Doctoral Thesis

Petrologic and stable isotope constraints on fluid-rock interaction, serpentinization and alternation of oceanic ultramafic rocks

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PETROLOGIC AND STABLE ISOTOPE CONSTRAINTS ON 
FLUID-ROCK INTERACTION, SERPENTINIZATION AND 
ALTERATION OF OCEANIC ULTRAMAFIC ROCKS

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presented by 
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ABSTRACT

The aim of this study is to constrain the mechanisms and effects of fluid-rock interaction and oceanic metamorphism of ultramafic rocks. Detailed petrologic and stable isotope investigations were performed on oceanic ultramafic rocks recovered during ODP legs in the Hess Deep Valley (Pacific Ocean, Leg 147), in the Tyrrhenian Sea (Leg 107), and on the Iberia Abyssal Plain (Leg 149). In addition, a large number of experiments were performed in order to calibrate a single-mineral oxygen isotope serpentine geothermometer.

The highly serpentinized sequence of dunites, harzburgites, troctolitic and gabbroic rocks recovered at Hess Deep (ODP Leg 147) represent a young shallow mantle section formed at the East Pacific Rise at a fast spreading ridge. The pervasive secondary replacement is dominated by lizardite, brucite, chrysotile, taenite (a FeNi-alloy, documented for the first time in ocean floor serpentinites), antigorite, magnetite, tremolite, talc, chlorite, and iowaite. Static serpentinization formed a typical mesh-textured pseudomorphic replacement of olivine and occurred at unusually high temperatures (>400°C). Lizardite, brucite and taenite progressively replace olivine in a first stage of serpentinization under strongly reducing conditions. Phase equilibria in the FeNi-alloy system indicate that taenite formed at a minimum temperature of 450°C. After (local) complete replacement of olivine and an increase in oxygen fugacity, brucite was partially replaced by chrysotile and taenite by magnetite. The presence of antigorite confirms the high temperature nature of serpentinization. Serpentine has relatively high Cl contents, which is probably present as a Fe-rich phase having the composition Fe2(OH)3Cl. 8180-values of serpentine are low (from 2.2 to 5.4‰), reflecting high temperature fluid-rock isotopic exchange. Serpentine-magnetite oxygen isotope thermometry yields temperatures between 350 and 545°C. Hydrogen isotope ratios of serpentine are also low, ranging from -69 to -59‰. The metamorphic evolution of the lower crust/upper mantle oceanic sequence is characterised by early near-axis fluid infiltration in the mafic rocks, with subsequent pervasive off-axis metamorphism under upper greenschist-facies conditions. A passive role of serpentinization is indicated by the low degree of deformation of the secondary phases. The results of this study suggest that serpentinization of peridotites at high temperature may be an important contribution to the overall 18O-budget in the oceanic lithosphere.

The peridotites drilled at Site 651 of ODP Leg 107 in the Tyrrhenian Basin, a back-arc basin related to a subduction zone, represent highly depleted, highly serpentinized upper mantle material. Secondary mineralogy is dominated by serpentine (lizardite/chrysotile), early amphibole (mainly tremolite to Mg-hornblende), talc and chlorite. Replacement of olivine formed a typical mesh-texture. Cl is partitioned into an Fe-rich and SiO2-poor phase (possibly Fe2(OH)3Cl). The 318O-values of serpentine range from 3 to 7.9‰, with δD-values ranging from -51 to -62‰. The oxygen isotope ratios of talc and amphibole (respectively 5‰ and 4.9‰ on average) allow an estimate of the evolution of the isotopic composition of the fluid during metamorphism. The oxygen composition of the fluid was strongly positive during all stages of metamorphism. Five different stages of metamorphism under decreasing temperature conditions are recognised: 1. early hydration at temperatures higher than 650°C by a magmatic or slab-derived fluid source, forming amphibole and followed by deformation caused by emplacement of the body to crustal levels; 2. metamorphism at temperatures of 450-650°C forming talc and chlorite from magmatic- or metamorphic-derived fluids; 3. limited fluid-rock interaction between 450°C and 350°C; 4. massive fluid infiltration and pervasive serpentinization under lower greenschist-facies conditions, at temperatures of approximately 300°C; 5. brittle deformation at low temperature, producing late crosscutting veins.

Five sites along the ocean-continent transition zone of the passive margin at the Iberia Abyssal Plain were drilled during ODP Leg 149. Primary mineralogy of ultramafic rocks consists of olivine, orthopyroxene, clinopyroxene, spinel and plagioclase. These phases are pervasively replaced by serpentine (lizardite and chrysotile), magnetite, brucite, calcite, clay, tremolite, chlorite, iowaite, and pyrite. Talc and antigorite are absent. Serpentine formed a mesh-textured pseudomorphic replacement of olivine, which is locally strongly sheared. Brecciation, calcitization and alteration by clay minerals are locally intense. Serpentine chemistry is similar to the chemistry of serpentinites from Legs 147 and 107. Chlorine contents the serpentines are relatively high. Stable isotope ratios of serpentine range from 5.3 to 9.3‰ and are 18O-enriched compared to primary mantle values. δD-values are very negative, ranging from -75 to -66‰. Serpentine-magnetite oxygen isotope thermometry yields a serpentinization temperature of approximately 150°C. 818O-values of clay minerals reflect equilibration at temperatures of less than 50°C. The metamorphic
evolution is characterised by subsolidus equilibration of websterites in the plagioclase-peridotite stability field, high temperature deformation forming mylonitic shear bands in the websterites, and formation of tremolite due to metasomatic activity. This stage was followed by massive serpentinization of the rocks at approximately 150°C and localised shearing, low temperature brittle deformation causing brecciation and allowing local massive calcitization, and finally alteration by clays at less than 50°C.

All serpentinites considered in this study show the following similarities: a high degree of secondary replacement; serpentine chemistry characterised by low Al and high Cl and B contents; strongly negative $\deltaD_{\text{serpentine}}$ and positive $\delta^{18}O_{\text{serpentinising fluid}}$. The main differences are: serpentinization temperature; presence or absence of taenite, talc and antigorite; $\delta^{18}O_{\text{serpentine}}$; degree and type of deformation; and degree of alteration after serpentinization. Amphibole and talc can be produced at temperatures higher than 500°C during early fluid-rock interaction. However, replacement of primary phases at this stage is limited and in contrast with the massive hydration caused by serpentinization. The role of serpentinization in the emplacement of ultramafic bodies may be active or passive, depending on the tectonic setting. Shearing of the serpentinite texture is not only indicative of diapirism, but may be caused by large-scale tectonic processes, particularly in rifted passive margins. The calculated negative $\deltaD_{\text{fluid}}$ values for all samples considered in this study are either an artifact of uncertainties in the presently available serpentine-water fractionation factors or reflect processes occurring during hydrothermal circulation and alteration. These processes are: a) production of methane and/or molecular hydrogen in hydrothermal fluids caused by reactions of serpentine formation, resulting in extremely D-depleted CH$_4$ and H$_2$; b) phase separation, producing various degrees of D-depletion in brines; c) pressure dependence on the hydrogen fractionation factors of minerals. Despite the large volumes of fluid required for serpentinization, local gradients in the hydrogen isotopic signatures of the serpentines suggest a lack of true open system conditions and indicate that the isotopic composition of the fluid was not buffered. Inferred serpentinization temperatures vary from 150° to higher than 400°C. The extremely high T-values at Hess Deep reflect the tectonic setting (rapidly rifted, very young crust produced at a fast spreading ridge) and furnish new limits for the hydration of ultramafic rocks in oceanic environments. Although the presence of antigorite in oceanic samples is an indication of high temperature, its absence can not be considered an indication of low serpentinization temperatures. Mantle sections exposed at the ocean floor are mostly highly serpentinized. As a consequence, through the formation of magnetite, these rocks may play an important role in the production of marine magnetic anomalies.

Boron contents were measured by Secondary Ion Mass Spectrometry (SIMS) in five oceanic serpentinites from different tectonic settings. Boron concentrations in serpentine are very high, ranging from 30 to 160 ppm. Brucite and clay minerals may adsorb higher quantities of boron than serpentine itself, contributing to an increase in total B contents in altered mantle rocks. The results of this study differ with previous studies and the assumption that boron is principally adsorbed by serpentine after the serpentinization process. The primary adsorption of boron is a direct process occurring during the formation of serpentine. Boron contents in oceanic serpentinites are not directly a function of the formation temperatures of the rocks (as assumed to date), but most likely are dependent on boron contents of the fluids and/or fluid/rock ratios during the hydration of the rocks. Consequently, boron concentrations alone can not be used as precise tracers for very low temperature fluid-rock interaction (i.e. "oceanic weathering").

The intracrystalline fractionation of oxygen isotopes in serpentine may be a useful method for the estimation of serpentinization temperatures, especially in oceanic environments. A large number of experiments were conducted in order to: determine which technical procedure yields the best results; constrain the effects of experimental conditions on the results; and design a useful fractionation curve. Partial fluorination at low temperatures is an inadequate method for the determination of the internal fractionation. In contrast, the thermal dehydroxylation method offers a simple way to determine the intracrystalline oxygen isotope fractionation of serpentine minerals. The extraction of structural water must be performed under ideal conditions (heating rate >350°C/min, dehydroxylation temperature 900-1000°C, maximal grain size of the mineral powders =1μm). The following fractionation curve has been calculated using natural samples, and piston cylinder re-equilibration experiments: $\Delta_{\text{nonOH-mineral}}(\% ) = 4.60 \times 10^{-9} T^2 - 2.89$.

In summary, this study presents new detailed isotopic, chemical, and petrologic data on oceanic serpentinites, as well as new limits for water-rock interaction and serpentinization of the oceanic mantle. The experimental work on the intracrystalline isotopic fractionation in serpentine furnishes a solid data base for similar studies on other minerals.
ZUSAMMENFASSUNG


Eine grosse Anzahl Experimente wurde durchgeführt, um die intrakristalline Fraktionierung von Sauerstoffisotopen im Serpentin zu bestimmen. Das Ziel dieser Experimente war: bestimmte Welche Prozedur die Reproduzierbarkeit liefert, die Charakterisierung der Effekte von technischen und experimentellen Bedingungen auf die Resultate, und die Festlegung einer nützlichen Fraktionierungskurve, die als Geothermometer angewendet werden kann. Partialle Fluorinierung durch ClF3 kann die erwünschten Resultate nicht liefern. Thermische Entwässerung im Vakuum stellt eine einfache und effiziente Methode für die Bestimmung der intrakristallinen Fraktionierung dar. Die Entwässerung der Proben muss bei idealen Bedingungen durchgeführt werden: Heizungsraten >350°C/min, Entwässerungstemperatur 900-1000°C, Korngröße der Proben ≤1 μm. Eine erste semi-empirische ermittelte Fraktionierungskurve, die als Geothermometer für ozeanischen Gestein angewendet werden kann, lautet: \[ \Delta_{\text{nonOH-mineral}}(\%o) = 4.60 \cdot 10^{-6}/T^2 - 2.89 \]