}(k))^2}{\sum \chi_{\text{obs}}^2(k)}} \times 100$$

Estimated errors: ($R_{\text{Eu-O}}, R_{\text{Eu-Si}}, R_{\text{Eu-Ca}}$) ~0.02 Å; ($N_{\text{O}}, N_{\text{Si}}, N_{\text{Ca}}$)~ 20 %; $\chi_{\text{obs}}$ and $\chi_{\text{calc}}$: experimental and theoretical data points.

The structural parameters determined for the Eu(III)-35-480 sample (high Eu loading) were similar to those observed in the Eu(III)-7-120 sample with low Eu loading (Table 2) confirming that Eu(III) incorporation into the tobermorite structure depends on metal loading and reaction time. Changes in the structural parameters indicate changes of the local coordination environment of Eu(III) due to progressive incorporation into the C-S-H structure as previously observed for Nd(III) uptake by 11 Å tobermorite (Chapter 3).

The experimental EXAFS parameters determined after prolonged reaction time could be assessed on the basis of structural information of non-doped 11 Å tobermorite (Merlino et al., 2001). In the latter structure, Ca from the central Ca sheet is surrounded by 7 oxygens ($R_{\text{Ca-O}} = 2.46$ Å), 3 - 4 Si ($R_{\text{Ca-Si}} = 3.67 - 3.73$ Å) and 4 - 5 Ca ($R_{\text{Ca-Ca}} = 3.80 - 3.96$ Å). The structural parameters listed in Table 2 indicate that the number of neighboring second shell Si atoms in the Eu(III)-7-120 and Eu(III)-35-480 samples range between 4.2 and 5.1 at $R_{\text{Eu-Si}}$ ~ 3.73 - 3.76 Å. The number of neighboring Ca atoms ranges between 3.7 and 4.2 at $R_{\text{Eu-Ca}}$ ~ 3.82 Å and confirms that high coordination numbers and long distances observed after prolonged reaction time indicate structural incorporation of Eu(III) into the framework of 11 Å tobermorite.
4. A mechanistic interpretation of Eu(III) immobilization in 11 Å tobermorite

Inner-sphere surface complex formation may dominate Eu(III) binding to 11 Å tobermorite at high Eu(III) loadings and short reaction times as indicated by TRLFS. Outer-sphere coordination could be ignored as it would imply that Eu(III) binds to C-S-H phases with intact hydration shell (~9 water molecules) (Park et al., 2006). The TRLFS results show that the number of H$_2$O/OH molecules is significantly lower in all samples (~ 4.7). Formation of an inner-sphere surface complex in the early stage of Eu(III) interaction with tobermorite is suggested from both TRLFS and EXAFS data. In the case of inner-sphere surface complexation Eu(III) is directly bonded to the surface of tobermorite via oxygen atoms and backscattering contributions from neighboring atoms of the solid phase (e.g. Si and Ca) are observed in the EXAFS spectra (DUFF et al., 2004) (See Chapter 4). If Eu(III) sorbs on the tobermorite surface via inner-sphere complex ~3 Si atoms from Si chains and 2 Ca at maximum from the Ca sheets in bulk-structure could be observed. Hence, our observation of ~4 Si and ~2.7 Ca atoms after one day reaction time suggests that a significant fraction of Eu(III) was bound on the surface as an inner-sphere complex. Nevertheless, presence of already incorporated Eu(III) species in the Eu(III)/tobermorite-35-1 sample in addition to inner-sphere surface complexation is indicated by the low number of neighboring oxygen atoms (N$_O$~6.9) compared to that expected in Eu(III) inner-sphere surface complexes (~8.7) (Stumpf et al., 2004). The latter conclusion is supported by TRLFS, as Eu(III) species with 1-2 and zero H$_2$O/OH molecules were already detected after one day reaction time.

Assuming equal fluorescence efficiency of the Eu(III) species, the contribution of each Eu(III) species to the overall fluorescence emission (and thus the relative abundance of this species) can be estimated. The results in Table 3 show that the relative portion of each Eu(III) species changes with time. For example, at high Eu(III) loading in the Eu(III)/tobermorite-7-1 sample, ~46% of Eu(III) species are present as inner-sphere surface complex (4.7 water molecules), ~36% of the Eu(III) species are bound in the interlayer (~2 water molecules) and ~18% of the Eu(III) species are taken up by the Ca sheets (zero water molecules). In the sample Eu(III)/tobermorite-7-570 after prolonged reaction time, the relative portion of the different Eu(III) species are 0% (inner-sphere complex), ~44% (interlayer species) and ~56% (incorporation in Ca sheet).
Table 3  
Relative abundance of the Eu(III)/tobermorite species as function of reaction time.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Reaction time</th>
<th>A1 (%)</th>
<th>$\tau_1$ $\mu$s (water)</th>
<th>A2 (%)</th>
<th>$\tau_2$ $\mu$s (water)</th>
<th>A3 (%)</th>
<th>$\tau_3$ $\mu$s (water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu(III)/tobermorite-7-1</td>
<td>1</td>
<td>46</td>
<td>200 (4.7)</td>
<td>36</td>
<td>647 (1)</td>
<td>18</td>
<td>2019 (0)</td>
</tr>
<tr>
<td>Eu(III)/tobermorite-7-570</td>
<td>570</td>
<td>0</td>
<td>-</td>
<td>44</td>
<td>598 (1.4)</td>
<td>56</td>
<td>2199 (0)</td>
</tr>
<tr>
<td>Eu(III)/tobermorite-0.4-1</td>
<td>1</td>
<td>0</td>
<td>-</td>
<td>66</td>
<td>580 (1.1)</td>
<td>34</td>
<td>1567 (0)</td>
</tr>
<tr>
<td>Eu(III)/tobermorite-0.4-310</td>
<td>310</td>
<td>0</td>
<td>-</td>
<td>47</td>
<td>540 (1.3)</td>
<td>53</td>
<td>2036 (0)</td>
</tr>
</tbody>
</table>

At low Eu(III) loading about ~66% of Eu(III) species have 1-2 H$_2$O/OH molecules, while ~34% of the Eu(III)/tobermorite species have zero H$_2$O/OH molecules in the first coordination sphere after one day reaction time. After 310 days the relative abundance of the Eu(III) species was ~47% (1-2 H$_2$O/OH molecules) and ~53% (zero H$_2$O/OH molecules). This clearly shows that, as already observed at high Eu(III) loadings, the portion of Eu(III) species with no H$_2$O/OH molecules in the first coordination sphere significantly increases with time, suggesting that Eu-Ca replacement in the Ca layers is the thermodynamically favorable process rather than surface complexation and Eu-Ca substitution in the interlayer. The species distribution was similar to the one observed at high Eu(III) loading and 570 days reaction time (~44% with 1-2 H$_2$O/OH molecules and ~56% with zero H$_2$O/OH molecules).

5. Conclusions

The results from the present study suggest that binding into the structure of C-S-H phases is the dominant mode of Eu(III) immobilization in cementitious materials. The latter finding, in combination with the observed long-term stability of C-S-H phases in the cementitious near field, implies that lanthanides, and trivalent actinides based on the chemical analogy, can be incorporated into the structure of C-S-H in the long term. This knowledge is essential for long-term predictions of the safe disposal of radioactive waste in cement-based repositories.
6. References


CHAPTER 7

A TRLFS and EXAFS study on the Eu(III) uptake by xonotlite

Abstract

Cement is an important component in repositories for low-level and intermediate-level radioactive waste. The uptake of Eu(III) by xonotlite has been investigated by the combined use of time-resolved laser fluorescence spectroscopy (TRLFS) and X-ray absorption fine structure (EXAFS) spectroscopy. Eu(III) doped xonotlite samples with varying metal loadings (0.4, 7 and 35 μmol Eu/g solid phase) and reaction time (1 - 570 days) were investigated. The structural environment of Eu(III) taken up by xonotlite was found to depend on both parameters. TRLFS indicates the presence of three Eu(III) species with different fluorescence lifetimes at high Eu(III) loadings (7 μmol Eu/g solid phase) and after one day reaction time. The emission lifetimes deduced from the different species correspond to ~4.7, ~1 and zero H₂O/OH molecules, suggesting presence of one surface species forming an inner-sphere surface complex and two species incorporated in the crystal lattice. After longer contact times (90 days, 570 days), the surface species has disappeared. At lower Eu(III) loadings (0.4 μmol Eu/g solid phase) and reaction times between 1 and 310 days only two Eu(III) species with ~1 - 2 and zero water molecules were detected, corresponding to Eu(III) being incorporated in the crystal structure. The results from EXAFS carried out on samples with high Eu loadings (35 μmol Eu/g) show that the distances between Eu(III) and neighboring Ca and Si atoms increase after prolonged reaction time, coinciding with higher numbers of neighboring Ca and Si atoms. The observed bond-distances and coordination numbers suggest incorporation into Ca layers in the structure of xonotlite. The study reveals that binding into the structure of xonotlite is the dominant mode of Eu(III) immobilization after long reaction time. This finding is essential for assessment of the safe disposal of actinides in cement-based repositories for radioactive waste, because incorporation into the crystal structure could prevent radionuclide release into the environment.
1. Introduction

Radionuclides released from a deep geological repository can be controlled and reduced by a suitable choice of engineered and geological barriers. Cement-based materials play an important role in multi-barrier concepts developed worldwide for the disposal of radioactive wastes (Chapman and McCombie, 2003). A large number of studies have demonstrated the waste loading potential of cement (Jantzen et al., 1984), but its long-term ability to retard the release of radionuclides from waste repositories and the chemical mechanism governing radionuclides immobilization are poorly understood on the molecular level. This knowledge, however, is essential for detailed long-term predictions of the environmental impact of cement-stabilized waste forms.

Calcium silicate hydrate (C-S-H) phases are considered to be particularly important in governing immobilization processes in cementitious materials, because they are the main constituent of fresh and degraded cement (~50 wt.%). Due to their stability during the evolution of the cementitious near field, long-term immobilization of radionuclides by C-S-H is crucial when uptake processes need to be extrapolated to time scales relevant for the safe disposal of radioactive waste (Berner, 1992). Among various hydrous C-S-H phases, xonotlite, Ca$_6$Si$_6$O$_{17}$(OH)$_2$, is formed as a by-product of the hardening Portland cement paste (Kalousek et al., 1977).

\[ \text{Figure 1} \quad \text{The crystal structure of xonotlite with position of hydrogen atoms, Si in the Si chains and Ca in the Ca layers.} \]
The layered structure of xonotlite is built up of sheets of six and seven coordinated Ca polyhedra, which are condensed by wollastonite-type silicate chains on both sides (Figure 1). The silica chains are built up by Si$_2$O$_7$ groups (“paired” silica tetrahedra) connected to the central Ca sheet and, via “bridging” Si tetrahedra, to the adjacent Ca layer. Four xonotlite polytypes can be distinguished according to the different arrangements of building layers along c direction (Gard, 1966). The nomenclature of xonotlite polytypes and the mechanism of defects formation in the crystal structure of xonotlite have been discussed in detail elsewhere (Churakov and Mandaliev, 2008; Hejny and Armbruster, 2001).

The retention of radionuclides by the complex cement matrix and cement minerals, in particular C-S-H phases, has been studied in the past by combining wet chemical methods with synchrotron- and laser-light-based spectroscopic techniques (Pointeau et al., 2001; Schlegel et al., 2004; Tits et al., 2003). Pointeau et al. (2001) investigated the interaction of Eu(III) with amorphous C-S-H phases with varying C/S ratio (0.34 - 1.65) and different pH (10.0 - 12.4), and 14 Å tobermorite using time-resolved laser fluorescence spectroscopy (TRLFS). The results of this study allowed distinction of two types of Eu(III) species with different fluorescence lifetimes (390 and 990 μs). The authors interpreted the first one as a site in the framework of C-S-H due to substitution for Ca and the second Eu(III) specie was proposed to be consistent with surface precipitation or complexation. Tits et al. (2003) studied the interaction of Eu(III) and Cm(III) with C-S-H phases with a C/S ratio of about 1.0 at pH 13.3, and reaction time up to 119 days in batch-type sorption experiments and using TRLFS at 20K. Three different Cm (III) species were observed. Based on the different fluorescence lifetimes and using the linear correlation between the decay rate and the number of the H$_2$O/OH molecules in the first coordination sphere of the Cm(III), the authors concluded that Cm (III) and Eu(III) are incorporated into the structure of the C-S-H phases by substituting for Ca. Schlegel et al. (2004) investigated the uptake of Eu(III) by C-S-H phases as function of C/S ratio and amount of the added Eu(III) using extended X-ray absorption fine structure (EXAFS) spectroscopy. The results suggested incorporation of Eu (III) into the structure of C-S-H phases at Ca structural sites, and possible precipitation of Eu(III)
and formation of C-S-H-like solid phase. The X-ray diffraction (XRD) and EXAFS study on Nd binding to 11 Å tobermorite and xonotlite showed that Nd(III) substitutes for Ca\(^{2+}\) in the interlayer and the Ca layers of 11 Å tobermorite as well as in the Ca sheets of xonotlite (see Chapter 3 for details). Nd binding coincides with the release of water from the interlayer of tobermorite and release of bridging Si tetrahedral in both C-S-H phases, thus resulting in more disordered structures. Furthermore, Nd(III) uptake by the Ca sheets of xonotlite and tobermorite was found to increase with time due to ongoing recrystallization.

The results of previous EXAFS and laser-light-based spectroscopic studies showed that C-S-H could play an important role in the immobilisation of lanthanides and trivalent actinides by cementitious materials. Nevertheless, the chemical mechanisms responsible for the immobilization of lanthanides and trivalent actinides by C-S-H phases, e.g. influence of reaction time, radionuclide concentration in the equilibrium solution of C-S-H phases, are still poorly understood. For example, previous spectroscopic studies do not allow for an unambiguous discrimination between the Eu(III) species formed in the early stages of the interaction with the solid phase and in the long-term. The present study aims at filling this existing gap in our knowledge. For the present study TRLFS and EXAFS were used to gain information on the local chemical speciation and coordination environment of Eu(III) taken up by xonotlite.

The aim of this study was to investigate Eu(III) uptake by xonotlite by the combined use of TRLFS and EXAFS, thus allowing surface species and species incorporated into the lattice of C-S-H to be distinguished from each other. Eu(III) was chosen as a non-radioactive analogue for trivalent actinides because its high fluorescence intensity allows speciation studies to be carried out in the \(\mu\)-mol concentration range (Stumpf et al., 2007a). The position of the main Eu(III) bands (\(^4\)D\(_0\) \(\rightarrow\) \(^7\)F\(_{1-4}\) transitions; \(J = 0, 1, 2, 3, 4\)) are almost independent of the chemical environment of the metal ion. Furthermore, the intensity of the \(^4\)D\(_0\) \(\rightarrow\) \(^7\)F\(_2\) transition changes significantly when the Eu(III) ion is complexed (Jorgensen and Judd, 1964). From the splitting of the fluorescence emission bands, in particular at low temperature, information on the ligand field and, hence, on the geometry of the coordination site of the Eu(III) ion can be deduced (Bünzli and Choppin, 1989). Only one transition is expected for each Eu(III)
species due to the non-degenerated ground state, $^7F_0$. TRLFS also allows the hydration status of the Eu(III) species to be determined using an empirical linear correlation between the reciprocal of the excited-state lifetime (i.e. the decay constant) with the number of H$_2$O/OH molecules in the first coordination sphere (Horrocks and Sudnick, 1979; Pointeau et al., 2001; Tits et al., 2003). Complementary information on atomic distances and coordination numbers of the Eu(III)/xonotlite species can be derived from the EXAFS (Stumpf et al., 2007b). Thus, the combined use of the two spectroscopic methods TRLFS and EXAFS is expected to provide complementary structural information essential for development of mechanistic picture of Eu(III) immobilization by xonotlite.

2. Materials and methods

2.1 Sample preparation

Throughout this study Fluka (Sigma-Aldrich, Buchs, Switzerland) or Merck (Dietikon, Switzerland) “pro analysis” chemicals and high-purity de-ionised water generated by a Milli-Q Gradient A10 system (Millipore, Bedford, USA) were used. All experiments were carried out in a glovebox under N$_2$ atmosphere and ambient temperature (CO$_2$, O$_2$ < 2ppm, T = 290 K ± 3 K). Xonotlite samples were synthesized as described in Chapter 2.

Eu(III) sorption samples used for the TRLFS measurements were prepared by adding appropriate volumes of a Eu(III) stock solution (10$^{-3}$ M) to xonotlite stock suspensions (5 g L$^{-1}$ (TRLFS) and 50 g L$^{-1}$ (EXAFS) solid materials suspended in their equilibrium solution) to achieve the required Eu(III) loadings (TRLFS: 0.4 and 7 μmol Eu/g solid phase; EXAFS: 7 and 35 μmol Eu/g solid phase). No changes in pH were determined after Eu(III) addition. The samples were equilibrated in the glovebox and sampled after 1, 90 and 570 days (TRLFS) or 1 and 480 days (EXAFS), respectively.

After phase separation by centrifugation (60 min at 95000 g) the Eu(III) treated samples were packed as a wet paste into Plexiglas sample holders and sealed with Kapton tape for the EXAFS measurements. TRLFS measurements were carried out on suspensions. Sample abbreviations are given in Table 1.
Table 1
Chemical conditions of the Eu(III) sample preparation for EXAFS and TRLFS measurements.

<table>
<thead>
<tr>
<th>Method</th>
<th>Abbreviation</th>
<th>Reaction time (days)</th>
<th>Eu(III) loading (μmol Eu/g xonotlite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXAFS</td>
<td>Eu(III)/xonotlite-35-1</td>
<td>1</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/xonotlite-35-28</td>
<td>28</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/xonotlite-35-480</td>
<td>480</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/xonotlite-7-120</td>
<td>120</td>
<td>7</td>
</tr>
<tr>
<td>TRLFS</td>
<td>Eu(III)/xonotlite-7-1</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/xonotlite-7-90</td>
<td>90</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/xonotlite-7-570</td>
<td>570</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/xonotlite-0.4-1</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>Eu(III)/xonotlite-0.4-310</td>
<td>310</td>
<td>0.4</td>
</tr>
</tbody>
</table>

2.2 TRLFS measurements

TRLFS measurements were performed with an excimer pumped dye laser system (Lambda Physics, EMG, 308 nm, Scanmate 2). Direct excitation of the Eu(III) $^5D_0$-level was carried out using the dye Coumarin 153 (emission at 522–600 nm). The Eu(III) fluorescence emission was detected by an optical multichannel system consisting of a Czerny Turner polychromator (Jobin Yvon HR 320) with 300/600/1200 lines/mm gratings and a gated, intensified photodiode array (Spectroscopy Instruments, ST180, IRY 700G). The laser pulse energy was controlled by a pyroelectric detector on a pulse to pulse basis. A pulse generator (Spectroscopy Instruments, DG 535) was used to measure the time dependent emission decay TRLFS experiments were carried out at T ≤ 20 K as decreasing temperature increases the fluorescence intensity and allow a better spectral resolution of the crystal-field splitting of the $^7F_J$ ($J = 1–4$) transitions, narrowing peak(s)
in the excitation spectra. The cooling system (Cryodyne Cryocooler model 22C, compressor 8200, CTI Cryogenics, USA) used helium as refrigerant and allowed continuous closed cycle cooling of the copper sample holder at the cold head. The laser beam was focused on the copper sample holder, and the fluorescence emission signal was collected with a glass fibre and directed onto the polychromator. Site selective excitation of the $^5D_0 \rightarrow ^7F_0$ transition experiments were carried out (300 lines/mm grating) from 576.0 to 582.0 nm. For each sample, several excitation wavelengths were selected to record emission spectra, (600 lines/mm grating, resolution $\sim$1 nm (Neon)), and to determine the emission lifetimes (300 lines/mm grating). The fluorescence lifetimes were determined by varying the delay time between laser pulse and camera gating with time intervals of 50 to 100 $\mu$s.

2.3 EXAFS data collection and reduction.

EXAFS spectra at the Eu L$_{III}$ edge (6977 eV) were collected at beamline BM26A (DUBBLE) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, and at the ANKA-XAS beamline of the Angstroemquelle Karlsruhe (ANKA). Both beamlines are equipped with a Si (111) double-crystal monochromator. Spectra were energy calibrated to the first inflection points of the K-absorption edge of a Fe foil (7112 eV). The EXAFS measurements were conducted at room temperature in fluorescence mode using a 9 channel monolithic Ge-solid-state detector at SNBL/ESRF and a five element Ge-detector at the ANKA-XAS. For each compound, depending on the metal loadings, between three and eight spectra were collected to achieve the required signal-to-noise ratio.

EXAFS data reduction was performed using the WinXAS 3.11 software package and following standard procedures (Ressler, 1998). Details on the EXAFS data reduction and fitting are shown in Chapters 3. Theoretical scattering paths for the fits were calculated using FEFF 8.2 (Ankudinov and Rehr, 2000) and the xonotlite structure (Hejny and Armbruster, 2001).

For the EXAFS analysis of Eu(III) doped xonotlite, the structural model proposed earlier by Schlegel et al. (2004) for Eu(III) retention by amorphous C-S-H phases with varying Ca/Si molar ratios was used. This model includes backscattering contributions
from Si atoms at \( R \sim 3.2 \text{ Å} \) and \( R \sim 3.7 - 3.75 \text{ Å} \), and Ca atoms at \( R \sim 3.79 - 3.84 \text{ Å} \) and is based on the assumption that Eu can replace Ca in the lattice of amorphous C-S-H phases. This assumption is justified with a view to similarities in the ionic radii of the two elements in sevenfold coordination (1.01 Å and 1.06 Å, respectively) (SHANNON, 1976). In this study the short Si distances at \( R \sim 3.2 \text{ Å} \) proposed by Schlegel et al. (2004) was not considered, as the EXAFS fits did not result in meaningful residual parameter including Si at short distance. The proposed model for Eu(III) retention only considers one Ca and one Si shell at similar distances, i.e.: \( R_{\text{Eu-Si}} \sim 3.70 - 3.75 \text{ Å} \); \( R_{\text{Eu-Ca}} \sim 3.75 - 3.80 \text{ Å} \). Note, however, that the spatial resolution, which is given by \( \Delta R = \pi/2\Delta k \), where \( \Delta k \) is the range of \( k \)-space being fit (\( \Delta k = 1.40 - 10.60 \text{ Å}^{-1} \)), was estimated to be \( \sim 0.16 \text{ Å} \), implying that the two shells can be hardly resolved. Statistical F-tests were performed in order to prove whether or not the proposed fitting model with backscattering contributions from Si and Ca at long distances can be justified (see Supporting Information in Chapter 3). Based the results from these tests and additional crystallographic considerations of the structure of non-doped xonotlite, it was concluded that a model, which includes O, and Si and Ca atoms at similar distances, can be applied to adequately reproduce the coordination environment of Eu in the xonotlite structure.

3. Results and discussion

3.1 TRLFS measurements at high Eu(III) loadings

Spectroscopic information on the Eu(III)/xonotlite species was derived from the excitation spectra of the \( ^5D_0 \rightarrow ^7F_0 \) transmission (Figure 2), fluorescence emission spectra of the \( ^5D_0 \rightarrow ^7F_J \) (\( J = 0, 1, 2 \)) transitions (Figures 3 - 5) and the fluorescence emission lifetime (Figure 6). In all samples the \( ^5D_0 \rightarrow ^7F_0 \) transitions were very large with a FWHM (full-width at half-maximum) larger than 1.6 nm (Figure 2). All bands showed a clear shoulder on the left side of the peak, strongly suggesting the presence of multiple Eu(III) species (Marques Fernandes et al., 2008).
Figure 2 Eu(III) excitation spectra of Eu(III) taken up by xonotlite (7 µmol Eu/g solid phase) after 1, 90 and 570 days measured at 18 K.

Figure 3 Fluorescence emission spectra of the 7D0 → 7F0,1,2 transitions in Eu(III) taken by xonotlite (7 µmol Eu/g solid phase) after 1 day reaction time measured at 18 K and various excitation wavelengths.

Figure 4 Fluorescence emission spectra of the 7D0 → 7F0 transition in Eu(III) taken by xonotlite (7 µmol Eu/g solid phase) after 1 day reaction time measured at 18 K and various excitation wavelengths.
The emission spectra at various excitation wavelengths in the range of the 
$^5D_0 \rightarrow ^7F_0$ transition (578.47 nm – 580.13 nm) were normalized to the peak area of the 
$^5D_0 \rightarrow ^7F_1$ transition, which is known to be largely independent of the environment of the 
Eu ion (Marques Fernandes et al., 2008). The $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ emission bands 
were split into at least three crystal field (CF) levels, which indicates low site symmetry 
around Eu(III) (Figure 3 and 4). Further, the emission spectra clearly varied with varying 
excitation wavelengths (Figure 4). The $^5D_0 \rightarrow ^7F_0$ transitions showed a strong red shift 
with increasing excitation wavelength. The $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ emission bands 
excitation at $\lambda = 579.5$ nm were each split at least threefold (Figure 5), corroborating low 
site symmetry around the Eu(III) ion. The spectra further showed that in all transitions the 
size and shape of the peak varied with the reaction time, suggesting again the presence of 
multiple Eu(III) sorbed species with varying, time-dependent relative portions.

The decay curve of the fluorescence emission after one day reaction time was 
fitted with a tri-exponential function, suggesting the presence of 3 Eu(III) species with 
different lifetimes ($\tau_1 = 200$ μs, $\tau_2 = 508$ μs and $\tau_3 = 1634$ μs). After prolonged reaction 
(90 and 570 days), however, only two Eu(III) species with different lifetimes were 
detected (90 days: $\tau_1 = 552$ μs and $\tau_2 = 1756$ μs; 570 days: $\tau_1 = 474$ μs and $\tau_2 = 2705$ μs).

According to the empirical method developed by Horrocks and Sudnick (1979) the 
number of H$_2$O/OH molecules in the first coordination sphere of Eu(III) species is related 
to the emission lifetime by:
where $k_{\text{obs}}$ is the observed decay rate of the excited state [ms$^{-1}$], which is related to the mean lifetime of Eu(III)/xonotlite species ($k_{\text{obs}} = 1/\tau$).

After one day equilibration about 4.7, 1.4 and zero H$_2$O/OH groups, respectively, were calculated to be bound in the first coordination sphere of the Eu(III) species. The uncertainties are ± 0.5 H$_2$O/OH$^-$ as suggested elsewhere (Horrocks and Sudnick, 1979). About 5 water molecules in the first Eu(III) coordination sphere were observed for Eu(III) inner-sphere complexes (Stumpf et al., 2007b). The presence of Eu(III)/xonotlite species with zero molecules is consistent with Eu(III) bound in the structure of xonotlite as Ca from the central Ca sheet is surrounded by zero water molecules in the xonotlite structure. Assuming that no other quench processes (e.g. metal to ligand transfer) occurred in the vicinity of Eu(III), our observation of 4.7, ~1 - 2 and zero nearest neighboring water molecules suggested that three Eu(III) species, i.e. a Eu(III) surface-bound inner-sphere complex and two Eu(III) species bound in the structure of xonotlite, existed in the early stage of Eu(III) interaction with xonotlite.

Based on the observed lifetimes it was estimated that 1.0 - 1.5 and zero H$_2$O/OH molecules were bound in the first coordination sphere of the Eu(III) species after reaction time $\geq$ 90 days. The estimated number of H$_2$O/OH groups for the Eu(III)/xonotlite
species with the shorter (1.0 - 1.5 H₂O/OH) and longer lifetime (zero H₂O/OH) were very similar for the different reaction times, indicating similar coordination environments of Eu(III) in the Eu(III)/xonotlite-7-90 and Eu(III)/xonotlite-7-570 samples. The absence of the species with the shortest lifetime (4.7 H₂O/OH) indicates incorporation into the xonotlite structure with time.

3.2 TRLFS measurements at low Eu(III) loadings

The Eu(III) ⁵D₀→⁷F₀ excitation spectra at low loadings exhibited slightly narrower excitation bands compared to those determined at high Eu(III) loading (compare Figures 2 and 7). Similar to the highly loaded samples the ⁵D₀→⁷F₀ transitions were very large with a FWHM larger than 1.6 - 1.7 nm at the lower loading, thus suggesting the presence of more than one Eu(III) species in xonotlite.

The ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ emission bands recorded after excitation at 579.5 nm were at least threefold split (Figure 8). Splitting into three crystal field levels of the ⁵D₀→⁷F₂ emission band was more pronounced after 310 days reaction time than in the one day sample, indicating even lower site symmetry around the Eu(III) ion after prolonged reaction time.

![Figure 7 Eu(III) excitation spectra of Eu(III) taken up by xonotlite (0.4 μmol Eu/g solid phase) after 1 and 310 days, measured at 20 K.](image)
The decay curves of the Eu(III) doped samples after 1 and 310 days reaction time could be fitted with a bi-exponential function, which suggested the presence of two Eu(III) species with two different lifetimes (Figure 9). The lifetimes after one day reaction time were determined to be $\tau_1 = 650 \, \mu s$ and $\tau_2 = 1700 \, \mu s$. Based on these lifetimes the number of H$_2$O/OH molecules was estimated at 1.1 and zero in the first coordination sphere of the Eu(III) species, indicating Eu(III) incorporation in the structure of xonotlite. After 310 days the fluorescence lifetimes of the Eu(III) species were estimated at $\tau_1 = 540 \, \mu s$ and $\tau_2 = 2432 \, \mu s$, corresponding to 1.3 and zero H$_2$O/OH molecules. Thus, the number of H$_2$O/OH molecules in the first coordination sphere of the Eu(III) species were very similar in the Eu(III)/xonotlite-0.4-1 and Eu(III)/xonotlite-0.4-
310 samples, showing that the coordination environment of Eu(III) did not change significantly within 310 days reaction time. Similar to the xonotlite samples with high Eu(III) loadings, the low number of H₂O/OH molecules in the first coordination sphere of Eu(III) species indicates incorporation into the Ca layers of xonotlite. The absence of the Eu(III) species with the shortest lifetime, corresponding to 4.7 H₂O/OH molecules, which was observed at high Eu(III) loading, reveals faster incorporation into the lattice of xonotlite in the less concentrated samples. This suggests that Eu-Ca replacement in the Ca layers is the thermodynamically favorable process of Eu(III) immobilization by xonotlite.

TRLFS is a surface sensitive method which provided insight into the different modes of Eu(III) binding to xonotlite. Nevertheless, structural information about incorporated Eu(III) species such as bond lengths and coordination numbers could not be derived from TRLFS measurements. Therefore, an EXAFS study on Eu(III) uptake by xonotlite was carried out.

4. EXAFS measurements

All EXAFS spectra showed a pronounced peak at $R + \Delta R \sim 2.0 \text{ Å}$ in the Fourier transform (FT), corresponding to backscattering contributions from the nearest neighboring oxygen shell (Figure 10). The latter shell could be fitted by assuming the presence of a single oxygen shell. The number (N) of neighboring oxygen atoms and the Eu-O distances were found to be similar within the experimental uncertainties for all samples, e.g. $N_O = 7.2 - 7.5$ and $R_{\text{Eu-O}} = 2.40 - 2.41 \text{ Å}$ (Table 2).

The $R_{\text{Eu-O}}$ distances for Eu(III)/xonotlite were longer than for six-fold coordinated Eu(III) in Eu₂O₃ ($R_{\text{Eu-O}}=2.35 \text{ Å}$) (Schlegel et al., 2004) and shorter than those reported for Eu(III)ₙₖ complexes ($N_O =8.7; R_{\text{Eu-O}}=2.47 \text{ Å}$) (D'Angelo et al., 2001), suggesting that Eu(III)/xonotlite was seven-fold or eight-fold coordinated.

The broad peak in the FTs at $R+\Delta R \sim 3.0 \text{ Å}$ was fitted by considering Eu-Si and Eu-Ca backscattering paths. For reaction time between 1 and 28 days (35 μmol Eu/g solid phase) the next nearest backscattering contributions were fitted with ~0.5 Si(1) atoms at 3.19 - 3.23 Å, ~3.9 - 4.4 Si(2) atoms at 3.70 - 3.71 Å and 2.6 - 2.9 Ca atoms at 3.77 - 3.79 Å. (Table 2).
**Figure 10**  a) $k^3$-weighted spectra and b) the corresponding RSFs of experimental (solid line) and fitted (dashed and dotted lines for the imaginary and the real part, respectively) Eu L\textsubscript{III}-EXAFS of Eu(III) doped xonotlite with varying Eu(III) loadings (7 and 35 μmol Eu/g solid phase), reaction time 1, 28, 120 and 480 days; c) $k^3$-weighted EXAFS function for the Fourier-backtransform spectra obtained from Figure 10b (range: R + ΔR = 1.7-4.0).

**Table 2**  Structural information obtained from EXAFS data analysis of Eu(III)-doped xonotlite.

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Eu conc. (μmol/g)</th>
<th>$N_0$</th>
<th>$R_{\text{Nd}-\text{O}}$ (Å)</th>
<th>$σ^2$</th>
<th>$N_{\text{Si}}$</th>
<th>$R_{\text{Nd}-\text{Si}}$ (Å)</th>
<th>$σ^2$</th>
<th>$N_{\text{Ca}}$</th>
<th>$R_{\text{Nd}-\text{Ca}}$ (Å)</th>
<th>$σ^2$</th>
<th>$ΔE_0$ (eV)</th>
<th>$R_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35</td>
<td>7.3</td>
<td>2.40</td>
<td>0.009</td>
<td>0.5</td>
<td>3.23</td>
<td>0.011</td>
<td>3.9</td>
<td>3.70</td>
<td>0.002</td>
<td>2.6</td>
<td>3.77</td>
</tr>
<tr>
<td>28</td>
<td>35</td>
<td>7.5</td>
<td>2.40</td>
<td>0.010</td>
<td>0.5</td>
<td>3.19</td>
<td>0.003</td>
<td>4.4</td>
<td>3.71</td>
<td>0.004</td>
<td>2.9</td>
<td>3.79</td>
</tr>
<tr>
<td>480</td>
<td>35</td>
<td>7.2</td>
<td>2.40</td>
<td>0.009</td>
<td>0.7</td>
<td>3.20</td>
<td>0.004</td>
<td>4.9</td>
<td>3.77</td>
<td>0.006</td>
<td>5.3</td>
<td>3.88</td>
</tr>
<tr>
<td>120</td>
<td>7</td>
<td>7.4</td>
<td>2.41</td>
<td>0.009</td>
<td>0.9</td>
<td>3.19</td>
<td>0.003</td>
<td>3.78</td>
<td>3.78</td>
<td>0.004</td>
<td>4.5</td>
<td>3.88</td>
</tr>
</tbody>
</table>

| Estimated errors: (R_{\text{Nd}-\text{O}}, R_{\text{Nd}-\text{Si}}, R_{\text{Nd}-\text{Ca}})~\pm 0.02 Å; (N_0, N_{\text{Si}}, N_{\text{Ca}})~\pm 20%; $σ_\text{fit}$ and $σ_\text{calc}$: experimental and theoretical data points. |
These interatomic distances and the coordination numbers, $N_{\text{Si}}$ and $N_{\text{Ca}}$, were in the range of Eu-Si and Eu-Ca distances reported earlier for Eu(III) doped amorphous C-S-H with similar C/S ratios ($\text{C/S} \approx 1.3$) and 31 days reaction time ($N_{\text{Si}(1)}=0.6$, $R_{\text{Eu-Si}(1)}=3.23$ Å; $N_{\text{Si}(2)}=4.2$, $R_{\text{Eu-Si}(2)}=3.23$ Å; $N_{\text{Ca}}=4.1$, $R_{\text{Eu-Ca}}=3.70$ Å) (Schlegel et al., 2004). Note that higher $N_{\text{Ca}}$ were observed in Eu(III) doped amorphous C-S-H compared to Eu(III)/xonotlite, suggesting higher amount of Eu incorporated into the C-S-H structure.

Between one and 480 days the Si(2) coordination number, $N_{\text{Si}(2)}$, increased from 3.9 to 4.9 and the Eu-Si(2) distances increased by 0.08 Å. The differences in both parameters were larger than the expected uncertainties, i.e. ± 20% for $N$ and ± 0.02 Å for $R$ from WinXAS 3.1.

The variations in the EXAFS parameters of the neighboring Ca atoms were more pronounced after 480 days reaction time (1 day: $N_{\text{Ca}} = 2.6$, $R_{\text{Nd-Ca}} = 3.77$ Å; 480 days: $N_{\text{Ca}} = 5.3$, $R_{\text{Nd-Ca}} = 3.88$ Å). Changes in the structural parameters between 1 and 28 days were within the uncertainty of the method (Table 2), indicating similar coordination environment of Eu(III)/xonotlite in these samples. Changes in the structural parameters of Eu(III)/xonotlite indicate changes of the local coordination environment of Eu(III) due to progressive incorporation into the xonotlite structure.

The structural parameters determined for the Eu(III)-35-480 sample (high Eu loading) were similar to those observed in the Eu(III)-7-120 sample with low Eu loading (Table 2), supporting incorporation in the structure. This further confirms that Eu(III) incorporation into the xonotlite structure depends on metal loading and reaction time.

5. Structural model for Eu(III) retention by xonotlite

The EXAFS spectra determined for Eu(III) taken up by xonotlite are not consistent with those of fully hydrated Eu(III) species, e.g. Eu(OH)$_3$ and Eu$_{aq}$ complexes. In the latter species Eu(III) is surrounded by about 9 water molecules at $R_{\text{Eu-O}} \approx 2.48$ Å (D’Angelo et al., 2001; Schlegel et al., 2004). Hence, Eu(III) uptake by xonotlite could be explained only by Eu(III) sorption or/and precipitation on xonotlite and incorporation into the xonotlite structure.
Previous studies suggested that Eu(III) can substitute for Ca in the C-S-H structure (Pointeau et al., 2001; Schlegel et al., 2004; Tits et al., 2003). Eu-Ca substitution could be attributed to similarity of the ionic radii of the two elements in sevenfold coordination (1.01 Å and 1.06 Å, respectively). Eu(III) interaction with the xonotlite structure in the early stage of the reaction can be assessed based on the observed lifetimes of the different Eu(III)/xonotlite species from TRLFS and the structural parameters determined from EXAFS. The number of neighboring cations from EXAFS, N_{Si} and N_{Ca}, is indicative of the different modes of Eu(III) complexation, e.g. formation of Eu(III) inner-sphere and/or outer-sphere surface complexes, precipitation and Eu(III) incorporation into the xonotlite structure (see Chapter 3 for more details).

Assuming equal fluorescence efficiency of the Eu(III) species, the contribution of each Eu(III) species to the overall fluorescence emission (and thus the relative abundance of the species), can be calculated. The portions of each Eu(III)/xonotlite species change with time (Table 3). After one day and high Eu(III) loading the portions determined for each Eu(III)/xonotlite species are ~45% of the species with 4.6 H_{2}O/OH molecules, ~42% of the species with ~1 H_{2}O/OH molecules and ~13% of the species with zero H_{2}O/OH molecules in the first coordination sphere of Eu(III). After 570 days reaction time only two Eu(III) species appear, corresponding to ~68% of the species with ~1 H_{2}O/OH molecules and ~32% of the species with zero H_{2}O/OH molecules in the first coordination sphere.

At low Eu(III) loading about ~59 % of the Eu(III) species have ~1 H_{2}O/OH molecules and ~41 % zero H_{2}O/OH molecules in the first coordination sphere. After 310 days the portions of each Eu(III) species amount to ~56 % of the Eu(III) species with ~1 H_{2}O/OH molecules and ~44 % of the species with zero H_{2}O/OH molecules in the first coordination sphere.

TRLFS indicates presence of three different Eu(III) species after one day reaction time and high Eu loading (7 μmol Eu/g solid phase numbers) with ~4.6, between 1 and 2 and zero H_{2}O/OH molecules in the first coordination sphere.

None of the observed species is consistent with Eu(III) outer-sphere complex (~9 water molecules) (Stumpf et al., 2002). Further, the EXAFS results also contradict presence of fully hydrated Eu(III) species, e.g. the number of next nearest
oxygens is lower and the R_{Eu-O} distances are shorter than those of the fully hydrated Eu(III) species. Note that ~5 water molecules in the first coordination sphere of Eu(III) indicate inner-sphere complex formation (Stumpf et al., 2007b). Inner-sphere surface complexation was indicated from the structural parameters determined for the second Eu(III) shell from EXAFS (Table 2), where backscattering contributions from neighboring atoms Si and Ca atoms appear in the EXAFS spectra. Presence of ~3.9 Si and ~2.6 Ca atoms in the second coordination shell of the Eu(III)/xonotlite species after one day reaction time clearly indicate that a significant portion of Eu(III) is present as inner-sphere surface complex.

The study of Schlegel et al. (2004) showed that Eu(III) coprecipitation with solution Ca and Si results in formation of Ca and Si containing Eu(III) (hydr)oxide (>70 μmol Eu/g solid phase. In the latter phases N₀ was estimated to vary between 6.8 and 9.6 and Eu-Si and Eu-Ca distances were found to be about R_{Eu-Si(2)} = 3.75 - 3.81 Å and R_{Eu-Ca}=3.80 - 3.89 Å. The latter N₀ was higher and the Eu-Si and Eu-Ca distances were longer than those observed in Eu(III)/xonotlite (Table 2). The results of the studies on Nd(III) uptake by 11 Å tobermorite and xonotlite (see Chapter 3 for more details) showed that lanthanide precipitation and formation of Ca and Si containing Eu(III) (hydr)oxide in the early stage of the reaction was more pronounced at higher metal loadings (>35 μmol Eu/g solid phase). Hence, the above findings indicate no compelling evidence for precipitation of Eu(III)-precipitates in the early stage of the reaction in the case of Eu(III)/xonotlite.

Table 3  Relative abundance of each Eu(III)/xonotlite species as function of reaction time.

<table>
<thead>
<tr>
<th>TRLFS/xonotlite</th>
<th>Reaction time (7 μmol Eu/g solid phase)</th>
<th>A1 (%)</th>
<th>τ₁ (μs(water))</th>
<th>A2 (%)</th>
<th>τ₂ (μs(water))</th>
<th>A3 (%)</th>
<th>τ₁ (μs(water))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>45</td>
<td>200 (4.7)</td>
<td>42</td>
<td>508 (1.4)</td>
<td>13</td>
<td>1634 (0)</td>
</tr>
<tr>
<td></td>
<td>570</td>
<td>0</td>
<td>n.a.</td>
<td>68</td>
<td>474 (1.5)</td>
<td>32</td>
<td>2705 (0)</td>
</tr>
<tr>
<td></td>
<td>0.4 μmol Eu/g solid phase</td>
<td>1</td>
<td>n.a.</td>
<td>59</td>
<td>650 (1.1)</td>
<td>41</td>
<td>1700 (0)</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>0</td>
<td>n.a.</td>
<td>56</td>
<td>540 (1.3)</td>
<td>44</td>
<td>2432 (0)</td>
</tr>
</tbody>
</table>
The presence of two Eu(III) species with zero and 1-2 H$_2$O/OH molecules in its first coordination sphere was consistent with Eu(III) bound into the structure of xonolitite. In xonolitite Ca in the Ca sheets is surrounded by 6 – 7 oxygens ($R_{Ca-O} = 2.38 – 2.46$ Å), 1 - 2 Si at short distances ($R_{Ca-Si} = 3.17 – 3.43$ Å), ~ 4 Si at longer distances ($R_{Ca-Si} = 3.67 – 3.73$ Å) and 5 - 6 Ca ($R_{Ca-Ca} = 3.68 – 3.81$ Å). Therefore, presence of ~ 1 Si atoms at shorter distance, ~ 4 Si atoms at longer distances and ~ 3 - 4 Ca atoms as determined from EXAFS (Table 2) indicates that the large portion of Nd is bound in the Ca sheets of xonolitite after prolonged reaction time. Thus, the coordination environment of Eu in xonolitite, including two Si distances at $R_{Eu-Si(1)} \approx 3.2$ Å and $R_{Eu-Si(2)} \approx 3.70 – 3.80$ Å, is very similar to that observed around the Ca positions in non-doped xonolitite. Note, that only one Si shell at $R_{Eu-Si(2)} \approx 3.70 – 3.80$ was observed in the case of Nd doped xonolitite, suggesting that Eu occupies sites in the xonolitite structure which are more alike Ca than in the case of Nd.
Ca from the Ca layers is surrounded by zero H$_2$O/OH molecules in the xonotlite structure (Hejny and Armbruster, 2001). Recently, Churakov and Mandaliev (2008) showed that the xonotlite structure contains OH groups and tends to defects formation within the Si chains. Such defects provide the necessary space for possible incorporation of foreign ions and water in the structure of xonotlite. Therefore, while the Eu species with zero H$_2$O/OH molecules replace Ca in the Ca sheets, the presence of Eu species with 1-2 H$_2$O/OH molecules suggest Eu-Ca replacement on position near to or on defects in the xonotlite structure (Figure 11). In this case charge compensation could be fulfilled by inclusion of additional OH/water molecules into the xonotlite structure.

6. Conclusion

At high Eu(III) loadings (7 and 35 μmol Eu/g solid phase) and short reaction time Eu(III) forms several species on xonotlite. Changes in the relative fraction of Eu(III) species can be determined from TRLFS. Eu(III) is predominantly bound on the external surface of xonotlite via inner-sphere complexes. Eu(III) is being incorporated into the xonotlite structure with time by substituting for Ca. Incorporation into the structure is further reflected by changes in the distances between Eu(III) and neighboring Si and Ca atoms, which become longer with time, and increasing numbers neighboring Si and Ca atoms. Eu(III) incorporation is faster at lower Eu loading and continues with time. The complementary information obtained from TRLFS and EXAFS allowed a chemical mechanistic model of the Eu(III) retention by C-S-H to be developed. The results from this study are in general agreement with previous investigations on Eu(III) retention by C-S-H.
7. References


SUMMARY

The present doctoral study aimed at improving our understanding of the underlying principles of lanthanide immobilization processes in cementitious materials. Trivalent lanthanides e.g., Nd(III) and Eu(III), were regarded as suitable chemical analogues for trivalent actinides based on their comparable ionic radii (Shannon, 1976) and similarities in their complexation behavior.

For the development of a mechanistic model of Nd(III) and Eu(III) uptake by C-S-H phases it was important to know the bond distances and the positions of all atoms in the structure, including the positions of the water molecules and the OH groups. Knowledge of the exact crystallographic positions was considered to be a prerequisite for the correct interpretation of the results from spectroscopic studies, e.g. the observed coordination numbers and bond-distances from EXAFS and number of H$_2$O/OH molecules from TRLFS. The OH content in the C-S-H phases was supposed to play an important role for the stability of the crystal structure of C-S-H phases by balancing the charge and providing hydrogen bonds in order to satisfy the overall charge in the structure (see Chapter 2). For example, in the case of xonotlite it was shown that defects in the structure were charge-balanced by OH groups. Thus, detailed knowledge of the atomic structure was a prerequisite for the development of the envisaged mechanistic uptake model.

Crystalline C-S-H phases 11 Å tobermorite and xonotlite were chosen in this study as analogue for the poorly ordered amorphous C-S-H phases based on the similarities of the structures. Although the structure of non-doped 11 Å tobermorite was well known from previous studies, the structural position and the number of OH groups in the xonotlite structure were not exactly known. Therefore, in the first part of the doctoral study, the structure of non-doped xonotlite was investigated by means of XRD with Rietveld refinement and \textit{ab initio} molecular dynamics. We found that, deviation of the C/S ratio from the unity, which was observed after 30 days of hydrothermal synthesis, was likely due to disorder in the structure and defects in the Si chains. Such defects could provide the necessary space for possible incorporation of metal cations and water in the structure of xonotlite. The results of the Rietveld refinement showed that one of the
xonotlite polytypes (M2a2bc) was the dominant phase under the given reaction conditions, which helped to develop a structural model for the interpretation of the results from the following spectroscopic studies using EXAFS, XRD and TRLFS on Nd doped samples.

The study on the retention of Nd by 11 Å tobermorite and xonotlite showed that the Nd concentration in solution is not controlled by a solubility-limiting phase with fixed stoichiometry, although the total Nd concentration in these systems exceeded the solubility product with respect to Nd(OH)₃. Formation of a secondary precipitate (“metastable” precipitate) on xonotlite at high Nd loadings (350 μmol / g) was indicated from SEM. This phase was not visible in the long-term experiments and at low Nd loadings as well as in the case of Nd doped tobermorite. The study showed that at low Nd loadings Nd could form several species on xonotlite and tobermorite. Nd was predominantly bound on the external surface of both crystalline C-S-H phases after one day of reaction time, it was incorporated in the interlayer of tobermorite after intermediate equilibration times (1 - 60 days) and predominantly incorporated in the Ca sheets of both crystalline C-S-H phases in the long run (≥ 60 days reaction time). Nd incorporation in the Ca sheets was faster at low Nd loadings and over prolonged periods of time. In the long-term experiments Nd binding in the Ca sheets of both C-S-H phases and in the interlayer of tobermorite was controlled by recrystallization processes. Various modes of Nd↔Ca substitution in the interlayer and the Ca sheets were discussed. Uptake in the interlayer and the Ca sheets of 11 Å tobermorite and xonotlite caused the release of bridging Si tetrahedra and the formation of disordered structures.

Nd immobilization by amorphous C-S-H phases was investigated as function of reaction time and metal loadings. As Nd doped amorphous C-S-H phases could not be investigated using XRD, the EXAFS data on amorphous C-S-H were interpreted based on the structural similarities between 11 Å tobermorite and amorphous C-S-H phases. Similar to crystalline C-S-H phases, Nd was found to bind on the surface of C-S-H (formation of inner-sphere surface complexes) after one day reaction time. Nd was incorporated in the structure of C-S-H phases after longer reaction times (up to 270 days).
The investigations on Nd uptake by amorphous C-S-H phases showed that Nd adsorption by the potentially present amorphous silica and portlandite could not be supported from the EXAFS data. The low coordination numbers of neighboring Ca and Si atoms, \( N_{Ca} \) and \( N_{Si} \), were consistent with the presence of Nd surface complexes in the early stage of Nd interaction with all C-S-H phases. After prolonged ageing of the Nd doped C-S-H phases, however, the structural parameter determined from EXAFS were markedly different from those in the early stage. The coordination numbers were higher and the bond-distances were longer than those determined for the one-day sample, regardless the C:S ratio of the C-S-H material and the Nd concentration (see Chapter 4). The same correlation between reaction time and changes in the structural parameters, e.g. higher coordination numbers and longer bond distances, was previously observed for the Nd doped crystalline C-S-H phases. Longer bond-distances and higher coordination numbers were interpreted in terms of Nd incorporation into the structures of amorphous C-S-H phases.

Nd uptake by hardened cement paste was investigated using on Nd doped cement samples reacted between 1 and 200 days. Micro-XRF measurements were carried out in order to determine the Nd distribution and to obtain information on the correlation between the distribution of Nd in the cement matrix and important cement-derived elements, such as Ca and Si. The structural parameters from the micro-XAS measurements, which were carried out on selected Nd hot spots, provided insight into the Nd coordination environment in the cement matrix. Structural information on Nd binding in intact HCP as obtained from the micro-spectroscopic studies was compared with that from the bulk-XAS measurements of Nd doped powder HCP samples and Nd doped amorphous C-S-H phases. Comparison of the structural data enabled us to substantiate the proposed mechanistic model of Nd interaction with C-S-H and cement.

Upon adding Nd to hydrating cement several Nd species could appear: Nd bound on the surface of clinker and secondary minerals (outer- and inner-sphere surface complexes), Nd co-precipitated in solids with fixed and variable (solid solution) stoichiometries, and Nd incorporated in the structure of secondary minerals. It was found that the speciation of Nd in hydrated cement was not dominated by the formation of Nd surface complexes (outer-sphere, inner-sphere) on cement phases other than C-S-H, such
as portlandite or amorphous silica, due to the large number of neighboring Ca and Si atoms determined for Nd in HCP. Bulk-EXAFS spectra further showed that formation of Nd(OH)\(_2\)\(_{(am)}\) in these systems could be excluded. Formation of a mixed Nd-Ca precipitate, however, could not be ruled out in view of similarities in the EXAFS parameters of the Nd doped samples reacted for 15 min. and one day. The shorter bond distances and lower coordination numbers observed in the latter samples compared to samples reacted over longer periods of time, however, indicated that, in addition to the formation of a Nd/Ca precipitate, a small portion of Nd was bound as surface complex in hydrating cement.

Nd incorporation into the structure of C-S-H phases in hydrating cement in the long term was indicated by high Ca and Si coordination numbers and elongated Nd-Ca and Nd-Si bond-distances after reaction times up to 200 days. The coordination environment of Nd in the denser “inner”-C-S-H of HCP and in synthetic C-S-H phases were different likely due differences in the crystallinity of “inner”-C-S-H formed in cement paste and the amorphous C-S-H phases prepared in the laboratory. The coordination numbers and bond distances observed in Nd doped HCP were similar to those determined for Nd doped crystalline C-S-H phases. This can be explained by considering that “inner”-C-S-H is a relatively well crystallized material compared to “outer”-C-S-H as previously revealed from BSE imaging.

The uptake of Eu(III) by 11 Å tobermorite and xonotlite was investigated by the combined use of TRLFS and EXAFS. The latter studies were designed in a fashion to verify whether or not the findings from the studies on Nd uptake by crystalline and amorphous C-S-H, and HCP are representative for other trivalent lanthanides, such as Eu(III). Eu(III) uptake by C-S-H phases was studied at very low metal loadings (0.4 \(\mu\)mol / g solid phase).

Eu(III) uptake by crystalline C-S-H phases occurred in a way similar to that of Nd taken up by these phases. TRLFS provided additional information on the lanthanide speciation, which was not directly accessible by EXAFS. TRLFS showed that various Eu(III) species could coexist after one day reaction time. Furthermore, formation of outer-sphere surface complexes could be ruled out due to the low number of water molecules observed in the coordination sphere. For both crystalline C-S-H phases three
different Eu(III) species with ~4.7, between 1 and 2 and zero water molecules in the coordination sphere were determined after one day reaction time. The Eu(III) species with the highest number of water molecules (~4.7 water molecules) was interpreted as Eu(III) inner-sphere complex formation. Inner-sphere surface complexation was also supported by EXAFS data. Presence of between zero and 2 water molecules indicated incorporation of Eu(III) into Ca sheets and the interlayer of tobermorite and xonotlite.

Eu(III) incorporation into the structure of crystalline C-S-H was found to depend on the reaction time. The Eu(III) species with ~4.7 water molecules in the first coordination sphere was not observed after prolonged reaction time. EXAFS further showed that the number of neighboring Si and Ca atoms and the Eu-Ca and Eu-Si bond-distances increased with time, indicating that Eu(III) was incorporated into the structure of C-S-H in the long term. This agrees with the observations made on Nd doped systems.

The mechanistic model developed in this study helps to improve our understanding of the immobilization of trivalent lanthanides and actinides in cementitious materials. This is essential for long-term predictions of immobilisation processes needed to assess the safe disposal of actinides in the cementitious near field of a repository for radioactive waste.
OUTLOOK

The results from the present studies on the Nd(III) and Eu(III) uptake by C-S-H phases provide some important insights into the different modes of radionuclide complexation in the these systems. In particular, a dependency of the Nd(III) and Eu(III) incorporation by C-S-H on reaction time and metal loadings is evident from the present studies which could be expressed in a loading-time (LT) diagram (Figure 1):

In Figure 1 the different modes of Nd(III) and Eu(III) complexation are expressed in terms of stability fields of the different Nd(III)/Eu(III) species, which were observed in these systems. At low metal and short reaction time (e.g. 1 day) 2 different species were observed from TRLFS (s. Chapters 6 and 7), corresponding to Nd(III)/Eu(III) bound in structure of C-S-H. The latter species have different numbers of water molecules (e.g. between 1 and 2, and zero water molecules) in its first coordination sphere and corresponds to Nd(III)/Eu(III) bound in the interlayer and the Ca sheets of C-S-H.

![Figure 1](image-url)  
*Figure 1* Schematic representation of the Nd(III) and Eu(III) incorporation on reaction time and metal loadings.
With increasing reaction time and constant metal loadings, the number of species does not change and both species are observed even after long reaction time (e.g. 400 days from EXAFS). Starting again at low metal loadings and 1 day reaction time, we increase slowly the metal loadings, thus producing an third Nd(III)/Eu(III) species. The latter species, which corresponds to Nd(III)/Eu(III) inner-sphere complex formation (data from TRLFS), seems to disappear if we increase the reaction time. Thus, again, only two species are stable in the long run (up to 570 days; data from TRLFS). However, at higher Nd(III)/Eu(III) loadings, a fourth species exists, which could be attributed to a surface precipitate (s. Chapter 3, data from SEM and EXAFS). At present, it is not clear whether or not the surface precipitate coexists with the Nd(III)/(Eu(III)) surface complexes observed at lower loadings. Therefore, the fourth species in Figure 1 is shown in parenthesis. With decreasing the Nd(III)/Eu(III) loadings, however, the data indicate the presence of only two species in these systems (note that the boundaries of the stability field of the different species are not well known). Based on the recrystallization experiments in this study, we suggest that at very high Nd(III)/Eu(III) loadings, the system will contain more than 2 species, regardless of the reaction time. The latter could be explained by the limitation in the exchange capacity of C-S-H phases (s. Chapter 3).

The present work reveals the complexity of the chemical behaviors of Nd(III) and Eu(III) taken up by C-S-H phases and cement. Based on the insights from this study, the following questions could be addressed in the future:

- How does the crystal structure of the investigated materials influence the sorption properties and the long-term fate of radionuclides?
- How far are uptake mechanisms of radionuclides in waste repository materials controlled by reaction conditions (e.g. higher temperature)?
- Do Nd(III) precipitates form at low metal loadings?

The work presented in the previous chapters also provides methodological and crystallographic background to address such research questions.
ACKNOWLEDGMENTS

I am grateful to my wife and my son, Christian, without whose love and encouragement, I would not have finished this thesis.

I would like to express my gratitude to my supervisor, Dr. Erich Wieland, whose knowledge, patience, and skill in many areas (e.g., ethics, interaction with people) added considerably to my experience. Without him and his experience this thesis would have not been possible. I would like to thank also the other members of our workgroup Dr. Jan Tits, Dr. Rainer Dähn, Dr. Sergey Churakov, and Dr. Marika Vespa for the assistance they provided at all levels of the thesis. Finally, I would like to thank Prof. Bernhard Wehrli for the useful discussions and the constructive comments throughout the thesis.

I owe Dr. Thorsten Stumpf (FZK) special thanks for his support, mentoring, and motivation throughout the thesis and for acting as co-examiner.

Dr. Clemens Walter (INE-FZK) is kindly thanked for providing useful information and the constructive comments throughout the TRLFS measuring campaigns.

Appreciation also goes out to Dominik Kunz (LES-psi) and Astrid Schaible (LES-psi) for the assistance during the measuring campaigns and the support during the laboratory work. Roland Brütsch (LWV-psi) and Sandra Köchli (psi) are thanked for the SEM/EDS and ICP-OES measurements. Dr. Frank Winnefeld (EMPA) is thanked for his assistance during the XRD measurements. Sebastian Büchner (INE-FZK) is thanked for the assistance during the TRLFS measuring campaigns. The staff of the beamline 10.3.2 at the ALS, of the microXAS beamline at SLS, of the DUBBLE beamline at ESRF and the XAS beamline at ANKA is thanked for the experimental assistance during the synchrotron-based investigations.

I would like to express my gratitude to Prof. Michael Schindler (Laurentian University, Canada) for his engagement and encouragements to apply for this PhD work.

Partial financial support was provided by the National Cooperative for the Disposal of Radioactive Waste (Nagra), Switzerland.
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Synopsis of Former Research Interests

Environmental Mineralogy

Uranyl oxide minerals are common constituents of the weathered zones in uranium mine and mill tailings. They form in soils contaminated with actinides and are likely to be common products of spent nuclear fuel in a geological repository such as the proposed Yucca Mountain repository in Nevada. Despite their environmental importance, our understanding of water – mineral – surface interactions such as crystal growth, dissolution and adsorption lags behind that for other mineral groups, owing primarily to the structural complexity of uranyl oxide minerals and experimental difficulties associated with small crystals of poor quality. In Münster, I worked on a new approach to study the dissolution and crystal growth of (environmentally relevant) minerals at the nanoscale level. The corresponding morphological features were recorded with an Atomic-Force Microscope (AFM). This project was relevant to environmental research because there were not much research on the interaction of solutions with minerals at the nanoscale level.