Combining cosmogenic $^{10}$Be and in situ $^{14}$C in earth surface sciences
a new $^{14}$C extraction system and two case studies on sediment transfer and surface exposure dating

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Combining cosmogenic $^{10}$Be and in situ $^{14}$C in Earth surface sciences: A new $^{14}$C extraction system and two case studies on sediment transfer and surface exposure dating

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In situ produced cosmogenic nuclides are widely applied in Earth surface sciences. Of these nuclides $^{14}$C has by far the shortest half-life ($t_{1/2} = 5730 \, \text{y}$) and is, thus, particularly sensitive to recent and rapid landscape changes. Combined with a long-lived nuclide, in situ $^{14}$C provides the opportunity to analyse complex surface histories, e.g. due to burial or pre-exposure, or to investigate the relation of sediment transport and storage in fluvial systems. However, routine in situ $^{14}$C analysis is difficult and has long been hindered by the low $^{14}$C concentrations in terrestrial rocks and the contamination by atmospheric $^{14}$C. This work focuses on the in situ $^{14}$C extraction system established at ETH Zürich and the application of in situ $^{14}$C in quantitative geomorphology and Quaternary geochronology.

The first part of this thesis describes in detail the setup of the ETH in situ $^{14}$C extraction system and gives an account of the analytical reproducibility and accuracy. Carbon is extracted from quartz samples (~5g) by heating for several hours at 1550-1600°C under an O$_2$-flow without the use of a flux agent, i.e. without melting the quartz. Atmospheric contamination is removed during a pre-heating step at ~700°C. Following sample outgassing, gas purification is achieved by a series of cryogenic traps and passage through hot Ag and Cu wool/mesh. The clean CO$_2$ gas is analysed with a gas ion source Accelerator Mass Spectrometry (AMS) system without prior graphitization and, thus, without the addition of $^{14}$C-free CO$_2$. Typically, samples are measured with a high analytical precision of <2%. By optimizing the analytical protocol, sample processing time could be shortened from three to now two days in total.

Measurements of the informal in situ $^{14}$C standard sample PP-4 show a good reproducibility of <5% and are consistent with published values. The procedural blank level significantly decreased since the first regular operation of the extraction line and is currently at ~$3.7 \times 10^4$ $^{14}$C atoms. Due to this low procedural blank, we have successfully applied in situ $^{14}$C surface exposure dating to an only ~300 year old rock avalanche (Val Ferret, Italy).

Additionally, we present a modified calculation scheme for in situ $^{14}$C concentrations which differs from that used for conventional radiocarbon dating. This new approach is based on the characteristics of cosmogenic in situ $^{14}$C production and proposes to omit the inappropriate $\delta^{13}$C correction, to correct for the year of measurement instead of AD 1950, and to account for the natural isotopic composition of carbon.
In the first of two application studies in situ $^{14}$C is analysed in combination with cosmogenic $^{10}$Be and $^{26}$Al in fluvial sediments from the eastern Altiplano, Bolivia, to evaluate and quantify denudation processes and sediment transfer times. Concentrations of the long-lived nuclides $^{10}$Be and $^{26}$Al imply consistently low catchment-wide denudation rates of ~ 4-32 mm ky$^{-1}$ (integrating over 20-170 ky) and are in good agreement with published modern sediment discharge data. These results suggest long-term (since the late Pleistocene) geomorphic and isotopic steady-state for the eastern Altiplano and are consistent with the low topographic gradients and the absence of significant tectonic activity on the eastern Altiplano. Concentrations of in situ $^{14}$C are comparatively low and disagree with the simple exposure history indicated by $^{10}$Be and $^{26}$Al. This discrepancy is interpreted to reflect $^{14}$C decay during at least one episode of recent sediment storage lasting ~ 11-20 ky. The influence of soil-mantled hillslopes on the in situ $^{14}$C concentration is evaluated and models for deep burial of the sediment and storage at shallow depths are discussed.

Results for in situ $^{14}$C are well consistent with the geomorphic setting and the fluvial processes on the eastern Altiplano and illustrate the importance of sediment storage in low-gradient landscapes. This study highlights the potential of in situ $^{14}$C to investigate sediment routing within fluvial systems and to provide fundamental information on the sediment residence time within a drainage basin.

In the second study $^{10}$Be and in situ $^{14}$C were combined to investigate the deglaciation history of the Gotthard Pass, Central Swiss Alps, and elucidate the effect of Lateglacial climate warming on the high Alpine mountain glaciers. Glacial erosional features preserved on the Gotthard Pass portray a progressive downwasting of LGM glaciers from their maximum extent and a gradual re-organization of the paleoflow pattern. $^{10}$Be exposure ages of ~ 16-15 ky indicate that first deglaciation of the pass area is associated with the decay of the large Gschnitz glacier system by the end of the Oldest Dryas. In conjunction with published data from other Alpine passes, these ages suggest that after the breakdown of the LGM ice masses large interconnected local glaciers persisted in the high Alps. In contrast to the rapid deglaciation proposed for the Alpine foreland high Alpine glaciers might have remained large possibly until the onset of the Bølling warming. Consistent with field observations proposing another glacier readvance within a small and topographically controlled glacier system, $^{10}$Be exposure ages of ~ 12-13 ky are interpreted to record the disintegration of Egesen stadial glaciers. From a boulder at the pass, a minimum age of 11.2 ± 05 ky is given for final deglaciation by the end of the Younger Dryas.
In situ $^{14}$C data are overall in good agreement with the $^{10}$Be ages and confirm continuous exposure since the end of the Younger Dryas. In situ $^{14}$C further allows to constrain the amount of Holocene snow cover that has to be incorporated in the exposure age calculations. However, our data also suggest that the currently used in situ $^{14}$C production rate might be underestimated.

Altogether, this work shows that great progress was made in the analysis of in situ produced $^{14}$C. Both case studies illustrate that useful information that can be revealed from in situ $^{14}$C and demonstrate the potential of combining in situ $^{14}$C with $^{10}$Be or other cosmogenic nuclides to unravel complexity in surface exposure and geomorphic processes.
Zusammenfassung


Trotz diverser potentieller Anwendungen ist die Analyse von in situ $^{14}$C nach wie vor schwierig. Dies liegt vor allem an der niedrigen Konzentration von in situ $^{14}$C in terrestrischen Gesteinen und dem Problem der Kontamination durch atmosphärisches $^{14}$C. Die vorliegende Arbeit beschäftigt sich mit der Entwicklung einer Extraktionsanlage für in situ $^{14}$C an der ETH Zürich und beschreibt zwei Anwendungen von in situ $^{14}$C im Bereich der quantitativen Geomorphologie und der Quartärgeologie/-geochronologie.

Im methodischen Teil dieser Arbeit wird zunächst der Aufbau und die Funktionsweise der in situ $^{14}$C Extraktionsanlage an der ETH im Detail erläutert und die analytische Reproduzierbarkeit und Genauigkeit betrachtet.

Die Extraktion von Kohlenstoff aus etwa 5 g Quarz erfolgt bei Temperaturen von 1550-1600°C in einem Fluss von hochreinem Sauerstoff. Atmosphärisches $^{14}$C wird zuvor bei etwa 700°C entfernt. Da während des Extraktionsprozesses kein Flussmittel zugegeben wird, wird die Quarzprobe nicht geschmolzen. Das extrahierte Gas durchläuft eine sorgfältige Reinigung unter Verwendung mehrerer Kühlfallen und der Reaktion mit heisser Silber- und Kupferwolle. Das gereinigte $\text{CO}_2$ wird ohne Graphitisierung mithilfe einer Gasquelle an einem Beschleunigermassenspektrometer (AMS) gemessen. Die Messgenauigkeit typischer Quarzproben beträgt <2%. Durch die Zusammenfassung mehrerer Analyseschritte während des Extraktionsprozesses, konnte die Probenaufbereitung optimiert und die Dauer für die Extraktion einer Probe von zwei auf drei Tage reduziert werden.
Messungen einer \textsuperscript{14}C Referenzprobe (PP-4) bestätigen eine gute Reproduzierbarkeit <5\% und sind konsistent mit den Ergebnissen anderer Labore. Der Systemblank konnte seit Inbetriebnahme der Extraktionsanlage deutlich reduziert werden und ist derzeit bei \(\sim 3.7 \times 10^4\) \textsuperscript{14}C Atomen. Am Beispiel der Datierung eines nur etwa 300 Jahre zurückliegenden Felssturzes in Val Ferret (Italien) konnte gezeigt werden, dass, aufgrund des niedrigen Blanks, auch sehr junge Expositionsalter erfolgreich bestimmt werden können.

Des Weiteren wird ein verändertes Verfahren zur Datenauswertung und Berechnung von \textit{in situ} \textsuperscript{14}C-Konzentrationen vorgeschlagen. Die modifizierte Datenauswertung berücksichtigt die Unterschiede zwischen \textit{in situ} produziertem und atmosphärischem \textsuperscript{14}C und beachtet die natürliche Isotopenzusammensetzung von Kohlenstoff. Es wird keine \(\delta^{13}C\)-Korrektur vorgenommen und die Daten werden auf das Jahr der Messung anstelle 1950 korrigiert.

In der ersten von zwei Studien zur Anwendung von \textit{in situ} \textsuperscript{14}C auf geologische Fragestellungen, wurde \textsuperscript{14}C in Kombination mit den langlebigen Nukliden \textsuperscript{10}Be und \textsuperscript{26}Al in Flusssedimenten vom östlichen Altiplano, Bolivien, gemessen. Ziel dieser Studie war es, die Denudationsprozesse und den Sedimenttransfer in Einzugsgebieten entlang der Ostgrenze des Altiplano zu bestimmen und zu untersuchen, wovon diese gesteuert werden. Die gemessenen \textsuperscript{10}Be und \textsuperscript{26}Al-Konzentrationen deuten übereinstimmend auf niedrige Denudationsraten zwischen \(\sim 4-32\) mm a\(^{-1}\) während der letzten 20-170 ka hin. Ähnliche Raten könnten auch von publizierten Messungen der heutigen Sedimentfracht in Flüssen des Untersuchungsgebietes abgeleitet werden. Diese Übereinstimmung legt nahe, dass sich das östliche Altiplano seit dem späten Pleistozän in einem geomorphologischen und isotopischen Gleichgewicht befindet, welches sich auch aus der flachen Topografie und der weitgehenden Abwesenheit tektonischer Aktivität andeutet. Die \textit{in situ} \textsuperscript{14}C-Konzentrationen sind vergleichsweise gering und verweisen auf komplexe Erosionsprozesse. Sie werden nicht als Resultat erhöhter Denudationsraten, sondern als Hinweis auf eine Zwischenlagerung des Sediments interpretiert, die mindestens über die letzten \(\sim 11-20\) ka andauerte. Modelle für eine tiefe Sedimentlagerung mit kompletter Abschirmung vor kosmischer Strahlung und einer Lagerung nahe der Oberfläche werden verglichen. In diesem Zusammenhang wird auch der Einfluss von Bodenbildung und -durchmischung auf die \textit{in situ} \textsuperscript{14}C-Konzentration diskutiert.

Die Ergebnisse der \textit{in situ} \textsuperscript{14}C-Analyse spiegeln die Morphologie und die episodisch auftretenden fluvialen Prozesse auf dem östlichen Altiplano wider und belegen, dass die Zwischenlagerung von Sediment bereits über kurze Distanzen von mehreren Kilometern eine grosse Rolle spielen kann. Diese Studie belegt, dass mithilfe von \textit{in situ} \textsuperscript{14}C Transferprozesse in fluvialen Sedimentsystemen untersucht
und wichtige Informationen über die Verweildauer des Sediments innerhalb eines Einzugsgebietes ermittelt werden können.


Die Resultate der \textit{in situ} \(^{14}\)C-Messungen stimmen mit den \(^{10}\)Be-Daten grösstenteils überein und bestätigen die Abwesenheit von Gletschern auf dem Gotthardpass während des Holozäns. Die \textit{in situ} \(^{14}\)C-Konzentrationen erlauben ausserdem Rückschlüsse auf die Holozäne Schneedeckung, welche in die Berechnung der Expositionsalter einfließen sollte. Schliesslich wird angedeutet, dass die zurzeit verwendete \textit{in situ} \(^{14}\)C-Produktionsrate zu niedrig sein könnte.

Zusammenfassend verdeutlicht diese Arbeit nicht nur die Fortschritte, die bei der Extraktion und Analyse von \textit{in situ} \(^{14}\)C erreicht wurden. Sie zeigt auch das Potenzial von \textit{in situ} \(^{14}\)C, insbesondere in Kombination mit \(^{10}\)Be, komplexe geomorphologische Vorgänge auf der Erdoberfläche zu untersuchen.
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I. Introduction

I.1. Motivation

Since the formation of the first continental crust about 4.4 Gy ago (cf. Wilde et al., 2001) the Earth’s surface has experienced permanent modification under the influence of endogenous (e.g., tectonics, volcanism) and exogenous (e.g., denudation processes) forces. Tectonics provoke surface uplift by mountain orogeny while weathering and erosion wear landscapes down. These processes are not only strongly linked to each other; they are also coupled to regional and global climate (e.g., Masek et al., 1994; Willett, 1999; Montgomery et al., 2001; Montgomery and Brandon, 2002). To understand the dynamics of the land surface it is important to recognize the complex interaction of geomorphic processes with the Earth’s atmosphere, hydrosphere and cryosphere and to constrain their spatial and temporal impact on landscape evolution. By quantifying the rates and conditions at which the Earth’s surface has changed in the past, e.g. in response to climate change, it is possible to understand modern changes and predict the future evolution.

The development of terrestrial cosmogenic nuclide analysis has provided a tool to Earth surface sciences that allows to directly determine the age of a geomorphic surface (‘surface exposure dating’) or to quantify rates of geomorphic processes. Being produced by the impact of cosmic rays on the Earth’s surface, the concentration of a cosmogenic nuclide within a rock records the time this rock has been uncovered, i.e. exposed, at the surface. This basic concept essentially depends on the knowledge of the accurate local production rate and usually also requires a number of assumptions, e.g., on the continuity of surface exposure or the uniformity of process rates. Many studies and publications have been dedicated to these topics and provide detailed information on the theory and applications of terrestrial cosmogenic nuclides (e.g., Lal, 1988, 1991; Masarik and Reedy, 1995; Biermann and Steig, 1996; Heisinger et al., 1997; Gosse and Phillips, 2001; Niedermann, 2002; Heimsath and Ehlers, 2005; Kirchner et al., 2006; Granger and Riebe, 2007; Dunai, 2010 and references therein). With the significant improvements made during the past 30 years on the understanding and analysis of cosmogenic nuclides the number of applications has rapidly increased. Today, cosmogenic nuclides are not only used in Quaternary geochronology but also in paleoclimatology, archaeology, soil sciences, glaciology or sedimentology (examples given in Cerling and Craig, 1994; Cockburn and Summerfield, 2004).

\(^{10}\text{Be, }^{26}\text{Al and }^{36}\text{Cl}\) are the most widely and routinely used cosmogenic radionuclides in Quaternary geochronology and Earth surface process studies. They
are usually analysed in quartz ($^{10}$Be, $^{26}$Al) or carbonates ($^{36}$Cl) and are extracted from these minerals using a wet chemistry. Isotopic measurements are performed by Accelerator Mass Spectrometry (AMS). With half-lives of about 1.4 ($^{10}$Be), 0.7 ($^{26}$Al) and 0.3 ($^{36}$Cl) My (Holden, 1990; Nishiizumi, 2004; Chmeleff et al., 2009; Korschinek et al., 2009) these radionuclides cover an age range of up to a few $10^6$ years. Older surfaces with very long exposure times are studied with stable noble gas isotopes, of which $^3$He and $^{21}$Ne are most commonly used (e.g., Schäfer et al., 1999; Niedermann, 2002; Kober et al., 2005; Evenstar et al., 2009). Cosmogenic radionuclides accumulate fast enough to be analytically detectable already after several hundred to a few thousand years of exposure (Schaefer et al., 2009; Akcar et al., 2011; Goehring et al., 2011a). On the other hand, their relatively long half-lives render them insensitive to changes in surface exposure or process rates occurring on equally short time-scales. To detect such short and recent disturbances, commonly referred to as complex exposures, a nuclide of much shorter half-life is required. This condition is met by in situ cosmogenic $^{14}$C, which is the subject of this dissertation.

In situ $^{14}$C has a short half-life of $5730 \pm 40$ years (Godwin, 1962) and is useful to investigate surface evolution and process rates throughout the Holocene to Latest Pleistocene. Because of its fast radioactive decay, isotopic inheritance and low erosion rates are negligible for in situ $^{14}$C exposure dating. Most importantly, in situ $^{14}$C reacts rapidly to short-term landscape modifications that are not recorded by the longer-lived cosmogenic nuclides. It therefore provides information and quantification of the dynamics and complexity of geomorphic systems and landscape evolution. Because in situ $^{14}$C is mainly measured in quartz, it can be easily analysed in combination with $^{10}$Be, $^{26}$Al or $^{21}$Ne. A more detailed description of the advantages and possible applications of in situ $^{14}$C will be given in chapter 1.2.2.

Although ‘conventional’ radiocarbon analysis has been a long-established dating technique and despite the wide interest in using in situ $^{14}$C in Earth surface sciences, the development of the in situ $^{14}$C analytics has lagged behind compared to the long-lived cosmogenic radionuclides. When the in situ $^{14}$C extraction system was built at the ETH Zürich noble gas laboratory, only few other laboratories worldwide were reporting in situ $^{14}$C results (Lifton et al., 2001; Naysmith et al., 2004; Yokoyama et al., 2004). In 2007 this dissertation was started with the primary task to establish routine in situ $^{14}$C analysis at ETH. The successful results of that work are presented here. In a second step, in situ $^{14}$C was then applied to two very different geologic/geomorphologic studies that illustrate the potential of in situ $^{14}$C to unravel the complexities of landscape formation and surface processes.
The following introductory chapters will focus on the characteristics of the \textit{in situ} \(^{14}\text{C}\) isotope, introduce possible applications in Earth surface sciences and give a short overview of the development of the \textit{in situ} \(^{14}\text{C}\) extraction method.

\textbf{I.2. \textit{In situ} cosmogenic \(^{14}\text{C}\)}

\textit{I.2.1. Production mechanisms and rates}

\textit{In situ} \(^{14}\text{C}\) produced in rocks (and soils) on the Earth surface is bound to the same production pathways as the long-lived cosmogenic nuclides \(^{10}\text{Be}\) and \(^{26}\text{Al}\). Detailed descriptions of the production systematics of terrestrial cosmogenic nuclides are given, e.g., by Lal, 1988; Heisinger and Nolte, 2000; Gosse and Phillips, 2001; Dunai, 2010.

When entering the Earth’s atmosphere, primary cosmic rays (mainly protons) collide with atmospheric particles and produce a cascade of secondary cosmic rays which then impact on the Earth’s surface. Because the secondary cosmic-ray flux is mainly composed of neutrons, the dominant production mechanism for all cosmogenic nuclides is spallation, i.e. the production of lighter atomic nuclei by the collision with highly energetic secondary neutrons that remove protons and neutrons from the target nuclei (cf. Dunai, 2010). For \textit{in situ} \(^{14}\text{C}\), the primary target for spallation reactions is O (\(^{16}\text{O}(n, 2\text{pn})^{14}\text{C}, {^{17}}\text{O}(n, \alpha)^{14}\text{C}\)); minor production occurs from Si (\(^{28}\text{Si}(n, x)^{14}\text{C}\)) (Dunai, 2010). Muon-induced reactions considerably add to the total sea level, high latitude (SLHL) production rate of \textit{in situ} \(^{14}\text{C}\) (at least 17\% according to Heisinger et al., 2002b; see discussion below) and therefore always need to be considered when \textit{in situ} \(^{14}\text{C}\) is applied in Earth’s surface studies. Compared to the neutron flux that decreases rapidly with depth muons have a significantly higher attenuation length and reach much deeper into the subsurface (Stone et al., 1998). Thus, muonic reactions become more important with increasing depth below the surface (Fig. I.2.1). For \textit{in situ} \(^{14}\text{C}\), negative muon capture in O (\(^{16}\text{O}(\mu-, \text{pn})^{14}\text{C}\)) greatly exceeds fast muon reactions (Heisinger et al., 2002b).

Thermal neutron capture that produces \(^{14}\text{C}\) in the atmosphere (\(^{14}\text{N}(n, p)^{14}\text{C}\)) (Libby et al., 1946) is usually considered to be negligible for \textit{in situ} \(^{14}\text{C}\) production due to the low amount of thermal neutron-producing \(\alpha\)-particles in quartz (Dunai, 2010). However, it was suggested that in cases of a high abundance of fluid inclusions containing N, neutron capture produced \textit{in situ} \(^{14}\text{C}\) from N may be in a detectable range (Kim et al., 2007b).
For the application of a cosmogenic nuclide in Earth sciences it is crucial to know at which rate the respective nuclide is produced in a target rock or mineral. In the past decade and led by the CRONUS-Earth (Cosmic-Ray Produced Nuclide Systematics on Earth; Phillips, 2010) and the CRONUS-EU projects (Stuart and Dunai, 2009), significant effort has been made to improve the knowledge on production rates and the understanding of the production systematics. As a result of this effort, models for altitudinal and latitudinal scaling have been refined and the production rate calibration dataset for cosmogenic $^{10}$Be and $^{26}$Al, and less also $^{36}$Cl, has greatly expanded. This should allow a much more accurate determination of the local production rates of these nuclides. However, because of the difficulties in the extraction of in situ $^{14}$C the corresponding production rate estimates are still based upon rather limited data. All rates quoted in the following are scaled to SLHL according to scaling scheme of Lal (1991)/Stone (2000).

Numerical calculations by Masarik and Reedy (1995) predicted a SLHL production rate of 18.6 at g$^{-1}$ y$^{-1}$ without including muon contribution. Some of the first empirical estimates on the in situ $^{14}$C production rate in terrestrial rocks were

Figure I.2.1. In situ $^{14}$C and $^{10}$Be production as a function of depth below surface; calculated using a rock density of 2.65 g cm$^{-3}$ and the depth dependency from Schaller et al. (2002). Muonic production rates are taken from Heisinger et al. (2002b), spallogenic production rates are from Balco et al. (2008, 2009) for $^{10}$Be and from Lifton (pers. comm.) for in situ $^{14}$C. (A) The absolute production rates of in situ $^{14}$C and $^{10}$Be at SLHL. The importance of muon-induced production increases with depth because muons have a higher attenuation length and penetrate deeper into the subsurface. (B) The decrease of the relative production rates with depth (surface production rates are 100%). Due to a comparatively high contribution of muonic production to the total production rate of in situ $^{14}$C, the relative production rate of in situ $^{14}$C at depth is higher compared to the relative production rate of $^{10}$Be.
obtained from whole rock samples: Production rates from granitic rocks sampled at high elevation, high latitude sites range from ~17 to 28 at g⁻¹ y⁻¹ with a mean value of ~ 23 at g⁻¹ y⁻¹ (Donahue et al., 1990, rescaled by Lifton et al., 2001). In contrast, about 37% lower production rates were determined from Hawaiian glacial tills and lava flows (Donahue et al., 1990). Further studies in basaltic rocks yielded a production rate of ~ 20 at g⁻¹ y⁻¹ (Jull et al., 1994). The production of \textit{in situ} ¹⁴C in limestone was studied by Handwerger et al. (1999) who reported a production rate of 18 ± 3 at g⁻¹ y⁻¹.

A first estimate on the ¹⁴C production rate in quartz was presented by Lal et al. (1990). \textit{In situ} ¹⁴C concentrations measured in quartz from Allan Hills, Antarctica, yielded a local production rate of 99 ± 12 at g⁻¹ y⁻¹ equivalent to a SLHL production rate of ~ 19 at g⁻¹ y⁻¹ (Lal et al, 1990). With significant improvements achieved in the \textit{in situ} ¹⁴C extraction procedures, Lifton et al. (2001) obtained a production rate of 15.1 ± 0.5 at g⁻¹ y⁻¹ from quartzites at Lake Bonneville (Utah). Based on additional analyses of the Lake Bonneville PP-4 quartz and data from a sampling site in Scotland Dugan et al. (2008) presented a revised production rate of 15.2 ± 0.3 at g⁻¹ y⁻¹.

An important and still unsettled question is the actual contribution of muonic \textit{in situ} ¹⁴C production. The only published values are those from Heisinger et al. (2002a, b) with 3.34 ± 0.27 at g⁻¹ y⁻¹ for negative muon capture and 0.44 ± 0.25 at g⁻¹ y⁻¹ for fast muon reactions. These rates were obtained experimentally by irradiation of SiO₂ targets with the respective muons and were then calculated from the muon fluxes as measured by AMS. Data from natural quartz samples, i.e. from depth profiles, have not yet confirmed these results. In contrast, a ~ 150 cm deep profile analysed by Kim et al. (2007a) has shown 2-3 times higher ¹⁴C concentrations at depth than expected, which was attributed to ¹⁴C production by thermal neutron capture in nitrogen present in the fluid inclusions in quartz. However, detailed analyses of \textit{in situ} ¹⁴C production at depth are still missing.

Quoting a number of 18.4 at g⁻¹ y⁻¹ for nucleonic \textit{in situ} ¹⁴C production, Heisinger et al. (2002b) give a total production rate of 21.3 at g⁻¹ y⁻¹. With reference to that value, negative muon capture would account for 15% and fast muon reactions for 2% of the total production rate. The production rates of Lifton et al. (2001) and Dugan et al. (2008) given above were calculated based on these relative muon contributions. However, the computation of production rates has been re-evaluated lately. Now the absolute muonic production rates as given in Heisinger et al. (2002b), i.e. 3.34 ± 0.27 and 0.44 ± 0.25 at g⁻¹ y⁻¹, instead of the percentages are used as fixed rates for muon-induced production at SLHL. This is based on the assumption that the muonic production rates of Heisinger et al. (2002a, b) are correct for SLHL production and independent of future revisions of the spallogenic
production rate. Following this approach and using published in situ $^{14}$C calibration data (Lifton et al., 2001; Miller et al., 2006; Dugan et al., 2008) a revised in situ $^{14}$C production rate of 12.29 ± 0.99 at g$^{-1}$ y$^{-1}$ for spallation has been calculated by N. Lifton (pers. comm.). Including the above values for muonic production (Heisinger et al., 2002b) gives a total production rate of 16.07 ± 1.06 at g$^{-1}$ y$^{-1}$.

Recently, new in situ $^{14}$C data has been obtained from a calibration site in New Zealand (Putnam et al., 2010). Preliminary results suggest a spallogenic production rate of 11.4 ± 0.34 at g$^{-1}$ y$^{-1}$ corresponding to a total production rate of ~ 15.2 at g$^{-1}$ y$^{-1}$ (Schimmelpfennig et al., 2011). This value is not equivalent to the 15.2 at g$^{-1}$ y$^{-1}$ of Dugan et al. (2008) but in fact slightly lower because it has been determined using the absolute muon production rates of Heisinger et al. (2002b).

I.2.2. Applications

Equivalent to the other cosmogenic nuclides in situ $^{14}$C can be used as a tool for exposure dating or to determine local or catchment-averaged process rates. It is limited to exposures of up to 2-3 half-lives before reaching a secular equilibrium or ‘steady-state’ between nuclide production and radioactive decay (Fig. I.2.2). However, the development of the in situ $^{14}$C method at ETH Zürich is not primarily motivated by the prospect of using in situ $^{14}$C as a single nuclide. In fact, especially cosmogenic $^{10}$Be analysis is now a well-established method and has proven to be widely applicable in surface exposure dating and denudation studies (e.g., Klein et al., 1986; Brook et al., 1995; Biermann and Steig, 1996; Braucher et al., 1998; Heimsath et al., 1999, 2001; Schaller et al., 2001; Clapp et al., 2002; Biermann and Nichols, 2004; Stock et al., 2004; Binnie et al., 2006; Ivy-Ochs et al., 2007; Dixon et al., 2009; Hein et al., 2009; Wittmann et al., 2010). Recently, even exposures of a few hundred years have been successfully dated with $^{10}$Be (Schaefer et al., 2009; Akçar et al., 2011; Goehring et al., 2011a). However, while such young exposures can now be well determined by $^{10}$Be, short intervals of surface cover or shielding cannot be recorded by $^{10}$Be or any other long-lived nuclide. In situ $^{14}$C, on the other hand, decays rapidly and is therefore sensitive to short-term interruptions in surface exposure, e.g. through cover by ice, snow, sediment, or recent changes in geomorphic process rates. It is of greatest benefit when applied in combination with another isotope of longer half-life.

For surface exposure dating, three main approaches can be taken in combining in situ $^{14}$C with one or more other isotopes: (i) For surfaces where in situ $^{14}$C is in isotopic steady-state, its concentration can be used to derive a local denudation rate or production rate, assuming that these have been constant over the considered time interval. This eliminates one unknown in the calculation of an accurate surface exposure age obtained, e.g., by $^{10}$Be analysis. (ii) For younger surfaces, comparing
the concentration obtained for \textit{in situ} $^{14}$C and a longer-lived nuclide from the same sample allows to distinguish between simple and complex exposure history. Episodes of intermittent surface cover can be quantified and information about climate variability or the progression of geomorphic processes within sedimentary or soil systems are gained (Fig. I.2.3). (iii) Dating surface exposures with long-lived nuclides assumes that the cosmogenic nuclide concentration within that surface was zero prior to its current exposure. For depositional surfaces or postglacial exposures this condition is not always fulfilled and introduces possible sources of error (Anderson et al., 1996; Gosse and Phillips, 2001; Stroeven et al., 2002; Dühnforth et al., 2010). The cosmogenic nuclide clock within a pre-exposed rock or sediment can be reset to zero either by deep erosion or long burial. While the long-lived nuclides require at least several $10^6$ to $10^7$ years of burial, \textit{in situ} $^{14}$C is completely decayed after only several $10^4$ to $10^5$ years (without erosion). Therefore, apart from studying glacially modified surfaces or the formation ages of sediment deposits, \textit{in situ} $^{14}$C might also be used to quantify the intensity of glacial erosion.

So far, the combined application of \textit{in situ} $^{14}$C with a long-lived nuclide has focussed on glacially influenced landscapes to solve questions of ice fluctuations and ice movement. For example, a study on glacial response to climate change has successfully combined \textit{in situ} $^{14}$C and $^{10}$Be analyses to trace a Late Holocene readvance of the Rhone Glacier, Switzerland (Goehring et al., 2011a). Similarly, the

![Diagram](Figure I.2.2. The increase in the concentrations of $^{26}$Al, $^{10}$Be and \textit{in situ} $^{14}$C (at SLHL) and their approach to steady-state as a function of exposure time and variable erosion rates. Compared to the long-lived cosmogenic nuclides $^{10}$Be and $^{26}$Al, \textit{in situ} $^{14}$C reaches steady-state very quickly. The effect of erosion is illustrated with the dashed lines for 5 and 15 mm ky$^{-1}$, respectively. The black rectangle at the lower left corner of diagram (A) represents the extent of diagram (B). Note that the y-axis in (B) is not logarithmic.)
expansion of a local ice cap during historic times could be revealed by comparing in situ $^{14}$C ages with $^{10}$Be and $^{26}$Al data from exposed bedrock in the Canadian Arctic (Miller et al., 2006). A reconstruction of the exposure-burial-exposure history of an Arctic landform based on combined in situ $^{14}$C – $^{36}$Cl analyses has been presented by Zreda and Lifton (2000). Lately, in situ $^{14}$C ages obtained from glacial clasts in Antarctica were used to exclude nuclide inheritance and confirm the deglaciation history as inferred from $^{10}$Be and $^{26}$Al ages (White et al., 2011).

Figure I.2.3. Changes in nuclide concentration for $^{26}$Al, $^{10}$Be and in situ $^{14}$C as a response to recent surface cover (A) and variation in erosion rate (B).

(A) After exposure at 20 ky nuclides accumulate until the surface is abruptly covered at 5 ky (no erosion). Solid lines represent nuclide concentrations for surface cover with complete shielding from further irradiation; dashed lines have been calculated for shielding by a 2 m thick snow layer ($\rho = 0.3$ g cm$^{-3}$, only applied to spallogenic production). Dotted lines illustrate the increase in concentration if the surface is continuously exposed. Due to its fast radioactive decay in situ $^{14}$C decreases rapidly during complete shielding while the concentrations of $^{10}$Be and $^{26}$Al hardly change. In the case of low nuclide production in a snow covered surface $^{10}$Be and $^{26}$Al concentrations increase slowly. For in situ $^{14}$C, decay outweighs accumulation so that the concentration decreases, but less rapidly than for complete shielding.

(B) Following an instantaneous decrease in erosion rate from 100 mm ky$^{-1}$ to 10 mm ky$^{-1}$ at $t = 0$ (not shown here) nuclide concentrations slowly adjust to a new steady-state. It is shown that in situ $^{14}$C regains equilibrium significantly faster than the long-lived $^{10}$Be and $^{26}$Al. Furthermore, the relative concentration change is much less for in situ $^{14}$C compared to $^{10}$Be and $^{26}$Al. The time difference for $^{10}$Be and $^{26}$Al to reach steady-state is too small to be resolved here.
The potential of *in situ* $^{14}$C to quantify geomorphic process rates has not yet been explored in much detail. Lal et al. (1996) presented model erosion rates obtained by $^{10}$Be and *in situ* $^{14}$C from a soil profile. The measured nuclide concentrations predicted a one order of magnitude higher $^{14}$C erosion rate compared to the $^{10}$Be rate. These results were interpreted to reflect a mid-Holocene increase in soil erosion following an episode of soil burial (Lal et al., 1996; Lal, 2001). For the study of catchment-averaged denudation rates, *in situ* $^{14}$C is limited to fast rates. In slowly eroding landscapes, the *in situ* $^{14}$C concentration is controlled by nuclide decay and no information on the denudation rate can be obtained (Lal, 1991; von Blanckenburg, 2005). On the other hand, the limited sensitivity of *in situ* $^{14}$C to low denudation rates offers the opportunity to gain information on parameters as soil mixing depth or sediment storage in a floodplain environment (Wittmann and von Blanckenburg, 2009). This topic will be discussed in detail in chapter III.

I.2.3. The history of *in situ* $^{14}$C extraction

Already in the 1940s the development of ‘conventional’ radiocarbon analysis started, using the radioactive carbon isotope $^{14}$C, produced by cosmic rays in the Earth’s atmosphere, as a dating tool for organic material (Libby, 1946; Anderson et al., 1947; Libby et al., 1949). In conjunction with the huge progress made on Accelerator Mass Spectrometry (AMS) (Jull and Burr, 2006 and references therein) radiocarbon dating quickly became one of the most widely used dating methods for a large variety of applications in, e.g., geochronology, archaeology and climatology (Hajdas, 2008, 2009). However, the development of analytical methods to extract *in situ* produced $^{14}$C from a rock or mineral happened more slowly. The first measurements of the $^{14}$C content in rocks were obtained from meteorites (Suess and Wänke, 1962; Goel and Kohmann, 1962). Because the cosmic rays are not attenuated by the Earth atmosphere or the geomagnetic field, the $^{14}$C concentration in extra-terrestrial material is much higher than in terrestrial rocks (Lal and Peters, 1967) and can therefore be more easily detected. Assuming $^{14}$C saturation by irradiation in space, the rapid radioactive decay of $^{14}$C was used as a tool to determine the terrestrial ages (the fall age) of meteorites (Cresswell et al., 1994 and references therein).

Early experiments on the carbon content in terrestrial basalts (and lunar rocks) employed sequential sample combustion under the presence of oxygen at temperatures of 420-1270°C for 40-90 min (DesMarais, 1978a). The sample gas was trapped with liquid nitrogen at -196°C and CO$_2$ was separated from SO$_2$ by distillation at -155°C and -95°C at a variable temperature trap (DesMarais, 1978b; DesMarais and Moore, 1984). With the development of terrestrial cosmogenic
nuclide dating, considerable research on the extraction of cosmogenic \textit{in situ} $^{14}$C was done at the University of Arizona. In one of the first studies on \textit{in situ} $^{14}$C in terrestrial rocks (and meteorites), whole rock samples (0.5-2 g) were mixed with iron chips (as combustion flux) and fused for up to 8 min in a flow of oxygen. The sample was then separated from water (at -78°C), the CO$_2$ pressure was measured and the gas was graphitized for AMS measurement (Jull et al., 1989). This procedure already included a pre-heating step at 500°C to remove atmospheric contaminants (Jull et al., 1989). To compensate for the low \textit{in situ} $^{14}$C concentration in terrestrial rocks, first analyses focussed on high-altitude samples that were at or close to saturation (Jull et al., 1989, 1992). The extraction procedure was subsequently refined, using a larger sample size of 10-60 g and including a more rigorous chemical pre-cleaning of the sample and a longer heating time of 1 hour at $\sim$ 1500°C (Jull et al., 1994). However, large and variable procedural blanks of about $(1.5 \pm 0.5) \times 10^6$ $^{14}$C atoms and variable $^{14}$C yields from the Mo crucible remained major problems (Jull et al., 1994).

At that time, other techniques to extract \textit{in situ} $^{14}$C from a rock or mineral were tested. Lal and Jull (1994) proposed an extraction procedure using wet sample digestion with hydrofluoric acid (HF). This method is based on the experience gained from \textit{in situ} $^{14}$C analysis in Antarctic ice samples (Lal et al., 1990) and separates $^{14}$C in the two phases $^{14}$CO and $^{14}$CO$_2$ in order to isolate the atmospheric $^{14}$C from the \textit{in situ} produced component. After the addition of CO and CO$_2$ carrier gases, the sample is dissolved inside a digestion vessel at 60-70°C for 8-10 hours after which CO$_2$ is trapped with liquid nitrogen. CO is combusted over hot CuO into CO$_2$ which is then collected separately (Lal and Jull, 1994). Reported blanks for a sample size of 15 g quartz are on the order of $\sim 1 \times 10^5$ at g$^{-1}$ for CO and $\sim 3 \times 10^5$ at g$^{-1}$ for the CO$_2$ extracts, respectively (Lal and Jull, 2001). The wet digestion method has the advantage not to be limited to small sample sizes which can be important for studying subsurface samples (Kim et al., 2007a). Nevertheless, it is a major disadvantage that the initial $^{14}$CO/$^{14}$CO$_2$ ratio in the quartz needs to be known to obtain accurate \textit{in situ} $^{14}$C concentrations and correct for environmental contamination. Although it has been observed from meteorites that \textit{in situ} $^{14}$C is primarily oxidized into $^{14}$CO while atmospheric $^{14}$C is retained as $^{14}$CO$_2$, quartz shows a comparatively large variability in the initial $^{14}$CO/$^{14}$CO$_2$ ratio (Cresswell et al., 1993, 1994; Lal and Jull, 1994). Significant uncertainties on the measurement of the $^{14}$CO/$^{14}$CO$_2$ ratio are further introduced by the partial conversion of CO into CO$_2$ during digestion limiting the applicability of the wet digestion method for terrestrial samples (Lal and Jull, 1994).

In a study on \textit{in situ} $^{14}$C in carbonates, Handwerger et al. (1999) took a similar approach using acidic sample dissolution for $^{14}$C extraction. About 10 g of sample are dissolved with $\sim$ 100 ml 100% phosphoric acid (H$_3$PO$_4$) for 1-2 hours, a CO
carrier is added and CO$_2$ is cryogenically isolated from any CO before the latter is converted into CO$_2$ using hot CuO (Handwerger et al., 1999). Contrary to silicates, \textit{in situ} $^{14}$C in carbonates essentially occurs in $^{14}$CO while the atmospheric signal is given by $^{14}$CO$_2$ and can easily be cryogenically separated (Handwerger et al., 1999).

Following the approach of stepwise sample combustion but redesigning the extraction system and modifying the analytical protocol, Lifton (1997) developed a new extraction procedure for \textit{in situ} $^{14}$C from silicate minerals. Major improvements involved: (i) a better analytical reproducibility by analysing quartz instead of whole rock samples, (ii) the reduction of extraction time and temperature by using a flux agent (LiBO$_2$) for quartz melting, (iii) the complete oxidation of all carbon species into CO avoiding the uncertainties associated with the $^{14}$CO/$^{14}$CO$_2$ ratio, (iv) a more careful gas cleaning by cryogenic sublimation and the passage through copper mesh and silver wool at 620°C, and (v) the rearrangement of the pump types and setup to prevent contamination from backstreaming oil vapours (Lifton et al., 2001). These and other modifications significantly increased the reproducibility and resulted in lower and stable blank values of $\sim 2 \times 10^5$ $^{14}$C atoms (Lifton et al., 2001). It was also proven that at temperatures $< 500^\circ$C the atmospheric $^{14}$C component can be successfully separated from the \textit{in situ} component (Lifton, 1997). In an attempt to omit the flux agent from the extraction procedure Yokoyama et al. (2004) presented an \textit{in situ} $^{14}$C extraction system that is based on the design of Lifton et al. (2001) but uses a carrier gas consisting of O$_2$-CO-CO$_2$-He. Subsequent to the 450°C pre-heating step to remove meteoric $^{14}$C, the quartz (1-6 g) is heated in a resistance furnace to temperatures of up to 1550°C. The carrier gas supports CO oxidation and eliminates contaminant nitrogen oxides. System blanks obtained from a shielded quartz sample are $\sim 2 \times 10^6$ $^{14}$C atoms (Yokoyama et al., 2004). However, ongoing work on this system has not been reported.

Based on the work of Lifton et al. (2001) a number of extraction systems were built that either copied the original design or implemented certain modifications. At the Scottish Universities Environmental Research Centre (SUERC) a system similar to the original extraction line at Arizona (Lifton, 1997) was established (Naysmith et al., 2004; Naysmith, 2007). With minor methodical modifications, a good analytical reproducibility and stable system blanks of $\sim 2 \times 10^5$ $^{14}$C atoms were obtained (Fülöp et al., 2010). At the University of Arizona, another simplified extraction system was constructed that allows reducing the time for a sample extraction from 3 to 2 days (Pigati et al., 2010a). Reported system blanks of $\sim 2 \times 10^5$ $^{14}$C atoms are in the same range as those of the original system (Lifton et al., 2001) or at SUERC (Fülöp et al., 2010). Recently, first data has been published from the Lamont-Doherty Earth Observatory where another \textit{in situ} $^{14}$C extraction system based on the
methods of Lifton et al. (2001) and Pigati et al. (2010a) is installed (Goehring et al., 2011a). Although quartz has proven to yield the most stable and reproducible analyses, the system of Pigati et al. (2010a) was also used to test in situ $^{14}$C extraction from olivines (Pigati et al., 2010b). Major problems encountered for olivines were: (i) the difficult separation from the pyroxenes (handpicking is not suitable for sample sizes of 5 g), (ii) a possible preferential selection of $^{14}$C released from the Fe-crystal lattice because of incomplete destruction of the Mg-crystal lattice during melting, and (iii) the possible chemical interaction of released $^{14}$C atoms with the crystal melt, the LiBO$_2$ flux and the Al$_2$O$_3$ sample boat (Pigati et al., 2010b). As a consequence, significant research is still needed in order to reliably measure in situ $^{14}$C in olivines (Pigati et al., 2010b).

The in situ $^{14}$C extraction system at ETH Zürich (Fig. I.2.4) is based on the general concept and follows the protocol of Lifton (1997) and Lifton et al. (2001). However, motivated by the experience with noble gas analysis at ETH, several modifications and adjustments were carried out. These will be presented and discussed in detail throughout Section II. There it will be shown that in situ $^{14}$C measurements at ETH are now performed routinely and with system blanks of about one order of magnitude lower than reported from all other labs (see above).

Figure I.2.4. The in situ $^{14}$C extraction system at ETH Zürich (in the foreground).
I.3. Organization of this dissertation

This dissertation is divided into four main parts. The first section (I) is a general introduction presenting the motivation for this work, information about the \textit{in situ} $^{14}$C isotope and the organization of this dissertation. It gives an overview of the present knowledge about \textit{in situ} $^{14}$C and summarizes the history and current state of \textit{in situ} $^{14}$C analysis.

The second section (II) represents the methodical part of this thesis and comprises two main chapters. Chapter II.1. describes the development of the \textit{in situ} $^{14}$C method at ETH provides a detailed description of the extraction system and its specific features. This chapter has been published in Quaternary Geochronology (2009). Chapter II.2. focuses on improvements and the performance of the \textit{in situ} $^{14}$C extraction system and summarizes the progress made since 2009 in view of analytical efficiency, precision and accuracy. It further presents a revised approach for \textit{in situ} $^{14}$C data reduction. This chapter is in press in Nuclear Instruments in Physics Research Section B: Beam interactions with materials and atoms, Proceedings to the AMS-12 conference.

The third (III) and fourth (IV) sections are the application part of this work and present two projects where \textit{in situ} $^{14}$C together with $^{10}$Be (and $^{26}$Al) has been used to study specific questions in geochronology and geomorphology. As a preface to the first study, chapter III.1. introduces the concept of using cosmogenic nuclides to determine surface denudation rates and discusses in detail at which conditions \textit{in situ} $^{14}$C can be applied for denudation rate studies. This is followed by chapter III.2. in which denudation processes on the Bolivian eastern Altiplano have been investigated and long-term catchment-wide denudation rates have been quantified by $^{10}$Be and $^{26}$Al. Using \textit{in situ} $^{14}$C to quantify sediment storage provided insights into the sediment routing system and the timescales of sediment transit. This chapter has been accepted for publication in Geomorphology.

Section IV deals with surface exposure dating in the Swiss Alps. This section is introduced by chapter IV.1. providing an overview of the Quaternary glacial chronology in the Alps with emphasis on the last glacial cycle. Subsequently, chapter IV.2. presents surface exposure ages from the Gotthard Pass (Central Switzerland) that give information on the deglaciation history of the high Alps. Exposure ages obtained by $^{10}$Be and \textit{in situ} $^{14}$C are compared and discussed in the context of the presently established Lateglacial chronology. This chapter has been submitted for publication in Quaternary Geochronology, Special Volume: Quaternary Landforms.
Conclusions are shortly summarized in Section V together with an outlook on future work that could and will be done to improve \textit{in situ} $^{14}$C analysis and fully exploit its potential for Earth surface sciences.
II. Methods - Analysing *in situ* cosmogenic $^{14}$C

II.1. The current performance of the *in situ* $^{14}$C extraction line at ETH

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ABSTRACT

We present the new $^{14}$C extraction line at ETH Zürich. This system is designed to extract *in situ* produced cosmogenic $^{14}$C from terrestrial quartz samples, and to obtain pure CO$_2$ gas for analysis with a gas ion source Accelerator Mass Spectrometry (AMS) system. Samples are degassed at 1550 to 1600°C without the use of a fluxing agent. Gas purification is achieved by a series of cryogenic traps and passage through hot Ag and Cu wool/mesh. Graphitization and, thus, sample dilution is not required. Tests to determine the CO$_2$ recovery after gas extraction and cleaning yielded consistently good recovery rates of >99.8% ($n=7$). The $^{14}$C blank contribution from the all-metal tubing system is negligible. Our preliminary procedural blank estimate – deriving mostly from the hot extraction furnace - is $<5 \times 10^5$ $^{14}$C atoms. Extraction tests on two quartz samples by stepped-heating show a quantitative separation of atmospheric $^{14}$C at $\leq 500^\circ$C from the *in situ* component above $1200^\circ$C. Based on these data, we estimate to achieve a complete $^{14}$C extraction from a quartz sample.

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II.1.1. Introduction

For more than two decades, terrestrially (in situ) produced cosmogenic nuclides, particularly the radionuclides $^{10}\text{Be}$, $^{26}\text{Al}$, $^{36}\text{Cl}$ and the stable noble gases $^3\text{He}$ and $^{21}\text{Ne}$, have been widely used in Quaternary geology and quantitative geomorphology (Lal, 1991, Gosse & Phillips, 2001, Cockburn & Summerfield, 2004). In situ $^{14}\text{C}$ has been added to this list only relatively recently. This is because of the difficulties in quantitatively extracting the minute amounts of $^{14}\text{C}$ produced in terrestrial surface rocks and separating them effectively from atmospherically produced $^{14}\text{C}$ (Lal & Jull, 1994; Lifton et al., 2001; Pigati et al., 2005). $^{14}\text{C}$ has a considerably shorter half-life ($t_{1/2}=5730$ yrs) than all the other cosmogenic nuclides used so far. Compared to these longer-lived and stable nuclides, it is therefore much more sensitive to recent and more rapid changes in climate and tectonics and their impact on landscape formation. This sensitivity also makes in situ $^{14}\text{C}$ a suitable monitor for production rate systematics during the past few tens of thousands of years (Lifton et al., 2005; 2008). In combination with nuclides with longer half-life, in situ $^{14}\text{C}$ is particularly useful for studying both exposure and erosion histories, as well as for analyzing complex histories (e.g. burial histories). In situ $^{14}\text{C}$ is produced by secondary neutrons (83%) and muons (17%) derived from interactions of high energy cosmic ray protons with atoms in the atmosphere (Masarik & Reedy, 1995; Heisinger et al., 2002). The main target element is oxygen, with minor contributions from Mg, Al, Si, and Fe (Jull et al., 1998). Pure quartz is the ideal sample material due to its simple chemistry and wide distribution; olivine and feldspar are other possible target minerals. Carbonates have been analyzed by Handwerger et al. (1999).

The only routinely operating $^{14}\text{C}$ extraction systems using sample fusion have been constructed at the University of Arizona (Lifton et al., 2001; Pigati, 2004). Their technique is based on the observation that in situ produced $^{14}\text{C}$ is released at a considerably higher temperature than contaminating $^{14}\text{C}$ derived from the atmosphere. All evolved carbon is collected as CO$_2$ (Lifton et al., 2001). Another extraction procedure uses wet, in vacuo sample digestion with HF (Lal & Jull, 1994; Kim et al., 2007) extracting in situ $^{14}\text{C}$ in the two chemical forms $^{14}\text{CO}$ and $^{14}\text{CO}_2$. The total net $^{14}\text{C}$ concentration is calculated from the concentrations in the CO phase. It therefore strongly relies on an estimate of the $^{14}\text{CO}^{14}\text{CO}_2$ ratio in the sample (Lal & Jull, 1994). Few other attempts to extract and measure in situ $^{14}\text{C}$ in quartz samples have been reported (e.g. Naysmith et al., 2004; Yokoyama et al., 2004).

We have followed Lifton and Pigati’s basic design in constructing an in situ $^{14}\text{C}$ extraction and purification system at the Department of Earth Sciences at ETH Zurich. A major difference between our line and those at U. Arizona is that we chose
to use a stainless steel-tubing construction rather than glass tubing. Also, we measure the $^{14}\text{C}/^{12}\text{C}$ ratio directly in gaseous CO$_2$ with the gas ion source of the MICADAS 200kV AMS system at ETH/PSI (Ruff et al., 2007; Synal et al., 2007), rather than in graphite. Here, we present the setup and current performance of this system. We also report our first yield and blank measurements as well as two series of stepped heating experiments on quartz. These initial data were collected under a variety of different time and temperature conditions, which were then used to define a final procedure for $^{14}\text{C}$ extraction.

II.1.2. Methods

II.1.2.1. The ETH $^{14}\text{C}$ extraction system

With some modifications we have adopted the single-pass design of Pigati (2004). We constructed an all-metal line (apart from two hot quartz-tube furnaces) using off-the-shelf components from Swagelok® with copper seals. Quartz samples are degassed in an electron bombardment furnace at 1550/1600ºC, and the extraction part of the system is directly connected to the gas purification devices. With our final sample being measured as CO$_2$ gas, we avoid a sample dilution with $^{14}\text{C}$-free CO$_2$ necessary for graphitization (e.g. Lifton et al., 2001).

The electron bombardment furnace is able to maintain the temperature required to achieve complete $^{14}\text{C}$ extraction without requiring a fluxing agent. (Fig. II.1.1). Electrons emitted from eight hot W filaments heat a Ta tube which encompasses a sapphire tube hosting the samples. The furnace consists of two vacuum systems separating the inside of the sapphire tube, and thus the sample, from the outside part, hosting the filaments. Temperatures are automatically raised in steps of 10ºC/min up to a final extraction temperature of ~1550ºC (for details see caption of Fig. II.1.1).

Samples are heated in an ultra-high-purity (UHP) O$_2$ atmosphere (99.9996%), at about 5 kPa, adjusted by a needle valve and monitored with a Baratron pressure transducer (MKS® 870B) positioned after the extraction furnace (Fig. II.1.2). For the stepped heating experiments described below a constant O$_2$ flow of $\sim 0.5-1 \times 10^{-6}$ mol/s at 5 kPa rather than a static O$_2$ atmosphere was chosen. Up to 5 g of quartz are placed into the platinum crucible which is hanging inside the sapphire tube on a 350 mm long Al$_2$O$_3$ rod. The Pt crucible withstands temperatures up to about 1750ºC which is well above the melting point of pure quartz of 1650ºC. However, melting of quartz is not required in our method as complete CO$_2$ degassing from quartz is achieved at $\leq 1550$ºC (Lifton et al., 2001; Yokohama et al., 2004). Care is required, however, since the nominal temperature set for the furnace is considerably higher than the actual sample temperature within the quartz-filled Pt crucible (up to 100ºC.
difference as monitored with a pyrometer). Also, in an empty crucible, a temperature gradient of ~ 100°C between walls and bottom is observed.

After sample degassing, any remaining sample material is mechanically removed from the Pt-crucible, which is then etched in a concentrated HF-bath at 80°C for several hours and rinsed thoroughly with Milli-Q® water, allowing re-use of the Pt-crucible after preheating under vacuum at 1600°C for several hours.

To ensure the conversion of all released carbon species into CO₂, the gases from the extraction unit pass through a U-shaped quartz tube filled with quartz beads (2 mm in diameter), held at 1100°C by a Carbolite® furnace. All evolved condensable gases including CO₂ are then trapped in a stainless steel helix trap cooled with liquid nitrogen (LN). Oxygen and other gases which are not condensed at LN temperature are continuously pumped off downstream from the helix. After extraction, LN is removed from the helix to release the CO₂ and other condensable gases. In order to separate CO₂ from the other gases, we followed Lifton et al. (2001) by using a combination of variable temperature traps (VTTs) at -78°C, -130°C and -
145°C (details in Section II.1.2.2.) and an Ag-wool and Cu-mesh mixture in a quartz tube held at 610°C by a second Carbolite® furnace. The VTTs consist of an outer aluminum cylinder tube with a heatable inner aluminum cylinder isolated with aluminum foil (-78°C) or metal-wool (-130°C and -145°C). VTT1 (-78°C) is filled with ethanol (95%) while the two others are filled with 2-Methylpentane. All VTTs are cooled on the exterior by LN while the temperature in the inner cylinder is regulated with a heater and feedback from a Pt 100 sensor to within ± 1°C. During gas purification the pressure in this part of the system can be monitored with two Pirani gauges. The final yield of the clean CO₂ gas is measured with a capacitance manometer (MKS Baratron® 622A) in the known volume between cooling finger 4 and the Pyrex® breakseal tube (see Fig. II.1.2). The gas is taken off the line in the breakseal tube which is attached via a fitting sealed with Viton O-rings. Before receiving a sample, each breakseal is evacuated and thoroughly heated with a glassblower’s torch until the pressure reaches background values (< 5 × 10⁻⁷ Pa). The CO₂-filled tube is sealed with the torch and taken to the AMS facility. For yield tests and some blank experiments a reservoir of ‘dead’ CO₂ is connected to the known volume area.

II.1.2.2. Sample treatment

Quartz samples are prepared by thorough chemical purification following Kohl and Nishiizumi (1992) and Ivy-Ochs (1996). Immediately before being loaded into the extraction furnace, samples are sonicated in 1:1 HNO₃/Milli-Q® water for 30 min, soaked in this acid solution for another 30 min, rinsed several times with Milli-Q® water and dried under an infrared lamp in a laminar flow hood for 1-2 hours. The sample is then weighed, placed into the Pt crucible in the extraction unit and heated under vacuum for one hour at ~160°C to remove sorbed water contamination. Subsequently the sample is heated at 500°C under an UHP-O₂ flow (at 5 kPa) for at least 2 hours to release atmospheric ¹⁴C contaminants (Lifton et al., 2001), which are pumped off continuously. Next, samples are heated in UHP-O₂ for several hours at 1550-1600°C, in order to release the in situ ¹⁴C component. Throughout the entire heating time condensable gases including CO₂ are trapped on the LN-cooled helix, while O₂ is constantly pumped off through valve D adjacent to the helix (between cooling finger 1 and 2 on Fig. II.1.2). The trapped gases are released from the helix and expanded to the cleaning unit, passing first VTT1 held at -78°C to remove water. The remaining unfrozen gases are transferred to finger 2, which is first immersed in LN. At a pressure of 0.05 Pa LN is replaced by VTT2 (-130°C). At this temperature, CO₂ sublimes again while SO₂ and any remaining water vapor stay trapped in VTT2. In a next step, CO₂ and other gases released from finger 2 are frozen onto cooling finger 3, which is likewise immersed first in LN, followed by an exchange of the LN with VTT3 (-145°C). Evolved CO₂ then passes
through the hot Ag-Cu wool/mesh to remove SO\textsubscript{x}, NO\textsubscript{x} and halide species before being frozen into finger 4. At finger 4, CO\textsubscript{2} sublimation is repeated (at -130°C), followed by freezing the clean CO\textsubscript{2} to the adjacent small finger in the known volume for pressure measurement. After the yield measurement, CO\textsubscript{2} is cryogenically transferred to the breakseal tube and taken off the line for AMS analysis.

**II.1.2.3. AMS measurement**

The CO\textsubscript{2} samples are measured with the gas ion source at the miniaturized MICADAS 200 kV AMS system at ETH/PSI (Synal et al., 2007). The breakseal tube is inserted into an ampoule cracker and sample CO\textsubscript{2} is released into the evacuated cracker system. The CO\textsubscript{2} is flushed with He carrier gas into a syringe until
a CO₂/He mixing ratio of 1:25 is reached. The gas is then pressed through a gas capillary into the ion source at a constant rate to allow stable measurement conditions (Ruff et al., 2007). This system circumvents the usual graphitization and allows the measurement of 1-50 µg carbon. A small sample size not only simplifies sample preparation and reduces degassing time. Most importantly, dilution with ‘dead’ CO₂ becomes unnecessary, thus minimizing the potential for further contamination. At least 200-500 µg C are typically needed for the production of graphite targets. As an example, for our test quartz sample only on the order of 50 µg of extracted CO₂ are expected from 5 g quartz. 50 µg carbon as CO₂ is more than is required for analysis in the gas ion source of MICADAS, allowing sample splitting and replicate measurements. Adding 150-450 µg of ‘dead’ CO₂ would increase our total procedural blank by 1.5-4.4 × 10⁵ atoms of ¹⁴C, as the CO₂ we use contains ~ 980 ¹⁴C at µg⁻¹ CO₂ (n=4, Table II.1.2). Graphitization would thus roughly double our blank level (see Section 4.1.).

II.1.2.4. Sample material

Test sample material for the stepped heating experiments is from a quartz vein (G111) from the Grimsel Pass, Switzerland. The sample was taken as part of a deglaciation study of the Grimsel Pass region, central Swiss Alps, and used for surface exposure dating with in situ cosmogenic ¹⁰Be and ²⁶Al (Ivy-Ochs, 1996; Kelly et al., 2006). The sample was collected at 46.57°N, 8.35°E at an altitude of 2400 m a.s.l. We have used the Excel spreadsheet provided by Lifton et al. (2005) for recalculating the ¹⁰Be age of G111 and make an assumption on the expected ¹⁴C concentration. A SLHL production rate of 5.1 ± 0.3 ¹⁰Be at g⁻¹ (Stone 2000) was adopted to calculate a ¹⁰Be age of 10700 ± 900 ys, not corrected for shielding or snow cover. Based on this age and a SLHL production rate of 15.2 ± 0.3 ¹⁴C at g⁻¹ (Dugan et al., 2008), the expected concentration of ¹⁴C is (5.11 ± 0.03) × 10⁵ ¹⁴C at g⁻¹.

II.1.2.5. Calculations

Eq. (1) gives the number of ¹⁴C atoms (N₁⁴) for a given experimental step (cf. Lifton, 1997):

\[ N_{14} = \frac{(¹⁴C/¹²C) \cdot N_A \cdot V_S}{V_A} - B \]  \hspace{1cm} (1)

where ¹⁴C/¹²C is the measured isotopic ratio corrected to an internal standard. Nₐ is Avogadro’s number, V_S is the volume of CO₂ collected in cc STP, V_A is the volume
of 1 mole CO₂ in cc STP and B is the number of ^14^C atoms of the associated blank. The corresponding uncertainty in the number of ^14^C atoms is given by:

$$\Delta N_{14} = \sqrt{\left(\frac{^{14}C/^{12}C \cdot N_A \cdot \Delta V_S}{V_A}\right)^2 + \left(\frac{\Delta(^{14}C/^{12}C) \cdot N_A \cdot V_S}{V_A}\right)^2 + \Delta B^2}$$

(2)

with $\Delta(^{14}C/^{12}C)$ given solely by counting statistics and $\Delta V_S = 0.0001$ given by the uncertainty of the capacitance manometer.

II.1.3. Results

II.1.3.1. Sample recovery

A number of yield tests were carried out to check the system performance and to ensure the complete recovery of CO₂. The data from twelve recovery tests using between about 3 and 290 μg of ‘dead’ CO₂ gas are shown in Table II.1.1. Five of these were designed to test the gas cleaning system. Thus, a known amount of CO₂ was cryogenically transferred to the LN-helix trap and subjected to the system gas cleaning procedure before it was measured again with the capacitance manometer (Fig. II.1.2). A blank contribution of about 0.07 μg CO₂ for this part of the ^14^C line has been determined and repeatedly confirmed during many months of testing. This blank was subtracted to calculate the quoted recovery rate. The mean recovery rate is 99.2% (n=5), with three experiments yielding 99.8% each. The two lowest values were observed in the tests using the lowest gas amounts. However, even in these experiments the recovery exceeded 97%.

For seven yield tests CO₂ gas was frozen into a removable ‘yield’ finger (Fig. II.1.2) which was manually transferred to the front end of the extraction line, upstream of the sample furnace. There it was released under an atmosphere of ~ 5 kPa UHP O₂ followed by the usual sample extraction and cleaning procedure (apart from not heating the extraction furnace). Calculations included a blank subtraction of 0.2 μg CO₂. This value has been determined in a number of blank tests following identical procedures as described here for the yield measurements. Six of these yield tests gave recovery rates between 99.8 – 100.1%. The only outlier of 102.4% was again observed in the experiment with the lowest gas amount, where the blank required a ~6% correction. Notably, however, three tests with equally low CO₂ gas showed recovery rates of exactly 100%.
Table II.1.1. Recovery tests with test CO$_2$ gas.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CO$_2$ mass (µg)$^a$</th>
<th>CO$<em>2$ yield$</em>{corr}$ (µg)$^a$</th>
<th>recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>310507$^b$</td>
<td>145.6</td>
<td>145.3$^c$</td>
<td>99.8</td>
</tr>
<tr>
<td>010607-1$^b$</td>
<td>155.9</td>
<td>155.6$^c$</td>
<td>99.8</td>
</tr>
<tr>
<td>010607-2$^b$</td>
<td>152.7</td>
<td>152.3$^c$</td>
<td>99.8</td>
</tr>
<tr>
<td>170707-1$^b$</td>
<td>6.9</td>
<td>6.8$^c$</td>
<td>98.9</td>
</tr>
<tr>
<td>310108$^b$</td>
<td>6.0</td>
<td>5.9$^c$</td>
<td>97.5</td>
</tr>
<tr>
<td>120607</td>
<td>220.4</td>
<td>220.0$^d$</td>
<td>99.8</td>
</tr>
<tr>
<td>130607</td>
<td>178.1</td>
<td>178.0$^d$</td>
<td>100.0</td>
</tr>
<tr>
<td>140607</td>
<td>289.1</td>
<td>289.3$^d$</td>
<td>100.1</td>
</tr>
<tr>
<td>170707-2</td>
<td>6.3</td>
<td>6.3$^d$</td>
<td>100.0</td>
</tr>
<tr>
<td>180707</td>
<td>6.4</td>
<td>6.4$^d$</td>
<td>100.0</td>
</tr>
<tr>
<td>180308</td>
<td>3.0</td>
<td>3.1$^d$</td>
<td>102.4</td>
</tr>
<tr>
<td>160908</td>
<td>3.5</td>
<td>3.5$^d$</td>
<td>100.0</td>
</tr>
</tbody>
</table>

$^a$ Uncertainty deriving from the CO$_2$ pressure reading is 0.25% for values > 29.7 µg and 0.07 µg for values < 29.7 µg.

$^b$ Recovery test starting at LN helix.

$^c$ 0.07 µg were subtracted as blank contribution.

$^d$ 0.2 µg were subtracted as blank contribution.

II.1.3.2. Blank results

Blank tests have been performed with varying temperatures in the extraction furnace and variable times of maximum heating temperature. Results are given in Table II.1.2 and Figure II.1.3. The Pt-crucible was included in five tests (see Table caption II.1.2). For samples 170707-4 and 180308 a known amount of ‘dead’ CO$_2$ gas was introduced into the line, mixed with UHP O$_2$ and processed through the entire extraction and clean-up procedure. All other blank tests were initially run without addition of CO$_2$. However, tests 250707-1, 190308 and 270707-1 eventually had to be diluted for AMS analysis, since they yielded ≤ 0.3 µg of blank CO$_2$.

First runs were done with the extraction furnace kept at room temperature to determine blank levels delivered by our all-metal line. All four measurements gave very low $^{14}$C amounts with at most $(5.31 \pm 2.19) \times 10^3$ $^{14}$C atoms (corrected for the blank associated with CO$_2$ dilution). This highest $^{14}$C concentration (sample 180308) was measured after allowing the blank gas to accumulate in the furnace for 1 hour. However, analysis 190308, performed under identical conditions, gives a considerably lower $^{14}$C blank, indicating that variable times in the ‘cold’ blank experiments are not critical. Note that for two samples (170707-4, 250707-1) dilution correction leads to negative results, corresponding with the observation that
the uncorrected blank data of all experiments at room temperature either overlap or fall below the $^{14}$C amount expected from the added ‘dead’ CO$_2$. A substantial $^{14}$C blank contribution from the all-metal extraction system can thus reliably be excluded.

Hot blank tests were carried out at extraction furnace temperatures of 500°C, 1350°C, 1400°C and 1550°C with the samples remaining at the respective maximum temperature for 10 minutes, 1 hour or 2 hours (Tab. II.1.2). Additional blanks at higher temperatures were prevented by technical difficulties. Contrary to the cold blanks, the blank values at 500°C increase considerably with heating time. Step 270707-1 (10 min at 500°C) gives a $^{14}$C blank of only $(2.47 \pm 2.10) \times 10^3$ $^{14}$C atoms, about four times less than step 170308-1 with 1 hour at 500°C. As expected, blanks also increase strongly with temperature. Three independent blank determinations at 1350°C (10 min) following identical heating procedures give equal results within error and released almost 25 times more $^{14}$C than the 10 minutes/500°C step. The additional 1-hr experiment at 1400°C released somewhat more $^{14}$C than each of the 1350°C steps, though this may also be explained by the longer heating time at 1400°C and/or the placement of the Pt-crucible in the furnace.

All the blank experiments described above were run in a static mode keeping the evolved gases and UHP O$_2$ in the extraction furnace for the time quoted, before pumping off the oxygen and freezing the CO$_2$ to the helix trap. However, in the course of the system tests we switched to the flow-through mode described above for sample treatment (Section II.1.2.2). With this changed procedure, three additional blank tests have been performed. The first two blanks (090708 and 100708) were run without the Pt-crucible for 2 hours at 1400°C and 1550°C and yielded $(3.37 \pm 0.94) \times 10^4$ $^{14}$C atoms and $(8.60 \pm 1.83) \times 10^4$ $^{14}$C atoms, respectively. Note that immediately before blank run 090708 the extraction furnace had been vented and then pumped and heated at 400°C for one night. The third blank experiment was performed with the Pt-crucible at 1400°C (2 hrs) and yielded $(1.86 \pm 0.92) \times 10^5$ $^{14}$C atoms. However, before running this blank test the Pt-crucible had been used for heating quartz and subsequently was cleaned as explained above (Section II.1.2.1) but without preheating at high temperatures. This fact accounts for the high $^{14}$C concentration and demonstrates that thorough preheating of the Pt-crucible is necessary prior to its reutilization.
Table II.1.2. Summary of CO$_2$ gas measurements and blank data. The Pt-crucible was included in tests 180308, 190308, 170308-1, 130308-2 and 190908. All blanks except no. 090708, 100708 and 190908 were run in a stationary mode, keeping O$_2$ and the blank gas in the extraction furnace for the time stated in the table. For blank runs 090708, 100708 and 190908 a continuous O$_2$ flow and CO$_2$ trapping as described in the section on sample treatment was applied. Note that after correcting results of diluted samples for the $^{14}$C addition associated with the dilution CO$_2$ gas, two samples obtain negative $^{14}$C values.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CO$_2$ mass ($\mu$g)$^a$</th>
<th>$^{14}$C/$^{12}$C ratio ($10^{-18}$)</th>
<th>$N_{14}$ total ($10^4$ atoms)</th>
<th>$N_{14}$ (at $\mu$g$^{-1}$ CO$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>'Dead' CO$_2$ gas</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>130707-3</td>
<td>20.2</td>
<td>1.62 ± 0.19</td>
<td>1.76 ± 0.20</td>
<td>879.26 ± 101.97</td>
</tr>
<tr>
<td>160707-3</td>
<td>6.6</td>
<td>1.46 ± 0.31</td>
<td>0.52 ± 0.11</td>
<td>790.06 ± 165.76</td>
</tr>
<tr>
<td>170707-1</td>
<td>9.5</td>
<td>2.08 ± 0.35</td>
<td>1.07 ± 0.18</td>
<td>1127.75 ± 191.23</td>
</tr>
<tr>
<td>170707-2</td>
<td>6.7</td>
<td>1.61 ± 0.36</td>
<td>0.58 ± 0.13</td>
<td>872.89 ± 197.62</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td></td>
<td></td>
<td></td>
<td>872.89 ± 72.97 $^b$</td>
</tr>
<tr>
<td><strong>Blanks</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>Temperature/duration$^e$</strong></td>
</tr>
<tr>
<td>170707-4$^c$</td>
<td>6.5 (6.3)</td>
<td>1.50 ± 0.59</td>
<td>-0.02 ± 0.21$^d$</td>
<td>RT/10 min</td>
</tr>
<tr>
<td>250707-1$^c$</td>
<td>6.4 (6.2)</td>
<td>1.00 ± 0.54</td>
<td>-0.20 ± 0.19$^d$</td>
<td>RT/10 min</td>
</tr>
<tr>
<td>180308$^c$</td>
<td>3.3 (3.0)</td>
<td>4.70 ± 1.30</td>
<td>0.53 ± 0.22$^d$</td>
<td>RT/1 h</td>
</tr>
<tr>
<td>190308$^c$</td>
<td>4.7 (4.4)</td>
<td>2.11 ± 0.75</td>
<td>0.11 ± 0.18$^d$</td>
<td>RT/1 h</td>
</tr>
<tr>
<td>270707-1$^c$</td>
<td>5.5 (5.3)</td>
<td>2.39 ± 0.71</td>
<td>0.25 ± 0.21$^d$</td>
<td>500$^\circ$C/10 min</td>
</tr>
<tr>
<td>170308-1</td>
<td>1.9</td>
<td>29.00 ± 4.91</td>
<td>2.82 ± 0.48</td>
<td>500$^\circ$C/1 h</td>
</tr>
<tr>
<td>260707-1</td>
<td>7.0</td>
<td>45.97 ± 2.20</td>
<td>17.55 ± 0.85</td>
<td>1350$^\circ$C/10 min</td>
</tr>
<tr>
<td>260707-2</td>
<td>5.6</td>
<td>57.86 ± 2.48</td>
<td>17.68 ± 0.77</td>
<td>1350$^\circ$C/10 min</td>
</tr>
<tr>
<td>270707-2</td>
<td>5.4</td>
<td>57.85 ± 3.07</td>
<td>16.97 ± 0.91</td>
<td>1350$^\circ$C/10 min</td>
</tr>
<tr>
<td>130308-2</td>
<td>6.5</td>
<td>87.49 ± 2.57</td>
<td>28.51 ± 0.87</td>
<td>1400$^\circ$C/1 h</td>
</tr>
<tr>
<td>090708</td>
<td>1.6</td>
<td>42.81 ± 11.87</td>
<td>3.37 ± 0.94</td>
<td>1400$^\circ$C/2 h</td>
</tr>
<tr>
<td>100708</td>
<td>2.2</td>
<td>79.16 ± 12.52</td>
<td>8.60 ± 1.38</td>
<td>1550$^\circ$C/2 h</td>
</tr>
<tr>
<td>190908</td>
<td>5.4</td>
<td>67.97 ± 3.30</td>
<td>18.58 ± 0.92</td>
<td>1400$^\circ$C/2 h</td>
</tr>
</tbody>
</table>

All errors are 1σ.

$^a$ Numbers in brackets give amount of CO$_2$ gas added. Uncertainty deriving from the CO$_2$ pressure reading is 0.07 $\mu$g.

$^b$ Standard error of the mean

$^c$ Samples diluted for AMS analysis

$^d$ Results corrected for CO$_2$ dilution using the mean $^{14}$C concentration of the dilution CO$_2$ gas as quoted above in this table.

$^e$ RT = room temperature; duration gives time of the extraction furnace at maximum temperature.
Further blank tests at >1500°C are in progress. Nevertheless the data presented here already document the good performance of the extraction system. The three last blank analyses (Tab. II.1.2) demonstrate that an overall reduction in blank contamination could already be achieved due to repeated heating of the extraction furnace and possibly also the exchange of the sapphire tube with a more robust one.

II.1.3.3. Stepped heating experiments

With a series of stepped heating experiments Lifton (1997) demonstrated that a two-step heating of quartz is an effective means of separating atmospherically produced $^{14}$C from the in situ component. Contaminant $^{14}$C is released from quartz at $\leq$500°C while in situ $^{14}$C starts diffusing only at higher temperatures ($\geq$1200°C). In order to verify the suitability of this procedure for our extraction line and also to check the recovery of in situ $^{14}$C from quartz in our system, we performed two stepped heating experiments on our internal standard sample G111. Results are presented in Table II.1.3. Values are not blank corrected. However, to evaluate the

Figure II.1.3. Carbon yield and corresponding number of $^{14}$C atoms measured in all line blanks and in the ‘dead’ CO$_2$ gas inserted for yield tests and to dilute some samples for AMS analyses. Values and uncertainties are given in Table II.1.2. Error bars for the carbon amounts are smaller than symbol size. RT = room temperature

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total amount of in situ $^{14}$C extracted in experiment 2, an estimated blank contribution for each temperature step is also given (details given below).

For the duration of each experiment the sample remained in the Pt-crucible. Each temperature step was completed in one day with the same sample always being heated from room temperature to the desired temperature and subsequently cooled down to room temperature again. CO$_2$ was collected during the entire heating and cooling cycle. Table II.1.3 gives the times during which the quartz remained at maximum temperature for each step. Unfortunately, experiment 1 could not be run to completion because the sapphire tube broke while we attempted to heat above 1400°C. Figure II.1.4 shows the amounts of CO$_2$ recovered at each heating step as well as the corresponding concentrations of $^{14}$C as measured by AMS (Tab. II.1.3).

Table II.1.3. Results of stepped heating experiments. Note that the $^{14}$C/$^{12}$C ratio is $10^{-12}$ atoms compared to $10^{-14}$ atoms in Table II.1.2. The 1200°C and 1500°C step of experiment 2 could not be measured by AMS. Therefore, numbers in brackets give estimates calculated on the basis of a power law correlation between the carbon yield and the amount of $^{14}$C of the other samples of experiment 2. Explanations on the blank estimate are given in Section II.1.3.3.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>CO$_2$ mass ($\mu$g)$^a$</th>
<th>$^{14}$C/$^{12}$C ratio ($10^{-12}$)</th>
<th>N$_{^{14}}$total ($10^5$ atoms)</th>
<th>Temperature/duration$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment 1 (5.02 g quartz)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>270308</td>
<td>13.1</td>
<td>$1.12 \pm 0.02$</td>
<td>$7.89 \pm 0.14$</td>
<td>400°C/1 h</td>
</tr>
<tr>
<td>280308</td>
<td>2.2</td>
<td>$1.21 \pm 0.08$</td>
<td>$1.46 \pm 0.10$</td>
<td>500°C/1 h</td>
</tr>
<tr>
<td>310308</td>
<td>2.9</td>
<td>$0.64 \pm 0.04$</td>
<td>$1.00 \pm 0.06$</td>
<td>700°C/1 h</td>
</tr>
<tr>
<td>010408</td>
<td>2.3</td>
<td>$0.62 \pm 0.04$</td>
<td>$0.77 \pm 0.06$</td>
<td>900°C/1 h</td>
</tr>
<tr>
<td>020408</td>
<td>2.6</td>
<td>$1.24 \pm 0.05$</td>
<td>$1.74 \pm 0.08$</td>
<td>1200°C/1 h</td>
</tr>
<tr>
<td>030408</td>
<td>1.4</td>
<td>$2.28 \pm 0.12$</td>
<td>$1.74 \pm 0.11$</td>
<td>1400°C/1 h</td>
</tr>
<tr>
<td><strong>Experiment 2 (4.94 g quartz)</strong></td>
<td></td>
<td></td>
<td></td>
<td><strong>Blank estimate [10$^5$ atoms]</strong></td>
</tr>
<tr>
<td>030608</td>
<td>17.5</td>
<td>$1.06 \pm 0.02$</td>
<td>$10.07 \pm 0.17$</td>
<td>0.56</td>
</tr>
<tr>
<td>040608</td>
<td>4.8</td>
<td>$0.91 \pm 0.03$</td>
<td>$2.37 \pm 0.09$</td>
<td>1.05</td>
</tr>
<tr>
<td>050608</td>
<td>6.3</td>
<td>(1.39)</td>
<td>(4.75)</td>
<td>1.70</td>
</tr>
<tr>
<td>060608</td>
<td>7.9</td>
<td>$1.59 \pm 0.04$</td>
<td>$6.79 \pm 0.16$</td>
<td>1.85</td>
</tr>
<tr>
<td>100608</td>
<td>9.9</td>
<td>(1.78)</td>
<td>(9.53)</td>
<td>2.75</td>
</tr>
<tr>
<td>120608</td>
<td>6.7</td>
<td>$3.68 \pm 0.06$</td>
<td>$13.31 \pm 0.25$</td>
<td>2.98</td>
</tr>
<tr>
<td>170608</td>
<td>7.6</td>
<td>$1.54 \pm 0.03$</td>
<td>$6.30 \pm 0.15$</td>
<td>4.47</td>
</tr>
<tr>
<td>180608</td>
<td>3.3</td>
<td>$1.98 \pm 0.07$</td>
<td>$3.50 \pm 0.13$</td>
<td>3.56</td>
</tr>
</tbody>
</table>

All errors are 1σ.

$^a$ Uncertainty deriving from the CO$_2$ pressure reading is 0.07 µg.

$^b$ Duration gives the time of the extraction furnace at maximum temperature.
The 1200°C and 1500°C steps of experiment 2 could not be measured because of a leak in the breakseal tubes. The corresponding $^{14}$C amounts shown in Figure II.1.4 are therefore rough estimates calculated on the basis of a power law correlation between the carbon yield and the amount of $^{14}$C of the other samples of experiment 2. Including these estimates, calculations give a total recovery of $4.7 \times 10^6$ $^{14}$C atoms during the entire experiment (excluding the 500°C step).

Both experiments released substantial amounts of $^{14}$C at $\leq 500$°C, followed by a rapid drop to much lower levels in the intermediate temperature range. The second experiment again released a significant contribution of $^{14}$C at $> 900$°C whereas only a slight increase in $^{14}$C at this temperature is observed in experiment 1. This bimodal release pattern is basically very similar to that observed by Lifton (1997) and suggests a good separation of atmospheric and in situ produced $^{14}$C, respectively. The relatively small CO$_2$ amounts released in the high temperature steps of experiment 1 indicate that one hour of sample heating is not enough to completely liberate carbon from the quartz lattice. In contrast, the large amounts of $^{14}$C between...
1400°C and 1550°C in experiment 2 followed by a drop in the second 1550°C and the subsequent 1600°C step strongly suggest a nearly quantitative release of carbon after two hours at 1500-1550°C.

To determine the $^{14}$C extraction efficiency in experiment 2 we estimated a procedural blank contribution for each temperature step (Tab. II.1.3). Estimates are based on blank analyses 170308-1 (1 hr at 500°C) and 190908 (2 hrs at 1400°C), which correspond most closely to the procedures used for the stepped heating experiment, and on the $^{14}$C yield from the final 1600°C step of the quartz extraction experiment (sample 180608), which was taken as a maximum blank at that temperature. Values for blank 170308-1 were doubled for the estimate of the 2-hour blank at 500°C. Two linear functions connecting these three values were then used to interpolate the remaining unknown blank data.

II.1.4. Discussion

II.4.1. Line performance

First tests of the ETH in situ $^{14}$C extraction line reveal a good performance of our all-metal system. Recovery rates of CO$_2$ gas added to the system are excellent and cold blanks from the system are low. The sample extraction furnace is the main source of blank $^{14}$C, with amounts continuously increasing with temperature and heating time. We take blank sample 190908 (2 hours at 1400°C) as a good approximation to our final procedural blank. Except for temperature (and maybe also time), this blank experiment follows exactly the procedure for sample extraction. However, it includes a Pt-crucible that has not yet been degassed at high temperatures and is therefore regarded as an upper blank limit for this temperature.

Blank samples 090708 and 100708, both run under identical experimental conditions, show a ~ 2.5 fold blank increase from 1400°C to 1550°C. Applying this observation to the 1400°C blank of (1.86 ± 0.92) × 10$^5$ $^{14}$C atoms (sample 190908), the maximum final procedural blank should not exceed 5 × 10$^5$ $^{14}$C atoms.

Nevertheless, we are confident that a thorough preheating of the Pt-crucible is an effective means to further reduce the contamination significantly. For comparison, Lifton et al. (2001) report an extraction blank of (2.27 ± 0.12) × 10$^5$ $^{14}$C atoms using the LiBO$_2$ flux and (6.64 ± 0.37) × 10$^5$ to (1.10 ± 0.05) × 10$^6$ $^{14}$C atoms for the flux-free method. Yokohama et al. (2004) report a higher procedural blank of (2.3 ± 0.2) × 10$^6$ $^{14}$C atoms.

The low $^{14}$C concentration of blank 090708 indicates that short atmospheric venting of the furnace during sample exchange does not considerably increase the blank level. With regard to sample reproducibility blank experiments are also encouraging as three blank runs at 1350°C using the same heating protocol yielded identical results within error (Table II.1.2).
II.1.4.2. Sample extraction

Stepped heating experiment 2 shows that the current performance of the extraction line and the adopted analytical protocol are adequate to quantitatively extract \textit{in situ} produced $^{14}\text{C}$ from a quartz sample. Furthermore, both experiments demonstrate that effective outgassing of quartz not only depends on the temperature but also significantly on the duration of heating. However, several uncertainties still exist. Although the available data indicate an effective release of carbon, gaps in the blank data at certain temperatures make it difficult to calculate an absolute $^{14}\text{C}$ yield for the 2\textsuperscript{nd} stepped heating test. Nevertheless, with estimations on the $^{14}\text{C}$ yield at 1200°C and 1500°C and after subtraction of extraction blanks for each step, a total recovery of $2.7 \times 10^6$ $^{14}\text{C}$ atoms or $5.5 \times 10^5$ $^{14}\text{C}$ at g\textsuperscript{-1}, respectively, can be calculated. Compared with the expected amount of $5.11 \times 10^5$ $^{14}\text{C}$ at g\textsuperscript{-1} (cf. Section 2.4) the recovery is 108\%, indicating an underestimation of the cumulative blank.

We anticipate that additional blank and standard sample analyses will eliminate these uncertainties and provide the basis for the eventually aimed two-step heating of quartz samples. Albeit the final procedure for sample treatment will closely resemble the procedure described above, the required duration of sample heating has yet to be verified.

II.1.5. Conclusions

We have constructed an extraction system that is able to quantitatively release \textit{in situ} produced $^{14}\text{C}$ from quartz samples. Stepped heating experiments demonstrate the removal of atmospheric $^{14}\text{C}$ contamination from the quartz surface at temperatures $\leq$500°C followed by the release of \textit{in situ} $^{14}\text{C}$ above 900°C. An electron bombardment furnace capable of heating quartz to 1550-1600°C for several hours under an UHP O\textsubscript{2} flow allows sample outgassing without the addition of a fluxing agent. A rigorous gas cleaning system results in clean CO\textsubscript{2} gas which can directly be measured with a gas ion source AMS system. Neither sample dilution by $^{14}\text{C}$-free CO\textsubscript{2} nor graphitization is needed. These improvements eliminate additional blank $^{14}\text{C}$ and simplify the extraction procedure. Currently, CO\textsubscript{2} samples ready for AMS analysis can be produced in one working day. Tests simulating the extraction procedure show a consistently high CO\textsubscript{2} recovery rate of $>99.8\%$ (n=7), confirming that virtually no CO\textsubscript{2} is lost during heating or gas cleaning. First extraction experiments using a purified quartz sample indicate very good extraction efficiency. A series of line blanks at different temperatures have identified the extraction furnace as major source of $^{14}\text{C}$ blank, which can, however, be reduced by thorough preheating of the furnace, including the Pt-crucible, prior to the emplacement of a new sample. The preliminary procedural blank is $<5 \times 10^5$ $^{14}\text{C}$ atoms, which is in good agreement with values reported by Lifton et al. (2001).
Current work focuses on further improvements of hot blank levels and additional stepped heating experiments on the internal standard sample followed by first samples with unknown $^{14}$C concentrations.

**Acknowledgements**

We would like to thank N. A. Lifton for sharing the philosophy of cosmogenic $^{14}$C extraction and measurements and endless support during construction and testing of the line. We thank U. Menet, A. Süsli, D. Niederer and B. Rütsche for continuous support during the construction of the line. We acknowledge the access to the AMS MICADAS system by M. Suter and A. Synal and thank S. Fahrni for support during the measurements. Thanks to S. Ivy-Ochs for providing quartz sample G111. A. Steinhof is acknowledged for easy supply of the ’dead‘ CO$_2$. We thank Nat Lifton and two anonymous reviewers for their constructive comments that helped to improve the manuscript.

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II.2. An update on \textit{in situ} cosmogenic $^{14}$C analysis at ETH Zürich *

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ABSTRACT

We present the improved performance of the modified \textit{in situ} cosmogenic $^{14}$C extraction system at ETH Zürich. Samples are now processed faster (2 days in total) and are measured with a high analytical precision of usually <2\% at the gas ion source of the MICADAS AMS facility. Measurements of the PP-4 standard sample show a good reproducibility and consistency with published values. Procedural blanks are very low at currently $\sim 4.7 \times 10^4$ $^{14}$C atoms. Analyses of samples from a ~300 year old rock avalanche prove that we can successfully apply \textit{in situ} $^{14}$C exposure dating to very young surfaces. Additionally, we present a modified calculation scheme for \textit{in situ} $^{14}$C concentrations which differs from that used for conventional radiocarbon dating. This new approach explicitly accounts for the characteristics of cosmogenic \textit{in situ} $^{14}$C production.

* In press in \textit{Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms}

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II.2.1. Introduction

Terrestrial cosmogenic nuclides are widely applied in Quaternary geochronology and Earth surface process studies. With its short half-life (5730 y) in situ cosmogenic $^{14}$C is of special interest, as it is particularly sensitive to fast and/or recent landscape changes that cannot be detected by the long-lived radionuclides ($^{10}$Be, $^{26}$Al, $^{36}$Cl). Combined with a long-lived isotope, in situ $^{14}$C provides the opportunity, e.g., to reconstruct short episodes of surface burial, to distinguish recent exposure from pre-exposure of surfaces (Miller et al., 2006) or to determine the timing of sediment storage in a fluvial system (Wittmann and von Blanckenburg, 2009). However, the often low in situ $^{14}$C concentrations in terrestrial rocks and the contamination by atmospheric $^{14}$C make routine in situ $^{14}$C analyses difficult. With the development of in situ $^{14}$C extraction systems based on high-temperature sample heating or melting, significant progress has been made during the past decade (Lifton et al., 2001; Hippe et al., 2009; Pigati et al., 2010; Fülöp et al., 2010; Goehring et al., 2011).

The in situ $^{14}$C extraction system at ETH Zürich has been first described by Hippe et al. (2009). Since then the system has been routinely running and further improved. Most importantly, the blank $^{14}$C contribution has been strongly reduced. By now a good database of system blanks, quartz and standard sample analyses has been acquired that allows an evaluation of the long-term analytical performance. Here, we present a summary of these data and discuss the analytical reproducibility and accuracy. We further describe our revised and more efficient analytical protocol and propose a new approach in data reduction that accounts for the differences between in situ produced $^{14}$C and conventional radiocarbon. Finally, the capability of in situ $^{14}$C for exposure dating of very young surfaces will be shown and discussed on $^{14}$C data obtained for a ~300 y old rock avalanche.

II.2.2. Methods

II.2.2.1. Modifications of the in situ $^{14}$C extraction system

Three main features characterize the ETH in situ $^{14}$C extraction system: (1) the all-metal tubing system, (2) the omission of sample graphitization, and (3) the extraction furnace heated by electron bombardment. The latter allows the extraction of $^{14}$C from a quartz sample without using a flux agent. We argue that the extraction without flux and the lack of a graphitization step leads to less $^{14}$C contamination and thus lower $^{14}$C blanks than systems and procedures using those other techniques. While the system setup in general has remained unchanged, the extraction furnace has seen minor, yet important changes. The tantalum tube inside the furnace (see
Fig. II.1.1) was replaced by a tungsten tube, which is physically more stable at high temperatures. Furthermore, the control grid bars were re-shaped providing the originally flat bars with a V-profile to prevent constant bending. Both modifications significantly increased the reliability of the extraction furnace.

**II.2.2.2. Current analytical procedures**

About 5 g of quartz are used for an *in situ* $^{14}$C analysis. Once loaded into the extraction furnace, the quartz sample is pre-heated at ~700°C (calibrated with a pyrometer) for 2 h under a flow of ultra-high-purity (UHP) O$_2$ to remove atmospheric contamination. The temperature of 700°C was chosen based on stepped-heating experiments showing that 500°C is sufficient to remove atmospheric $^{14}$C (Lifton et al., 2001) but that the *in situ* component is not released below 900°C (Hippe et al., 2009). This pre-heating step is crucial because the amount of contaminant $^{14}$C can be similar or even higher than the *in situ* $^{14}$C amount. Next, the furnace is cooled to room temperature and the large amounts of water and other gases released during pre-heating are pumped off (usually overnight) until the system pressure is about $10^{-7}$–$10^{-6}$ Pa. For *in situ* $^{14}$C extraction the sample is then heated under a UHP O$_2$-flow to 1550-1600°C for $2 \times 2$ h. The quartz is not melted under these conditions but slight sintering was observed for a few samples. Following extraction, the gas is cleaned and taken off for AMS analysis as previously described (Hippe et al., 2009).

In our initial procedure, two high-temperature heating steps of 2 h duration each were made to guarantee complete extraction of *in situ* $^{14}$C from the quartz. The second extraction step was performed the next day after the furnace had been cooled to room temperature overnight. In our modified procedure, samples are heated at 1550-1600°C for 2 h, cooled to 1000°C for 30 min, and heated again for 2 h at 1550-1600°C. With the additional 1000°C step the quartz to crosses the tridymite-crystobalite transformation temperature at 1470°C twice more. The associated transformation of the quartz crystal lattice may help to promote the release of any remaining *in situ* $^{14}$C.

The entire extraction (incl. gas cleaning) now requires ~ 10 h and is accomplished in 1 day. Fig. II.2.1 compares present and previous sample processing procedures.

**II.2.2.3. AMS measurement**

The purified CO$_2$ gas can be measured without graphitization at the MICADAS AMS system at ETH using the gas ion source (Ruff et al., 2007; Synal et al., 2007; Wacker et al., 2010; Fahrni et al., 2012). The current setup of the gas feeding system allows CO$_2$ amounts equivalent to ~ 45 µg carbon to be released into
the ion source. Typically, our samples yield sufficient CO$_2$ (~5-30 µg carbon) to be measured without further CO$_2$-addition. Procedural blanks, however, yield only little CO$_2$ (1-2 µg carbon) and therefore require the addition of $^{14}$C-free CO$_2$ to provide sufficient gas for AMS analysis (Tab. II.2.1). Samples containing more than 40 µg carbon are split into separate breakseal tubes before being taken off the extraction system.

The $^{14}$C/$^{12}$C ratios obtained from a quartz sample are usually significantly higher than ratios measured, e.g., for modern organic samples. This creates a good signal-to-background ratio and allows a high analytical precision. An example of a $^{14}$C measurement from a quartz sample on the MICADAS system is given in Fig. II.2.2. Due to the small sample size (5.1 µg carbon) the $^{14}$C/$^{12}$C ratio is ~7 times the modern ratio and is measured with a counting error lower than 1%.

**II.2.2.4. Data processing**

AMS radiocarbon data are commonly reported as F$^{14}$C (or F$_m$), the measured fraction modern carbon, normalized to a δ$^{13}$C of -25‰$_{VPDB}$ and AD 1950 (Donahue et al., 1990; Reimer et al., 2004). Radiocarbon ages are typically calculated based on this value. The same procedure has so far also been applied to calculate concentrations of *in situ* $^{14}$C in quartz. However, the main purpose of a δ$^{13}$C...
correction is to compensate for natural isotopic fractionation in biochemical processes. The normalization to AD 1950 accounts for the anthropogenic release of ‘bomb’ $^{14}C$ in the atmosphere. Both effects are not relevant for the production of in situ $^{14}C$ in quartz. As such, we argue that normalization to these parameters is not correct and changes the ‘true’ $^{14}C/^{12}C$ ratio of the sample.

Because raw data for in situ $^{14}C$ analyses are often obtained from the AMS laboratories in the same way as classical radiocarbon data, we will describe in the following how we determine the absolute (‘true’) $^{14}C/^{12}C$ ratio from reported $F^{14}C$ and $\delta^{13}C$ values. Additionally, as an easier way, we calculate the absolute $^{14}C/^{12}C$ ratio directly from the measured raw $^{14}C/^{12}C$ data. We propose that this procedure should be used for in situ $^{14}C$ data reduction. Below, the subscripts $S$ and $OX$ refer to sample and the oxalic acid standard OX-I, respectively.

The $F^{14}C$ is defined as the ratio of the sample activity to the standard activity (Stuiver and Polach, 1977), which is equivalent to the ratio of the sample $^{14}C/^{12}C$ (or $^{14}C/^{13}C$) ratio to the standard $^{14}C/^{12}C$ (or $^{14}C/^{13}C$) ratio 1950 (Donahue et al., 1990; Reimer et al., 2004). By definition, the standard $^{14}C/^{12}C$ ratio is 95% of the specific activity of the international standard oxalic acid (OX-I), in AD 1950 and normalized to $\delta^{13}C = -19\%_{VPDB}$ (Stuiver and Polach, 1977). To calculate today’s absolute $^{14}C/^{12}C$ ratio of a sample, the $\delta^{13}C$ fractionation correction included in the $F^{14}C_S$ is

Figure II.2.2. The raw values over the course of a measurement on the MICADAS AMS for a typical small quartz sample. The target is pre-sputtered for 1-2 minutes before the gas enters the source and the current rises quickly. For this sample, after only 3 additional minutes the actual measurement is finished.
undone again using the measured $\delta^{13}_{S\ meas}$. Also, the decay of the standard from 1950 to the year of measurement is taken into account ($\lambda_{14C}=1/8267$ y$^{-1}$):

$$
\left(\frac{^{14}C}{^{12}C}\right)_{S\ abs} = 0.95 \cdot \left(\frac{^{14}C}{^{12}C}\right)_{OX\ [-19]} \cdot F^{14}_{S} \cdot \left[1 + \frac{\delta^{13}_{S\ meas}}{1000} \right] \cdot e^{1950\ \text{year}}_{8267}
$$

Note that for laboratories using a different standard than OX-I, the first term of Eq. 3 has to be modified accordingly [cf. Donahue et al., 1990]. With the $^{14}C/^{12}C$ ratio obtained in Eq. 3 the amount of in situ $^{14}C$ is calculated by (modified after Lifton et al., 2001):

$$
N_{14} = \frac{\left(\frac{^{14}C}{^{12}C}\right)_{S\ abs} \cdot 0.989 \cdot N_{A} \cdot V_{S}}{V_{A} \cdot B} \cdot e^{1950\ \text{year}}_{8267}
$$

$N_{A}$ is Avogadro’s number ($6.022 \times 10^{23}$ mol$^{-1}$), $V_{S}$ is the volume of collected CO$_2$, $V_{A}$ is the volume of 1 mol CO$_2$, $B$ is the number of $^{14}C$ atoms of the associated processing blank and $M$ is the mass of the quartz sample. The factor of 0.989 accounts for the abundance of $^{12}C$ in the sample which can be approximated by the natural abundance of the $^{12}C$ isotope.

However, the $\left(\frac{^{14}C}{^{12}C}\right)_{S\ abs}$ can also be directly calculated from the measured ratios $\left(\frac{^{14}C}{^{12}C}\right)_{OX\ meas}$ and $\left(\frac{^{14}C}{^{12}C}\right)_{S\ meas}$, both only background corrected. With the $^{14}C/^{12}C$ isotopic ratio of OX-I the measured $^{14}C/^{12}C$ sample ratio can be normalized by:

$$
\left(\frac{^{14}C}{^{12}C}\right)_{S\ abs} = \frac{\left(\frac{^{14}C}{^{12}C}\right)_{OX\ [-19]} \cdot \left(\frac{^{14}C}{^{12}C}\right)_{S\ meas}}{\left(\frac{^{14}C}{^{12}C}\right)_{OX\ meas}} \cdot e^{1950\ \text{year}}_{8267}
$$

For those laboratories that measure $^{14}C/^{13}C$ ratios, the $\left(\frac{^{14}C}{^{12}C}\right)_{S\ abs}$ can be obtained from the background corrected ratios $\left(\frac{^{14}C}{^{13}C}\right)_{OX\ meas}$ and $\left(\frac{^{14}C}{^{13}C}\right)_{S\ meas}$ using the relations [13]:

$$
\left(\frac{^{14}C}{^{12}C}\right)_{OX\ meas} = \left(\frac{^{14}C}{^{13}C}\right)_{OX\ meas} \cdot 0.981 \cdot \left(\frac{^{13}C}{^{12}C}\right)_{VPDB}
$$

$$
\left(\frac{^{14}C}{^{12}C}\right)_{S\ meas} = \left(\frac{^{14}C}{^{13}C}\right)_{S\ meas} \cdot \left[1 + \frac{\delta^{13}_{S\ meas}}{1000}\right] \cdot \left(\frac{^{13}C}{^{12}C}\right)_{VPDB}
$$

where the $^{13}C/^{12}C$ ratio of the VPDB standard is $11237.2 \times 10^{-6}$ [15, 16].

Following the approach given in Roberts and Southon (2007) and based on a half-life of 5730 y, the $^{14}C/^{12}C$ ratio of OX-I (in AD 1950) is:

$$
\left(\frac{^{14}C}{^{12}C}\right)_{OX\ [-19]} = 1.251 \cdot 10^{-12}
$$
We compared the total amount of $^{14}$C obtained for our entire dataset of more than 120 analyses (blanks, quartz extractions, $^{14}$C-free CO$_2$ gas measurements) by the equations given above and the original calculations (Donahue et al., 1990; Lifton et al., 2001). Depending on the $\delta^{13}$C value of each single measurement, results based on our new approach can be either higher or lower or not significantly different from the values calculated after the original approach. For our blanks that are usually measured with a very low $\delta^{13}$C (Tab. II.2.1), the calculated values are up to 7% lower using the new approach. In contrast, our measurements of $^{14}$C from quartz samples usually give a $\delta^{13}$C > 25‰ so that the amount of $^{14}$C calculated as proposed above is on average 1-2% higher compared to results from the original calculations.

II.2.3. Analytical performance

II.2.3.1. Blank levels and reproducibility

System blanks were determined following the protocol for sample extraction but without placing quartz in the sample holder. Blank data obtained since 2010 are summarized in Table II.2.1 and in Fig. II.2.3. Since the first regular operation of the extraction furnace in spring 2010, the average blank level significantly decreased (cf. Hippe et al., 2009). The mean extraction blanks for the two subsequent high-temperature steps of the previous extraction procedure are $(2.83 \pm 1.02) \times 10^4$ $^{14}$C atoms ($\pm$ 1 stdev, n=11), and $(1.51 \pm 0.66) \times 10^4$ $^{14}$C (±1 stdev, n=10), respectively. Higher blanks were observed immediately after major repairing of the extraction furnace, but values decreased again after repeated heating cycles of the furnace (Fig. II.2.3). These high values are not included in the average blanks given above, as samples are only processed when blank levels are low again. Preliminary blank data for the modified, 2 x 2 h extraction procedure are $(3.95 \pm 1.18) \times 10^4$ $^{14}$C atoms (±1 stdev, n=4). Our blank levels are thus about a factor of 4 to 6 lower than those reported for all other in situ $^{14}$C extraction systems (Lifton et al., 2001; Fülöp et al., 2010; Pigati et al., 2010; Goehring et al., 2011).

The extraction efficiency and analytical reproducibility of our system was tested with a quartzite sample (PP-4) used as an internal reference at the University of Arizona (Lifton et al., 2001). The measured in situ $^{14}$C concentrations for five PP-4 aliquots are given in Table II.2.2, calculated according to both the original and the new procedure proposed above. For ease of comparison, we will here discuss the PP-4 data as derived from the original calculation scheme (Fig. II.2.4). Our weighted mean of $(3.94 \pm 0.07) \times 10^5$ at g$^{-1}$ (1 σ) agrees within 1σ with the data measured by Lifton et al. (2001) and at SUERC (Fülöp et al., 2010). It is, however, some 10% higher than more recent results from the University of Arizona (Miller et al., 2006;
Table II.2.1. Summary of blank data obtained since 2010. All errors are 1 σ. Only single blanks marked with a * were included into the calculation of the mean blank (see Fig. II.2.3).

<table>
<thead>
<tr>
<th>Sample ID (AMS ID)</th>
<th>Sample mass (μg CO₂)</th>
<th>Fraction modern P^14C</th>
<th>δ^{13}C_{\Delta}</th>
<th>^14C/^12C</th>
<th>^14C</th>
<th>^14C (10^6 at g^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bl_220210 (38967.09)</td>
<td>6.8 (-- )</td>
<td>0.391 ± 0.032</td>
<td>-35.86</td>
<td>0.452 ± 0.037</td>
<td>15.22 ± 1.26</td>
<td></td>
</tr>
<tr>
<td>bl_260210 (38967.11)</td>
<td>2.7 (-- )</td>
<td>0.501 ± 0.022</td>
<td>-32.35</td>
<td>0.609 ± 0.027</td>
<td>8.12 ± 0.39</td>
<td></td>
</tr>
<tr>
<td>bl_120310 (38967.13)</td>
<td>2.8 (7.4)</td>
<td>0.166 ± 0.007</td>
<td>-37.87</td>
<td>0.191 ± 0.008</td>
<td>9.56 ± 0.44</td>
<td></td>
</tr>
<tr>
<td>bl_180310 (38967.16)</td>
<td>3.6 (3.7)</td>
<td>0.160 ± 0.009</td>
<td>-43.12</td>
<td>0.182 ± 0.010</td>
<td>6.57 ± 0.36</td>
<td></td>
</tr>
<tr>
<td>bl_160410 (38967.18)</td>
<td>1.9 (7.5)</td>
<td>0.096 ± 0.005</td>
<td>-47.05</td>
<td>0.108 ± 0.005</td>
<td>4.86 ± 0.25</td>
<td></td>
</tr>
<tr>
<td>bl_020610 (38967.19)</td>
<td>1.9 (7.7)</td>
<td>0.235 ± 0.006</td>
<td>-48.67</td>
<td>0.264 ± 0.007</td>
<td>12.45 ± 0.35</td>
<td></td>
</tr>
<tr>
<td>bl_280610 (38967.23)</td>
<td>1.1 (7.4)</td>
<td>0.053 ± 0.004</td>
<td>-54.76</td>
<td>0.058 ± 0.004</td>
<td>2.27 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>bl_260810 (38967.25)</td>
<td>0.9 (7.4)</td>
<td>0.054 ± 0.004</td>
<td>-45.23</td>
<td>0.062 ± 0.005</td>
<td>2.35 ± 0.22</td>
<td></td>
</tr>
<tr>
<td>bl_210910 (38967.27)</td>
<td>1.0 (6.9)</td>
<td>0.089 ± 0.005</td>
<td>-50.81</td>
<td>0.099 ± 0.006</td>
<td>3.70 ± 0.25</td>
<td></td>
</tr>
<tr>
<td>bl_121010 (38967.30)</td>
<td>1.2 (7.4)</td>
<td>0.090 ± 0.006</td>
<td>-48.47</td>
<td>0.101 ± 0.006</td>
<td>4.13 ± 0.28</td>
<td></td>
</tr>
<tr>
<td>bl_261010 (38967.32)</td>
<td>1.9 (7.4)</td>
<td>0.061 ± 0.005</td>
<td>-53.06</td>
<td>0.067 ± 0.006</td>
<td>2.94 ± 0.27</td>
<td></td>
</tr>
<tr>
<td>bl_011210 (38967.34)</td>
<td>11.6 (-- )</td>
<td>0.137 ± 0.004</td>
<td>-26.54</td>
<td>0.162 ± 0.005</td>
<td>9.34 ± 0.28</td>
<td></td>
</tr>
<tr>
<td>bl_031210 (38967.35)</td>
<td>6.5 (-- )</td>
<td>0.129 ± 0.006</td>
<td>-22.47</td>
<td>0.153 ± 0.007</td>
<td>4.93 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>bl_131210 (38967.37)</td>
<td>4.1 (7.4)</td>
<td>0.061 ± 0.003</td>
<td>-42.15</td>
<td>0.070 ± 0.004</td>
<td>3.79 ± 0.22</td>
<td></td>
</tr>
<tr>
<td>bl_110111 (38967.38)</td>
<td>2.9 (7.4)</td>
<td>0.031 ± 0.002</td>
<td>-45.77</td>
<td>0.035 ± 0.002</td>
<td>1.61 ± 0.12</td>
<td></td>
</tr>
<tr>
<td>bl_280111 (38967.40)</td>
<td>1.1 (7.4)</td>
<td>0.026 ± 0.006</td>
<td>-35.15</td>
<td>0.031 ± 0.007</td>
<td>1.10 ± 0.30</td>
<td></td>
</tr>
<tr>
<td>bl_180211 (38967.42)</td>
<td>1.6 (7.3)</td>
<td>0.085 ± 0.004</td>
<td>-46.16</td>
<td>0.096 ± 0.004</td>
<td>4.07 ± 0.19</td>
<td></td>
</tr>
<tr>
<td>bl_070311 (38967.44)</td>
<td>1.8 (7.3)</td>
<td>0.126 ± 0.004</td>
<td>-41.71</td>
<td>0.143 ± 0.005</td>
<td>6.33 ± 0.23</td>
<td></td>
</tr>
<tr>
<td>bl_210311 (38967.46)</td>
<td>1.2 (7.8)</td>
<td>0.063 ± 0.003</td>
<td>-45.44</td>
<td>0.071 ± 0.004</td>
<td>2.98 ± 0.17</td>
<td></td>
</tr>
<tr>
<td>bl_300311 (38967.31)</td>
<td>1.0 (7.4)</td>
<td>0.051 ± 0.004</td>
<td>-46.78</td>
<td>0.057 ± 0.005</td>
<td>2.20 ± 0.22</td>
<td></td>
</tr>
</tbody>
</table>

Mean value ± stdev

<table>
<thead>
<tr>
<th>First extraction step (initial procedure)</th>
<th>Second extraction step (initial procedure)</th>
<th>Extraction (new procedure)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean value ± stdev</strong></td>
<td><strong>Mean value ± stdev</strong></td>
<td><strong>Mean value ± stdev</strong></td>
</tr>
<tr>
<td><strong>3.84 ± 1.17</strong></td>
<td><strong>2.80 ± 1.02</strong></td>
<td><strong>1.48 ± 0.66</strong></td>
</tr>
</tbody>
</table>

*Numbers in brackets give amount of ‘dead’ CO₂ gas added. Uncertainty deriving from the CO₂ pressure reading is 0.07 μg.

b Normalized to δ^{13}C of -25%OVP at 85 and AD 1950.

*Calculated after Eq. 3.

*Calculated after Eq. 4. Corrected for the addition of ‘dead’ CO₂ gas with a mean ^14C concentration of 315 ± 118 at μg^-1 CO₂ (1 σ, n=12).
Pigati et al., 2010). Considering our very low blanks, this discrepancy is unlikely caused by a systematic blank underestimation. Other explanations could be an inhomogeneity of the PP-4 sample material or differences in the $^{14}$C diffusivity from a quartz melt (other in situ $^{14}$C extraction systems) compared to the diffusivity from solid quartz grains (our system).

![Figure II.2.3. Blank development since 2010. Only blanks marked by filled symbols were included into the calculation of the long-term mean blanks. Increased blanks due to repairing of the extraction furnace (hollow symbols) as well as an outlier (attributed to the use of an old Pt-crucible that has not been cleaned after the usual procedure) were excluded. Red rectangles are first blank data performed after the new extraction protocol (Fig. II.2.1).](image-url)
Table II.2.2. Summary of data for sample PP-4. All errors are 1σ. PP-4_1a and PP-4_4 were performed according to the original extraction protocol. PP-4_5a and PP-4_5b both derive from onelong 4 h extraction. PP-4_5a was collected after the first 2 h of heating; PP-4_5b shows the $^{14}$C released in the following 2 h. PP-4_5c is the post-extraction step performed on the following day to check for complete sample degassing. PP-4_7 and PP-4_8 were performed after the new extraction protocol. PP-4_7a was collected after the first 2 h of heating at 1550 °C, PP-4_7b after the final 2 h at 1600 °C. For PP-4_8 the entire gas was taken off as a single sample.

<table>
<thead>
<tr>
<th>Sample ID (AMS ID)</th>
<th>Temperature/duration</th>
<th>Sample mass (g qtz)</th>
<th>CO$_2$ yield (µg)$^a$</th>
<th>Fraction modern F$^{14}$C$^b$</th>
<th>δ$^{13}$C$_{\text{meas}}$</th>
<th>$^{14}$C/$^{12}$C$_{\text{abs}}$ (10$^{-12}$)$^c$</th>
<th>$^{14}$C (10$^5$ at g$^{-1}$)$^d$</th>
<th>$^{14}$C$_{\text{meas}}$ (10$^5$ at g$^{-1}$)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP-4_1a (39920.01)</td>
<td>1600°C/2 h</td>
<td>5.16</td>
<td>22.6 (--)</td>
<td>1.333 ± 0.013</td>
<td>-11.83</td>
<td>1.615 ± 0.016</td>
<td>3.42 ± 0.04</td>
<td>3.35 ± 0.04</td>
</tr>
<tr>
<td>PP-4_1b (39921.01)</td>
<td>1650°C/2 h</td>
<td>5.16</td>
<td>4.2 (--)</td>
<td>0.822 ± 0.024</td>
<td>-26.97</td>
<td>0.966 ± 0.029</td>
<td>0.32 ± 0.02</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PP-4_4a (40887.01)</td>
<td>1600°C/2 h</td>
<td>4.91</td>
<td>16.7 (--)</td>
<td>1.707 ± 0.021</td>
<td>-15.45</td>
<td>2.054 ± 0.025</td>
<td>3.43 ± 0.05</td>
<td>3.39 ± 0.05</td>
</tr>
<tr>
<td>PP-4_4b (40888.01)</td>
<td>1650°C/2 h</td>
<td>4.91</td>
<td>2.5 (7.7)</td>
<td>0.183 ± 0.005</td>
<td>-46.78</td>
<td>0.207 ± 0.006</td>
<td>0.18 ± 0.01</td>
<td>0.19 ± 0.02</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.61 ± 0.05</td>
<td>3.58 ± 0.05</td>
</tr>
<tr>
<td><strong>Total$_{corr}^f$</strong></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PP-4_5a (41521.01)</td>
<td>1600°C/2 h</td>
<td>5.30</td>
<td>16.2 (--)</td>
<td>1.903 ± 0.017</td>
<td>-13.05</td>
<td>2.301 ± 0.021</td>
<td>3.45 ± 0.04</td>
<td>3.40 ± 0.04</td>
</tr>
<tr>
<td>PP-4_5b (41521.02)</td>
<td>1650°C/2 h</td>
<td>5.30</td>
<td>1.4 (7.9)</td>
<td>0.214 ± 0.007</td>
<td>-46.08</td>
<td>0.242 ± 0.008</td>
<td>0.18 ± 0.01</td>
<td>0.19 ± 0.01</td>
</tr>
<tr>
<td>PP-4_5c (41521.03)</td>
<td>1650°C/2 h</td>
<td>5.30</td>
<td>0.9 (7.5)</td>
<td>0.071 ± 0.005</td>
<td>-49.25</td>
<td>0.080 ± 0.006</td>
<td>0.03 ± 0.01</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.67 ± 0.05</td>
<td>3.62 ± 0.04</td>
</tr>
<tr>
<td><strong>Total$_{corr}^f$</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>PP-4_7a (43023.1.1)</td>
<td>1600°C/2 h</td>
<td>5.26</td>
<td>17.7 (--)</td>
<td>1.707 ± 0.022</td>
<td>-26.52</td>
<td>2.008 ± 0.026</td>
<td>3.33 ± 0.05</td>
<td>3.37 ± 0.05</td>
</tr>
<tr>
<td>PP-4_7b (43023.1.2)</td>
<td>1650°C/2 h</td>
<td>5.26</td>
<td>1.9 (7.4)</td>
<td>0.345 ± 0.012</td>
<td>-52.02</td>
<td>0.385 ± 0.013</td>
<td>0.31 ± 0.02</td>
<td>0.33 ± 0.02</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.64 ± 0.05</td>
<td>3.70 ± 0.05</td>
</tr>
<tr>
<td><strong>Total$_{corr}^f$</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.02 ± 0.16</td>
<td>3.85 ± 0.15</td>
</tr>
<tr>
<td>PP-4_8 (43023.2.1)</td>
<td>1650°C/2 × 2 h</td>
<td>4.97</td>
<td>17.3 (--)</td>
<td>1.755 ± 0.020</td>
<td>-13.35</td>
<td>2.121 ± 0.025</td>
<td>3.60 ± 0.05</td>
<td>3.54 ± 0.05</td>
</tr>
<tr>
<td>PP-4_8$_{corr}^f$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.94 ± 0.07</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Numbers in brackets give amount of 'dead' CO$_2$ gas added. Uncertainty deriving from the CO$_2$ pressure reading is 0.07 µg.

$^b$ Normalized to δ$^{13}$C of -25‰$_{VPDB}$ and AD 1950.

$^c$ Calculated after Eq. 3.

$^d$ Calculated after Eq. 4. Blank corrected and corrected for the addition of 'dead' CO$_2$ gas with a mean $^{14}$C concentration of 315 ± 118 at µg$^{-1}$ CO$_2$ (1σ, n=12).

$^e$ Calculated after Eq. 5 in Lifton et al. (2001). Blank corrected (blanks calculated after the same equations as quartz samples) and corrected for the addition of 'dead' CO$_2$ gas with a mean 14C concentration of 336 ± 126 at µg$^{-1}$ CO$_2$ (1σ, n=12).

$^f$ Correction factors: 1.0779 ± 0.0106 (production at ground surface), 1.0064 ± 0.0255 (no topographic shielding) and 1.0027 ± 0.0266 (pure SiO$_2$) (Miller et al., 2006). All errors propagated.
II.2.3.2. In situ $^{14}$C surface exposure dating of very young surfaces

To explore the possibility of dating very young surfaces with our in situ $^{14}$C system, we have analysed $^{14}$C in two quartz samples from the historically recorded, AD 1717 rock avalanche in Val Ferret, Italy (Deline and Kirkbride, 2009). The measured in situ $^{14}$C concentrations and the calculated surface exposure ages are given in Table II.2.3. We used a sea level-high latitude production rate of 15.2 ± 0.3 at g$^{-1}$y$^{-1}$ (Dugan et al., 2008) and the scaling scheme of Stone (2000). The ages obtained for Trio-8 and Trio-10 are 228 ± 45 y (1σ) and 433 ± 50 y (1σ), corresponding to AD 1780 and AD 1576, respectively. The age of Trio-8 agrees within 2σ with the true age of the rock avalanche of 291 y (back from the sampling year 2008 to AD 1717). The $^{14}$C age of Trio-10 is clearly higher than expected. If this was due to an underestimated blank, the true blank for this sample would have to be more than twice as high as our long-term average blank. This seems rather unlikely in view of the observed scatter of the blank values. The high $^{14}$C concentration of Trio-10 might rather indicate nuclide inheritance. Nevertheless, blank uncertainties are clearly a major source of uncertainty when analysing samples with such low $^{14}$C concentrations. Still, the Val Ferret example shows that with careful blank determinations we are able to determine surface in situ $^{14}$C exposure ages of a few 100 y with reasonable accuracy.

Figure II.2.4. In situ $^{14}$C concentrations of the PP-4 quartz sample compared to published data. For comparison, our data were calculated after the original approach of Donahue et al. (1990) and Lifton et al. (2001). All errors are 1 σ (for ETH single data 1 σ errors include AMS statistical error and errors of the associated blank).
Table II.2.3: In situ $^{14}$C data and exposure ages for the ~ 300 y old samples from Val Ferret, Italy.

<table>
<thead>
<tr>
<th>Sample ID (AMS ID)</th>
<th>Sample mass (g qtz)</th>
<th>$^{14}$C yield (μg)</th>
<th>Fraction modern $P^{14}$C</th>
<th>$^{13}$C S meas ($^{14}$C/$^{12}$C)</th>
<th>$^{13}$C S abs ($^{10}$-$^{12}$)</th>
<th>$^{14}$C age (years)</th>
<th>Correction factor</th>
<th>Scaling factor</th>
<th>Error (_{\text{total}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trio-8a (43021.2.1)</td>
<td>5.22</td>
<td>1.1 (7.7)</td>
<td>0.166 ± 0.008</td>
<td>-42.08</td>
<td>0.189 ± 0.009</td>
<td>1.01 ± 0.21</td>
<td>0.27 ± 0.07</td>
<td>1.28 ± 0.25</td>
<td>3.958</td>
</tr>
<tr>
<td>Trio-8b (43021.2.2)</td>
<td>5.22</td>
<td>0.7 (7.5)</td>
<td>0.068 ± 0.006</td>
<td>-45.57</td>
<td>0.077 ± 0.007</td>
<td>0.27 ± 0.14</td>
<td>0.493 ± 0.018</td>
<td>0.90 ± 0.22</td>
<td>3.879</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trio-10a (43022.1.1)</td>
<td>5.15</td>
<td>5.1 (5.1)</td>
<td>0.496 ± 0.015</td>
<td>-10.98</td>
<td>0.493 ± 0.018</td>
<td>0.38 ± 0.14</td>
<td>0.085 ± 0.006</td>
<td>0.27 ± 0.14</td>
<td>3.958</td>
</tr>
<tr>
<td>Trio-10b (43022.1.2)</td>
<td>5.15</td>
<td>1.2 (7.5)</td>
<td>0.075 ± 0.006</td>
<td>-45.48</td>
<td>0.077 ± 0.007</td>
<td>0.27 ± 0.14</td>
<td>0.493 ± 0.018</td>
<td>0.90 ± 0.22</td>
<td>3.879</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
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</tbody>
</table>

*Numbers in brackets give amount of ‘dead’ CO$_2$ gas added. Uncertainty deriving from the CO$_2$ pressure reading is 0.07 μg.*

*b Normalized to δ$^{13}$C of -25‰ vs. VPDB and AD 1980.*

*c Calculated after Eq. 3. Corrected for the blank and for the addition of ‘dead’ CO$_2$ gas with a mean $^{14}$C concentration of 315 ± 118 atoms μg$^{-1}$ CO$_2$ (1 σ, n=12). The blank contributed 39% and 27% to total measured $^{14}$C for Trio-8 and Trio-10, respectively.*

*d Calculated after Eq. 4. Corrected for topographic shielding and dip of surface (Dunne et al., 1999) and for sample thickness.*

*e Corrected for scaling after Stone (2000). Scaling parameters: Trio-8: 1775 m a.s.l., 45.873 °N; Trio-10: 1746 m a.s.l., 45.862 °N.*

*f Corrected for topographic shielding and dip of surface (Dunne et al., 1999) and for sample thickness.*

*g Calculated using a sea level-high latitude production rate of 15.2 ± 0.3 at g$^{-1}$ y$^{-1}$ (Dugan et al., 2008). Production by spallation, stopped and fast muons were taken into account separately (Heisinger et al., 2002b; Schaller et al., 2002).*
II.2.4. Conclusions

With small modifications of the extraction system and a shorter extraction procedure, the efficiency and reproducibility of in situ $^{14}$C analysis at ETH Zürich has been significantly improved. Typical quartz samples ($^{14}$C concentrations of $>10^5$ at g$^{-1}$) are measured with a precision of better than 2%, while for samples with low $^{14}$C concentrations (few $10^4$ at g$^{-1}$) a precision of <6% is usually achieved. The analyses of a reference sample (PP-4) show a good reproducibility of <5% and are in reasonable agreement with published data. Our very low blank levels allow us to analyse quartz samples with exposure ages as low as a few hundred years. Furthermore, we propose a revised approach for in situ $^{14}$C data reduction that (1) omits the conventionally used but for in situ $^{14}$C inappropriate $\delta^{13}$C correction, (2) corrects for the year of measurement, and (3) accounts for the natural isotopic composition of carbon.

Acknowledgements

The authors wish to thank A. Süsli, D. Niederer and U. Menet for their continuous support at the extraction system. We sincerely thank N. Lifton for his advice, endless patience and excellent discussions that greatly benefited this work. We thank T. Dunai for pointing out the shortcomings of conventional data reduction for in situ 14C data, and T. Jull for constructive discussions. Critical reviews by N. Lifton and an anonymous reviewer are greatly appreciated. K.H. is funded by a grant of the SNF awarded to C.S.
III. Applications

Part 1 – In situ $^{14}$C in quantitative geomorphology

III.1. Studying Earth surface processes

III.1.1. The concept of catchment-wide denudation rates

The modification of a landscape is in a large part controlled by weathering and erosion processes which can be described quantitatively by local or catchment-averaged denudation rates. The concentration of a cosmogenic nuclide ($N$, at g$^{-1}$) in a surface sample provides an estimate of a time-integrated, local denudation rate ($\varepsilon$) capturing the total loss of nuclides from a rock or soil by physical erosion and chemical weathering. In general, the accumulation of cosmogenic nuclides in an eroding surface is given by (e.g. Lal, 1991; Cerling and Craig, 1994):

$$N(t) = N_{inh}(0)e^{-\lambda t} + \sum_i \frac{P_i(0)}{\lambda + \rho \varepsilon / \Lambda_i} (1 - e^{-t(\lambda + \rho \varepsilon / \Lambda_i)})$$  \hspace{1cm} (8)

$P_i(0)$ (at g$^{-1}$ y$^{-1}$) is the on-site surface production rate for each production pathway (indicated by the subscript $i$) of a specific cosmogenic nuclide, $\lambda$ (y$^{-1}$) is the decay constant of that nuclide, $t$ (y) the time since exposure, $\rho$ (g cm$^{-3}$) is the rock density and $\Lambda_i$ (g cm$^{-2}$) is the mean attenuation length of the respective cosmic-ray particle considered for nuclide production. $N_{inh}(0)$ describes any ‘inherited’ concentration, i.e. any concentration acquired from a previous exposure. To account for the thickness $x$ (cm) of a rock sample $P_i(0)$ is replaced by an averaged production rate $\langle P_i \rangle$ that integrates over the entire slab thickness (Granger and Riebe, 2007):

$$\langle P_i \rangle = P_i(0) \frac{\Lambda_i}{\rho x} (1 - e^{-\rho x / \Lambda_i})$$ \hspace{1cm} (9)

In the case of long-term constant denudation, the nuclide concentration at the surface is in steady-state and does no longer depend on the time. Assuming negligible inheritance Eq. (8) reduces to (Lal, 1991):

$$N(x) = \sum_i \frac{\langle P_i \rangle}{\lambda + \rho \varepsilon / \Lambda_i}$$ \hspace{1cm} (10)

However, to estimate the average denudation of a larger area or catchment, the measurement of the cosmogenic nuclide concentration in river sediments rather than in a large number of single surface samples has proven to be a more adequate and effective approach (e.g. Lal, 1991; Brown et al., 1995; Schaller et al., 2001; von
The concept of a catchment-averaged (=catchment-wide) denudation rate considers the cosmogenic nuclide concentration in the sediment leaving a drainage basin to reflect an average cosmogenic nuclide concentration representative for the entire catchment (Brown et al., 1995; Biermann and Steig, 1996; Granger et al., 1996). Catchment-wide denudation rates are not only averaged over a certain basin area but also over a time interval, sometimes called the averaging time (T\textsubscript{ave}) or the ‘apparent age’ (T\textsubscript{app}) (von Blanckenburg, 2005; Dunai, 2010). This interval describes the time required to remove one mean attenuation path length Λ/ρ (often defined as z\textsuperscript{*}), i.e. the time a grain resides within a depth of Λ/ρ ~ 60 cm for bedrock and ~100 cm for soil, and is dependent on the denudation rate itself with T\textsubscript{ave} = Λ/ρε (or z\textsuperscript{*}/ε) (Lal, 1991; Dunai, 2010).

The calculation of a catchment-wide denudation rate from a cosmogenic nuclide concentration is based on several fundamental assumptions (von Blanckenburg, 2005):

1. Denudation has to remain constant over the time interval the denudation rate is integrated, i.e. the cosmogenic nuclide production equals removal by erosion and decay. This mass balance may be disturbed in landscapes dominated by landslides or other mass-wasting processes. Nevertheless, by adjusting the size of a sampled catchment the effect of landslides can be averaged out and adequate long-term denudation rates can be obtained (Niemi et al., 2005).

2. Quartz is contributed uniformly to the sampled sediment from the entire catchment. This condition might be violated in catchments comprising different rock types of highly variable quartz content, e.g. carbonates that do not contribute any quartz at all. In that case, a correction for the non-uniform quartz distribution based on petrologic information should be made (Safran et al., 2005).

3. The analysed quartz grain size must be released by all contributing rock types to avoid that results are biased towards a single delivering lithology.

4. Quartz should not be enriched by subsurface weathering. This can be important in tropical landscapes with intense regolith weathering (Riebe et al., 2001).

5. Sediment transit times have to be short compared to the denudation timescale. Sediment storage can modify the cosmogenic nuclide inventory, either by nuclide accumulation during surface or shallow depth storage or by nuclide decay during deep sediment burial. However, from modelling sediment storage and mixing in various active floodplain settings of largely different river systems hypothetical storage times of 70 ky to 2 My have been proposed for the long-lived \textsuperscript{10}Be and \textsuperscript{26}Al isotopes in order to change the nuclide concentrations sufficiently to be analytically resolvable (Wittmann and von Blanckenburg, 2009). It was further shown that the effect of sediment storage in each individual catchment strongly depends on the
channel depth, i.e. storage depth, and the channel migration rate (Wittmann and von Blanckenburg, 2009). On the example of the eastern Andes it was proposed that the cosmogenic $^{10}$Be signal from the sediment-producing hinterland areas can be preserved despite sediment floodplain storage and can thus be measured in the foreland river sediments. It was further proposed to calculate floodplain-corrected denudation rates employing an average production rate based on a ‘floodplain-corrected’ sediment source area (Wittmann and von Blanckenburg, 2009; Wittmann et al., 2009). In contrast to the long-lived nuclides, in situ $^{14}$C is supposed to be more sensitive to floodplain storage. According to the modelling of Wittmann and von Blanckenburg (2009) a residence time of <20 kyr can significantly change the in situ $^{14}$C concentration within a sediment sample. In our study on catchment-wide denudation rates on the Bolivian Altiplano we were able to proof this rapid impact of floodplain storage on the in situ $^{14}$C concentration (see Chapter III.2).

(6) The integration timescale has to be short compared to the timescale of radioactive decay of the respective cosmogenic nuclide, i.e. $\Lambda/\varepsilon \rho \ll 1/\lambda$. This condition is crucial for the application of in situ $^{14}$C for catchment-wide denudation studies because it means that in the case of low denudation rates ($\epsilon < 80$-100 mm ky$^{-1}$ for $\rho = 2.0$-$2.5$ g cm$^{-3}$) the in situ $^{14}$C concentration is controlled by radioactive decay and mixing processes in the subsurface and therefore no information on $\varepsilon$ can be obtained. This issue will be discussed in further detail below.

### III.1.2. Using in situ cosmogenic $^{14}$C in denudation rate studies

Catchment-wide denudation rates are often studied in landscapes having soil or regolith-mantled hillslopes. Mainly bioturbation accounts for a vertical mixing of the soil layer and modifies the cosmogenic nuclide inventory. Figure III.1.1 shows different depth profiles (modified after Granger and Riebe, 2007) that illustrate the cosmogenic nuclide concentration in bedrock (or any other parent material) overlain by a well-mixed soil layer. In the no-erosion case (Fig. III.1.1.A) the nuclide concentration measured at the surface equals a mean concentration $\langle N \rangle$ derived from the mean production rate integrated over the soil depth $x$ (cm). Substituting Eq. (8) and (9) and solving for simple exposure gives (Granger and Riebe, 2007):

$$\langle N \rangle = \sum_i \frac{P_i^{(0)}}{\lambda} \frac{\Delta t}{\rho x} (1 - e^{-\rho x/\Delta t}) (1 - e^{-t/\lambda})$$

Eq. (11) also holds for the case of steady denudation because the material removed by erosion has the same average cosmogenic nuclide concentration as the mixed soil layer. As a prerequisite the thickness of the mixed soil is considered to remain stable. In an eroding profile, fresh regolith at the top of the underlying bedrock contributes additional material to the mixed layer. Material is added from
below at the same rate (ε) as material is removed by denudation (Fig. III.1.1). In the bedrock nuclides are produced as a function of the soil depth (x):

$$N(x) = \sum_i \frac{P_i(0)}{\lambda + \rho \varepsilon / \Lambda_i} e^{-\rho x / \Lambda_i} (1 - e^{-(\lambda + \rho \varepsilon / \Lambda_i) t})$$  \hspace{1cm} (12)

The cosmogenic nuclide concentration at the surface/within the mixed soil is then given by the mean production in the mixed layer \(\langle P_i \rangle\), the loss of nuclides by decay and denudation and the concentration added from the bedrock \(N(x)\) (Brown et al., 1995; Granger and Riebe, 2007):

$$\frac{d\langle N \rangle}{dt} = \langle P_i \rangle - \langle N \rangle \lambda - \langle N \rangle \frac{\varepsilon}{\rho x} + N(x) \frac{\varepsilon}{\rho x}$$  \hspace{1cm} (13)

Solving Eq. (13) for steady-state conditions describes the nuclide concentration in the soil profile as:

$$\langle N \rangle \left(\lambda + \frac{\varepsilon}{\rho x}\right) = \sum_i P_i(0) \frac{\Lambda_i}{\rho x} (1 - e^{-\rho x / \Lambda_i}) + \sum_i \frac{P_i(0)}{\lambda + \rho \varepsilon / \Lambda_i} e^{-\rho x / \Lambda_i} \frac{\varepsilon}{\rho x}$$  \hspace{1cm} (14)

Long-lived cosmogenic nuclides fulfil the condition \(\Lambda / \varepsilon \rho \ll 1 / \lambda\) also for very small denudation rates, e.g. as low as 0.3-0.4 mm ky\(^{-1}\) for \(^{10}\)Be or 0.6-0.8 mm ky\(^{-1}\) for \(^{26}\)Al (\(\rho = 2.0-2.5\) g cm\(^{-3}\)). Therefore, Eq. (14) can be simplified by ignoring radioactive decay to:

$$\langle N \rangle \left(\frac{\varepsilon}{\rho x}\right) = \sum_i P_i(0) \frac{\Lambda_i}{\rho x} (1 - e^{-\rho x / \Lambda_i}) + \frac{1}{\rho \varepsilon / \Lambda_i} e^{-\rho x / \Lambda_i} \frac{\varepsilon}{\rho x}$$  \hspace{1cm} (15)

and finally to (Granger and Riebe, 2007):

$$\langle N \rangle \approx \sum_i P_i(0) \frac{\Lambda_i}{\varepsilon}$$  \hspace{1cm} (16)

Eq. (16) is valid for the long-lived cosmogenic nuclides, e.g. \(^{10}\)Be or \(^{26}\)Al, and illustrates that the cosmogenic nuclide concentration of these isotopes is insensitive to the soil depth and thus equals the concentration of an eroding rock surface (Fig. III.1.1.B). Therefore, the long-lived nuclides can provide accurate long-term, basin-wide denudation rates even soil-mantled landscapes without considering the soil depths within a catchment.

For \textit{in situ} \(^{14}\)C, however, condition \(\Lambda / \varepsilon \rho \ll 1 / \lambda\) is not met for small denudation rates, i.e. \(\Lambda / \varepsilon \rho \sim 1 / \lambda\) for \(\varepsilon = 80-100\) mm ky\(^{-1}\) (\(\rho = 2.0-2.5\) g cm\(^{-3}\)). At lower denudation rates the nuclide losses are controlled by radioactive decay rather than by denudation. With \(\Lambda / \varepsilon \rho \gg 1 / \lambda\) and \(\rho x / \varepsilon \gg 1 / \lambda\) Eq. (14) changes to:
\[ \langle N \rangle \approx \sum_i \frac{P_i(0)}{\lambda} \left[ \frac{\Delta_i}{\rho x} \left( 1 - e^{-\frac{\rho x}{\Delta_i}} \right) + e^{-\frac{\rho x}{\Delta_i}} \frac{\varepsilon}{\lambda \rho x} \right] \]  

(17)

For low denudation rates the term \( \varepsilon/\lambda \rho x \) is small and can be ignored. Eq. (17) then further reduces to:

\[ \langle N \rangle \approx \sum_i \frac{P_i(0)}{\lambda} \frac{\Delta_i}{\rho x} \]

(18)

The important implication from Eq. (18) is that the concentration of in situ \( ^{14} \text{C} \) in a slowly eroding soil profile provides no direct information on the denudation rate but strongly depends on the mixing depth (Fig. III.1.1. C and D). Thus, in situ \( ^{14} \text{C} \) could be used to study local soil dynamics and to obtain information on the mixing properties of a soil layer without analysing an entire depth profile. However, this application has not yet been explored.

The considerations presented above illustrate important differences between the long-lived nuclides and in situ \( ^{14} \text{C} \) with regard to their applicability for catchment-wide denudation studies. Very high to very low denudation rates can be obtained from \(^{10} \text{Be}\) or \(^{26} \text{Al}\) allowing these nuclides to be applied in most natural settings, regardless of the presence of mixed soil (Fig. III.1.1.D). Even complex exposure histories do not necessarily strongly perturb the long-term denudation signal. The long half-lives average out episodes of intermittent surface cover/burial, sediment storage or any other change in exposure that occur on a comparatively short timescale. While this is of great benefit when studying long-term denudation processes, it also provides a rather simplified image of the processes modifying the Earth’s surface. Complex surface exposure histories or changes in geomorphic processes are often not captured. However, this can be achieved with in situ \( ^{14} \text{C} \). Due to its fast decay, even short intervals of surface cover or sediment storage (over the last several \( 10^3 \) years) are traceable. Although the interpretation of in situ \( ^{14} \text{C} \) concentrations can be quite complex with regard to the influence of soil mixing as described above, the application of in situ \( ^{14} \text{C} \) is not limited to fast-eroding settings. On the example of the Bolivian Altiplano we show in the following that with reasonable assumptions on the soil depths, in situ \( ^{14} \text{C} \) can be well used to determine sediment transfer times even in slowly-eroding landscapes.
Figure III.1.1. The development of the $^{10}$Be and in situ $^{14}$C concentrations with depth for a surface covered with a well-mixed soil layer. Saprolite that is usually present at the transition from bedrock to soil is ignored here for simplicity. Calculated for a substrate density of 2.0 g cm$^{-3}$ using the depth dependency of Schaller et al. (2009) and Eq. (22) (see Section III.2.) modified after Brown et al. (1995) and Schaller et al. (2009). Muonic production rates are taken from Heisinger et al. (2002b), spallogenic production rates are from Balco et al. (2008, 2009) for $^{10}$Be and 12.29 ± 0.99 at g$^{-1}$ y$^{-1}$ for in situ $^{14}$C (Lifton, pers. comm.).

(A) In the no-denudation case, the concentration of a cosmogenic nuclide within the mixed soil layer is an average concentration $\langle N \rangle$ integrating over the soil depth $x$. (B) If denudation is included, the concentration of $^{10}$Be at the surface equals the concentration expected for an unmixed profile without soil. In contrast, in situ $^{14}$C has an average concentration because the
denudation rate is too low to exceed the effect of soil mixing and radioactive decay during residence in the soil. (C) The nuclide concentrations for two different denudation rates. The $^{10}$Be concentration at the surface is much lower for a five times higher denudation rate whereas the in situ $^{14}$C concentration changes comparatively little. The denudation rate of 50 mm ky$^{-1}$ is still too low to have a strong influence on in situ $^{14}$C. (D) In contrast, for a soil mixing depth of 200 cm instead of 100 cm, the in situ $^{14}$C concentration decreases by nearly 30% whereas the change in the $^{10}$Be concentration is insignificant.
III.2. Quantifying denudation rates and sediment storage on the eastern Altiplano, Bolivia, using cosmogenic $^{10}$Be, $^{26}$Al, and $\textit{in situ}$ $^{14}$C

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ABSTRACT

Denudation processes and sediment transfer are investigated in a high-elevation, low-relief environment (eastern Altiplano, Bolivia) using $^{10}$Be, $^{26}$Al, and $\textit{in situ}$ $^{14}$C analysis in fluvial sediments. Concentrations of the long-lived nuclides $^{10}$Be and $^{26}$Al yield consistently low catchment-wide denudation rates of $\sim 3$-29 mm ky$^{-1}$ (integrating over 21-194 ky), which reflect the low geomorphic gradients and the discontinuity of fluvial transport along the eastern Altiplano margin. No significant correlation is recorded between denudation rates of individual catchments and morphological basin parameters (slope, area, elevation). This is attributed to the overall little variability in morphology. The agreement between the denudation rates and published modern sediment discharge data suggests steady landscape evolution of the eastern Altiplano from the latest Pleistocene until today. While $^{10}$Be and $^{26}$Al provide long-term estimates on sediment production, $\textit{in situ}$ cosmogenic $^{14}$C is used to trace short-term sediment storage. $\textit{In situ}$ $^{14}$C concentrations are comparatively low indicating that $^{14}$C decayed during alluvial storage over at least the past $\sim 11$-20 ky. We assume storage at shallow depth (2 m) and consider the influence of soil-mantled hillslopes on the $\textit{in situ}$ $^{14}$C concentration. Our results illustrate the importance of sediment storage even over short distances and demonstrate the potential of $\textit{in situ}$ $^{14}$C to study sediment routing and transfer times within drainage systems. However, this study also demonstrates that the long-lived $^{10}$Be and $^{26}$Al nuclides can provide adequate estimates on long-term denudation rates even if sediment transport is not fast but interrupted by several thousands of years of storage.

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III.2.1. Introduction

Denudation is one of the key elements that define the topographic evolution of mountain belts and shape landscapes (e.g., Horton, 1999; Willett, 1999; Whipple, 2009). In continental sedimentary systems, denudation marks the starting point of complex mass transfer processes and defines the input rates of material entering the drainage system (Allen, 2002). Understanding the processes that control long-term denudation and sediment transfer is fundamental to reconstruct mass flux and the large-scale geodynamic and geomorphic evolution of mountainous landscapes. Observational constraints and the quantification of denudation rates and transfer times provide the basis for geodynamic modelling of landscape evolution (e.g., Ehlers and Poulsen, 2009).

In the central Andes denudation processes have been studied in widely different tectonic, climatic, and topographic settings (e.g., Montgomery et al., 2001; Safran et al., 2005; Zeilinger and Schlunegger, 2007; Kober et al., 2009; Insel et al., 2010). However, one of the most prominent features of the Central Andes, the large intramontane Altiplano basin, has yet received little attention. The Altiplano is a tectonically passive, high elevation plateau, bounded by the tectonically active mountain chains of the Eastern and Western Cordillera. The Altiplano forms one of the largest, internally drained, continental sedimentary basins and has been an important region of sediment accumulation in the Cenozoic (Lamb et al., 1997). The Altiplano plateau acts as a large-scale climatic barrier separating the eastern continental moisture from the western SE-Pacific moisture sources (Garreaud et al., 2003). Therefore, it is considered to play an important role for the South American climate and atmospheric circulation (Garreaud et al., 2003; Barnes and Ehlers, 2009; Ehlers and Poulsen, 2009). Low denudation rates, resulting from this specific climatic and tectonic situation, have been proposed as an essential condition for the large accumulation of material resulting in plateau formation (Masek et al., 1994; Montgomery et al., 2001, Norton and Schlunegger, 2011). However, data that quantify denudation on the Altiplano are sparse and mainly limited to a few sediment discharge measurements (Guyot et al., 1990, 1992) that reflect the modern situation. To gain insights into the landscape-forming processes that occur over millennial and longer timescales, this study applies cosmogenic nuclide analysis and investigates denudation rates and processes as well as sediment transfer on the Bolivian Altiplano.

Our study focusses on an area along the eastern Altiplano-Rio La Paz drainage divide (Fig. III.2.1). With the headwaters of the Rio La Paz cutting into the Altiplano, a sharp transition between the flat plateau and the rapidly incising systems of the Rio La Paz and the Eastern Cordillera was formed (Safran et al.,
2005; Zeilinger and Schlunegger, 2007). For the Rio La Paz a strong feedback between erosional unloading by focussed incision and crustal rebound has been suggested (Zeilinger and Schlunegger, 2007). It was proposed that this feedback mechanism causes weak flexural rebound along the Altiplano-Rio La Paz drainage divide and, thus, maintains internal drainage along the eastern Altiplano. Here, we investigate to which extent the processes east of the drainage divide have an impact on the landscape evolution of the adjacent Altiplano.

We present catchment-averaged denudation rates and evaluate sediment storage based on the analysis of the three cosmogenic nuclides $^{10}$Be, $^{26}$Al, and \textit{in situ} $^{14}$C in river-borne sediment. The key aspect is the widely different half-lives of these isotopes ($^{10}$Be 1.4 My, $^{26}$Al 0.7 My, and $^{14}$C 5730 y, respectively), which cover different time intervals and thereby give information on temporal changes in surface exposure or denudation. The $^{10}$Be–$^{26}$Al nuclide pair is commonly used to unravel complex exposure and denudation histories and to gain information on the long-term stability or variability of geologic and/or climatic conditions (e.g., Biermann et al., 1999; Granger and Muzikar, 2001). The measurement of $^{10}$Be or $^{26}$Al concentrations from river sediments provides spatially averaged denudation rates over any defined catchment size (e.g., Brown et al., 1995; Biermann and Steig, 1996; von Blanckenburg, 2005) and allows identifying and/or isolating climatic, topographic, and lithological factors that control local and regional denudation. These cosmogenic nuclide-derived denudation rates integrate over variable climate conditions that have prevailed on the Altiplano throughout the late Quaternary (e.g., Baker et al., 2001; Placzek et al., 2006). By comparing these rates with published sediment discharge data (Guyot et al., 1990, 1992), temporal changes in surface denudation – as have been proposed for the eastern Andean fold-and-thrust belt (Insel et al., 2010) – can be evaluated. Here, the analysis of the long-lived nuclides $^{10}$Be and $^{26}$Al is combined with measurements of the short-lived \textit{in situ} $^{14}$C isotope. We will show that \textit{in situ} $^{14}$C is a unique tool to directly determine the duration of sediment storage and, thus, provides a new method to investigate transport-storage relations within a fluvial system. The combination of all three isotopes will characterize and quantify denudation processes on the eastern Altiplano and illustrate the importance of sediment storage in such a landscape. This will therefore provide a better understanding of the source-to-sink processes that modify intramontane basins over timescales of thousands to a few hundred thousand years.
III.2.2. Study area

III.2.2.1. Geologic setting

The Altiplano is a ~ 250-km-wide plateau within the central Andes representing a distinct morphotectonic unit formed of coalesced sedimentary basins. Since the Eocene, sediment from a proto-cordillera, which today is the Eastern Cordillera, and the volcanic arc in the west (today the Western Cordillera) was accumulated rapidly within the Altiplano basin (Lamb et al., 1997). Plateau formation is assumed to result from crustal thickening caused by horizontal shortening involving thermal weakening of the crustal base from subduction-related
processes (Isacks, 1988; Allmendinger et al., 1997). Ege et al. (2007) proposed the early Oligocene (33-27 My) as the time of the onset of exhumation of the present plateau area with initial deformation localized at the eastward propagating frontal thrusts (Elger et al., 2005). For the principal phase of uplift, opposing geodynamic models have suggested rapid plateau rise during the late Miocene (e.g., Garzione et al., 2008) as well as constant and slow plateau growth over the last 25 My (Ehlers and Poulsen, 2009). At the eastern Altiplano, tectonic activity continued until ~ 7 My (Ege et al., 2007), but weak Plio-Pleistocene deformation on the northern Bolivian Altiplano was found along a NW-SE oriented thrust fault south of La Paz and in some weak regional folding (Dewey and Lamb, 1992). Minor normal fault systems running parallel to and cutting through the Altiplano edge have been attributed to late Pleistocene tectonic activity due to ongoing shortening (Imaizumi et al., 2000).

Today, the Bolivian Altiplano basin fill is composed of thick deposits of Paleogene/Neogene to Quaternary sediments and volcanic rocks from ignimbrite eruptions in the late Miocene to Pliocene (Allmendinger et al., 1997). Few topographic highs, mainly along the eastern Altiplano margin, expose the underlying Palaeozoic and Mesozoic basement of Ordovician to Cretaceous rocks. Small exposures of Neogene granitic plutons occur on the eastern Altiplano in proximity to the Cordillera Real (Fig. III.2.2).

### III.2.2.2. Geomorphology and climate

The Altiplano plateau has an average elevation of ~ 3800 m and is characterized by a flat, low-relief surface and smooth hillslopes. Vegetation is limited to grass and sporadic small bushes forming a steppe landscape. The Altiplano basin is drained internally. The drainage network on the eastern Altiplano shows a tectonic imprint with major, higher order channels following the main structural trend (NW-SE). In contrast, smaller tributaries directly draining the Altiplano margin run mostly in a NE-SW direction, roughly perpendicular to the main streams (Fig. 2). In the SE, channel direction changes gradually and tributary streams run parallel to the Cordillera. Precipitation on the Altiplano is largely restricted to the summer season (Nov-Mar) and depends on the westward transport of moisture from the interior of the continent (Garreaud and Aceituno, 2001; Garreaud et al., 2003). This accounts for a west-to-east gradient in rainfall from ~ 250 mm y\(^{-1}\) at the Western Cordillera to ~ 560 mm y\(^{-1}\) in the La Paz area (Bookhagen and Strecker, 2008). A strong intra-annual variability in rainfall causes most small streams to dry out partially or completely during the dry season. Thus, fluvial sediment transport is limited to the rainy season, which is characterized by episodic, often heavy rainfall and flooding (Guyot et al., 1992; Garreaud et al., 2003). However, given the low relief of the landscape, the occurrence of landslides...
or debris flows is unlikely or spatially insignificant. Aeolian sediment transport occurs during the dry season but is of minor importance.

Within several kilometres from the Altiplano margin, the landscape is characterized by rounded hills comprising mainly Palaeozoic units. With increasing distance from the Rio La Paz–Altiplano drainage divide, these hills are replaced by...
alluvial fans and floodplains. Ephemeral channels cutting into the sedimentary deposits have created small terraces (up to ~ 2 m; Fig. III.2.3A). Coarse gravel deposits that are frequently exposed in these terraces record episodic events of increased fluvial energy and capacity.

Modern glaciations in the Bolivian Eastern Cordillera are mainly restricted to the high peaks above 6000 m altitude (Clapperton et al., 1997). Modern equilibrium-line altitudes (ELA) in the area of La Paz have been determined to be in the range of 5100-5300 m for glaciers facing the Altiplano (Seltzer, 1992; Francou et al., 1995). Glacial deposits (boulders, gravel, clay) and moraines occurring NW of La Paz (Fig. III.2.2; GEOBOL, 1991-1994; Smith et al., 2005) illustrate the limited downward extent of glaciers onto the Altiplano during the Late Pleistocene and have been used to assess a depression of the ELA during the last local glacial maximum of between ~ 300-800 m (Klein et al., 1999; Smith et al., 2005). The timing of moraine deposition has been dated by $^{10}$Be to ~ 34-23 ky BP (Smith et al., 2005, 2008).

Figure III.2.3. Sampling sites on the eastern Altiplano, all views are upstream. (A) Site 22-3; channel incision is ~ 2 m. (B) Ephemeral channel at site 19-1. (C) Site 24-4, this catchment is one with the steepest slopes and highest relief (as seen in the background). (D) Site 18-2, cut bank is ~ 1 m high.
Table III.2.1. Sample locations, basin characteristics, cosmogenic nuclide data (\(^{10}\text{Be}\) and \(^{26}\text{Al}\)), and calculated denudation rates; all errors are 1\(\sigma\).

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<tr>
<th>Sample ID</th>
<th>Sampling location</th>
<th>Basin area (km(^2))</th>
<th>Mean altitude (m)</th>
<th>Palaeo -zoic rocks (%)</th>
<th>Mean slope (°)</th>
<th>Measured concentrations(^a)</th>
<th>(^{26}\text{Al/}{^{10}\text{Be}})</th>
<th>Production rates(^b)</th>
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<td>(^{10}\text{Be}) (10(^5) at g(^{-1}))</td>
<td>(^{36}\text{Al}) (10(^6) at g(^{-1}))</td>
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<td>(^{10}\text{Be}) (10(^5) at g(^{-1}))</td>
<td>(^{36}\text{Al}) (10(^6) at g(^{-1}))</td>
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<td>(^{10}\text{Be}) (10(^5) at g(^{-1}))</td>
<td>(^{36}\text{Al}) (10(^6) at g(^{-1}))</td>
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<td>24-6</td>
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<td>(^{10}\text{Be}) (10(^5) at g(^{-1}))</td>
<td>(^{36}\text{Al}) (10(^6) at g(^{-1}))</td>
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<td>24-7</td>
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<td>(^{10}\text{Be}) (10(^5) at g(^{-1}))</td>
<td>(^{36}\text{Al}) (10(^6) at g(^{-1}))</td>
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<tr>
<td>24-8</td>
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<td></td>
<td></td>
<td></td>
<td>(^{10}\text{Be}) (10(^5) at g(^{-1}))</td>
<td>(^{36}\text{Al}) (10(^6) at g(^{-1}))</td>
<td></td>
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</tbody>
</table>

\(^a\) Analyses were normalized to the ETH AMS standards S2007N for Be (calibrated to 07KNSTD) and ZAL94N (calibrated to KNSTD) for Al (Kubik and Christl, 2010).

\(^b\) Total basin-wide production rates from spallogenic and muonic production. Errors are 8.7 % for \(^{10}\text{Be}\) and 8.6 % for \(^{26}\text{Al}\), respectively (Stone, 2000; Balco et al., 2008).

\(^c\) Errors include the statistical error of the AMS and ICP-MS (for \(^{26}\text{Al}\) analyses), including the blank error and the uncertainty of the production rates.

\(^d\) Including only the drainage area south of the Lago Titicaca.
III.2.3. Methods

III.2.3.1. Drainage characteristics and sampling strategy

The study area extends over a distance of ~ 150 km along the eastern margin of the Bolivian Altiplano between 16° and 17°S. The sampling area is divided into a northern part draining toward the Lago Titicaca in the NW, and a southern part whose streams flow into the Rio Desaguadero draining toward the Lago Poopo and the Salars de Coipasa and Uyuni in the south (Fig. III.2.1). Samples were taken from 19 catchments, of which 16 directly border the Altiplano–Rio La Paz drainage divide (Fig. III.2.2). Sediment samples were collected from the active stream or in the part of the river channel that seemed to have been active most recently (Fig. III.2.3). The associated catchment sizes range from 14 km² to 1420 km² (Table III.2.1). Sampling of adjacent catchments with different sizes but otherwise similar parameters allows us to check for the influence of catchment size on the rate of surface denudation. Sample 18-5 was taken from the main stream comprising all sampled subcatchments draining toward the NW. An additional sample (123) was taken farther SW on the Altiplano from the Rio Desaguadero (Fig. III.2.2). Sample 123 represents a large-scale spatial average of northern Altiplano denudation because its drainage area (~ 18,000 km²) includes the central Altiplano, the Western Cordillera, and the Lago Titicaca.

III.2.3.2. Multiple cosmogenic nuclide analysis

The $^{10}$Be isotope is the most commonly used cosmogenic nuclide for the investigation of Earth surface denudation and has been successfully applied to obtain basin-averaged denudation rates in a variety of settings (e.g., Brown et al., 1995; Biermann and Steig, 1996; Schaller et al., 2001; Wittmann et al., 2007; Binnie et al., 2008; Kober et al., 2009). In the simplest case, the cosmogenic nuclide concentration of a sediment sample is entirely attributed to the nuclide accumulation on the hillslopes. Later changes in the cosmogenic nuclide inventory during the transit of the sediment through a catchment are considered to be negligible if transport times are short (von Blanckenburg, 2005; Wittmann and von Blanckenburg, 2009). This assumption might hold for many natural settings where long transit times (10⁵-10⁶ years) are usually not assumed (e.g., Dietrich and Dunne, 1978; Nakamura et al., 1995; Lancaster and Casebeer, 2007). Studies on surface denudation rates are therefore often based entirely on the $^{10}$Be isotope. In slowly evolving landscapes, however, the cosmogenic nuclide concentration in the sediment might be distorted by longer residence times within a basin. Cosmogenic nuclides might further accumulate during near-surface floodplain storage or the concentration might decrease by radioactive decay during deep sediment burial. In such a case, information about the nature and duration of transport processes can be
obtained by the combined analysis of two or more nuclides with different half-lives (cf. Wittmann and von Blanckenburg, 2009).

In view of the episodic character of erosional processes on the eastern Altiplano and of the low geomorphic gradients, sediment storage in our study area is likely. To test this assumption and to verify that $^{10}$Be concentrations are adequate long-term denudation proxies, we have combined $^{10}$Be analyses with $^{26}$Al and in situ $^{14}$C measurements. The $^{26}$Al/$^{10}$Be ratio records the medium- to long-term denudation history in the range of $10^4$ to $10^6$ years, but short-term storage episodes are not resolvable with these long-lived nuclides (Wittmann and von Blanckenburg, 2009). The short-lived in situ $^{14}$C, however, is sensitive to variations in the order of $10^3$ to $10^4$ years and can provide constraints on surface evolution and processes during the Holocene and late Pleistocene.

III.2.3. Sample preparation

All three nuclides – $^{10}$Be, $^{26}$Al, and in situ $^{14}$C – were analysed in quartz. Sediment samples were sieved to a grain size of 0.25-1 mm. Quartz was isolated by chemical dissolution with weak HF (Kohl and Nishiizumi, 1992) and, if necessary, by additional magnetic and/or heavy liquid separation. For $^{10}$Be and $^{26}$Al analysis, quartz separates were dissolved in concentrated hydrofluoric (HF) and nitric (HNO$_3$) acid along with 0.3 g of an in-house $^9$Be carrier solution. A small aliquot was taken from each sample solution for the measurement of the Al concentration. Separation of Be and Al was achieved by anion and cation exchange and pH-sensitive precipitations (Ivy-Ochs, 1996; Ochs and Ivy-Ochs, 1997). The $^{10}$Be/$^9$Be and $^{26}$Al/$^{27}$Al ratios were measured at the ETH Zurich accelerator mass spectrometry (AMS) facility (Synal et al., 1997). The mean subtracted blank represents mainly the $^{10}$Be/$^9$Be ratio of the carrier material added and has a $^{10}$Be/$^9$Be ratio of $(4.2 \pm 2.0) \times 10^{-15}$ ($n = 5$). The Al concentration was determined by standard addition to the untreated aliquots of the dissolved samples using inductively coupled plasma mass spectrometry (ICP-MS). The average of two repeat measurements of four standard addition aliquots per sample was taken. In total, $^{10}$Be concentrations were obtained for 20 samples; $^{26}$Al concentrations were measured for 13 of those (Table III.2.1).

In situ $^{14}$C concentrations were obtained for four samples (18-7, 24-3, 24-6, and 25-4). Sample extraction was performed at ETH Zürich following the methods of Hippe et al. (2009, 2012). About 5 g of clean quartz was preheated at ~700°C to remove atmospheric $^{14}$C contamination. In situ produced $^{14}$C was then extracted during two subsequent heating steps at 1550-1600°C. The $^{14}$C concentrations were measured separately for both extraction steps and finally added to yield a total concentration (Table III.2.2). Sample 24-3 was degassed after a modified extraction protocol during one single extraction step (cf. Hippe et al., 2012). Samples were
measured with the gas ion source of the MICADAS AMS system at ETH Zürich (Ruff et al., 2007; Synal et al., 2007; Wacker et al., 2010). Subtracted long-term average processing blanks are \((2.80 \pm 1.02) \times 10^4\) \(^{14}\)C atoms \((\pm 1\ \text{stdev}, \ n = 11)\) for the first and \((1.48 \pm 0.66) \times 10^4\) \(^{14}\)C \((\pm 1\ \text{stdev}, \ n = 10)\) for the second extraction step, respectively, and \((4.55 \pm 2.19) \times 10^4\) \(^{14}\)C \((\pm 1\ \text{stdev}, \ n = 9)\) for the modified extraction method. To check for analytical reproducibility, two aliquots of sample 18-7 were analysed. The two independent runs (separated by two months) gave identical results within \(1\sigma\) and we use the mean value from both analyses for further calculations.

### III.2.3.4. Data reduction and denudation rate calculations

In order to calculate catchment-wide denudation rates from the measured cosmogenic nuclide concentrations, catchment-averaged nuclide production rates were computed based on a digital elevation model (DEM) at 30-m resolution (ASTER GDEM). Scaling to altitude and latitude was done following the scheme of Lal (1991)/Stone (2000). Topographic shielding corrections were calculated to be < \(1\%\) and were therefore neglected. No shielding correction for snow or vegetation cover was deemed necessary. Denudation rates were calculated based on the formalism of Schaller et al. (2002), where nuclide production by spallation, stopped,

### Table III.2.2. In situ \(^{14}\)C data\(^a\). All errors are \(1\sigma\).

<table>
<thead>
<tr>
<th>Sample ID (AMS ID)</th>
<th>Sample mass (g)</th>
<th>CO(_2) yield (µg)(^b)</th>
<th>Fraction modern F(^{14})C</th>
<th>(\delta^{13})C(_{\text{meas}})</th>
<th>(^{14})C/(^{12})C(_{\text{abs}}) (10(^{-12}))(^c)</th>
<th>(^{14})C (10(^3) at g(^{-1}))(^d)</th>
<th>(^{10})Be/(^{14})C (^{10})Be/(^{14})C</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-7e (40446.01)</td>
<td>5.17</td>
<td>13.6 (-- (--)</td>
<td>1.661 ± 0.017</td>
<td>-16.30</td>
<td>1.996 ± 0.020</td>
<td>2.57 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>18-7f (40446.02)</td>
<td>5.17</td>
<td>19. (7.9)</td>
<td>0.320 ± 0.008</td>
<td>-49.84</td>
<td>0.358 ± 0.009</td>
<td>0.31 ± 0.02</td>
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<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.88 ± 0.04</td>
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<tr>
<td>18-7g (40885.01)</td>
<td>5.63</td>
<td>16.7 (--</td>
<td>1.406 ± 0.014</td>
<td>-16.92</td>
<td>1.687 ± 0.016</td>
<td>2.47 ± 0.03</td>
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<tr>
<td>18-7h (40886.01)</td>
<td>5.63</td>
<td>2.5 (7.7)</td>
<td>0.367 ± 0.009</td>
<td>-45.04</td>
<td>0.416 ± 0.010</td>
<td>0.35 ± 0.01</td>
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<tr>
<td>Total</td>
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<td></td>
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<td>2.82 ± 0.03</td>
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<tr>
<td>Mean</td>
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<td>2.85 ± 0.02</td>
<td>15.2 ± 0.5</td>
</tr>
<tr>
<td>24-3 (45659.1)</td>
<td>5.16</td>
<td>7.7 (--)</td>
<td>0.549 ± 0.008</td>
<td>-24.37</td>
<td>0.649 ± 0.009</td>
<td>3.49 ± 0.06</td>
<td>3.1 ± 0.2</td>
</tr>
<tr>
<td>24-6a (40447.01)</td>
<td>5.30</td>
<td>28.4 (-- (--)</td>
<td>0.985 ± 0.011</td>
<td>-21.07</td>
<td>1.172 ± 0.013</td>
<td>3.11 ± 0.04</td>
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</tr>
<tr>
<td>24-6b (40447.02)</td>
<td>5.30</td>
<td>3.9 (7.4)</td>
<td>0.524 ± 0.008</td>
<td>-41.08</td>
<td>0.598 ± 0.009</td>
<td>0.61 ± 0.02</td>
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<tr>
<td>Total</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3.72 ± 0.04</td>
<td>11.3 ± 0.4</td>
</tr>
<tr>
<td>25-4b (41520.01)</td>
<td>4.92</td>
<td>10.1 (-- (--)</td>
<td>1.569 ± 0.018</td>
<td>-16.61</td>
<td>1.883 ± 0.022</td>
<td>1.88 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>25-4c (41520.02)</td>
<td>4.92</td>
<td>2.1 (7.9)</td>
<td>0.604 ± 0.010</td>
<td>-45.07</td>
<td>0.684 ± 0.012</td>
<td>0.66 ± 0.02</td>
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<td></td>
<td></td>
<td>2.54 ± 0.04</td>
<td>9.7 ± 0.3</td>
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</tbody>
</table>

\(^a\) For samples 18-7, 24-6, and 25-4, the results of both extraction steps and the total concentration are given. Sample 24-3 was extracted in one single heating step. For sample 18-7 two aliquots have been measured. The mean value of both total concentrations has been used for all further calculations.

\(^b\) Numbers in brackets give amount of ‘dead’ CO\(_2\) gas added. Uncertainty deriving from the CO\(_2\) pressure reading is 0.07 µg.

\(^c\) Normalized to \(\delta^{13}\)C of -25‰ VPDB and AD 1950.

\(^d\) Calculated after Eq. 3.

\(^e\) Calculated after Eq. 4. Blank corrected and corrected for the addition of ‘dead’ CO\(_2\) gas with a mean \(^{14}\)C concentration of 315 ± 118 at µg\(^{-1}\) CO\(_2\) (1\(\sigma\), \(n=12\)).
and fast muons, respectively, is taken into account separately. For all isotopes, statistical errors together with blank errors and errors on the production rates were propagated in all calculations. For $^{26}$Al and $^{10}$Be, the sea level high latitude (SLHL) spallation production rates adopted in this study are $30.2 \pm 2.6$ at g$^{-1}$ y$^{-1}$ and $4.49 \pm 0.39$ at g$^{-1}$ y$^{-1}$ (Stone, 2000; Balco et al., 2008), respectively, using the revised $^{10}$Be half-life of $1.387 \pm 0.012$ My (Chmeleff et al., 2010; Korschinek et al., 2010). For $^{14}$C, a SLHL spallation production rate of $12.29 \pm 0.99$ at g$^{-1}$ y$^{-1}$ was used, based on a re-evaluation of published in situ $^{14}$C calibration data (Lifton, pers. comm.). The contribution due to muonic production was calculated separately for stopped and fast muons applying the online accessible MATLAB code of the CRONUS calculator (Balco et al., 2008), which implements the results of Heisinger et al. (2002a,b) from irradiation experiments. Parameters were adjusted to allow muon scaling for in situ $^{14}$C based on the muon cross-sections as published in Heisinger et al. (2002a,b). For comparison, the muonic contribution of $^{10}$Be and $^{26}$Al has additionally been calculated using muon production rates recently obtained from natural samples together with the scaling approach and the specific attenuation lengths as presented by Braucher et al. (2011). For both nuclides, local muonic production rates derived this way are up to ~ 90% lower than the respective values deduced from Heisinger et al. (2002a,b). However, $^{10}$Be and $^{26}$Al production rates derived by both approaches differ by less than 2% from each other, since the muonic contributions to these two nuclides are small. Accordingly, denudation rates calculated for both muon schemes (Heisinger et al., 2002a,b, Braucher et al., 2011) agree within 1σ. For in situ $^{14}$C, however, reliable estimates of the muonic production should be more important because of the significantly higher muon contribution (Heisinger et al., 2002b). Analyses of natural samples are therefore an important task for future research.

For a correct interpretation of the obtained in situ $^{14}$C concentrations, the presence of a soil or regolith layer on the eroding hillslopes also has to be considered. As in most natural settings, denudation on the Altiplano takes place on exposed bedrock surfaces as well as in the soil layer covering the bedrock or sediment. This layer is assumed to be well-mixed by, e.g., bioturbation and/or seasonal freezing. The concentrations of the long-lived $^{10}$Be and $^{26}$Al nuclides are hardly affected by a mixed soil cover because their half-lives are much longer than the typical integration timescales associated with $^{10}$Be or $^{26}$Al denudation rates (Biermann and Steig, 1996; Granger et al., 1996). Thus, the steady-state $^{10}$Be or $^{26}$Al concentration at an eroding geomorphic surface is the same for a well-mixed soil profile or for bare bedrock (cf. Fig. 8 in Granger and Riebe, 2007). However, if denudation rates are low, the integration timescale, i.e., the time required to erode the depth of one absorption length of cosmic rays in the subsurface ($t = \Lambda/\varepsilon^*\rho$ with $\varepsilon$
being the denudation rate, \( \Lambda \) the mean absorption length, and \( \rho \) the substrate density; Lal, 1991), can easily exceed the short half-life of \(^{14}\text{C}\). In such settings, the in situ \(^{14}\text{C}\) concentration is essentially controlled by the radioactive decay and the depth of the mixed soil layer (see Appendix for details). To account for this mixed layer, all results presented below that involve in situ \(^{14}\text{C}\) data were calculated following the equations given in Brown et al. (1995) and Schaller et al. (2009) (see Eq. 12 in Appendix). We emphasize that our approach of analysing river sediment assumes a constant mixing depth for the entire catchment. From field observations and with regard to the overall homogeneity in climate, bedrock, and geomorphology on the eastern Altiplano, we consider this to be a valid assumption for this study.

III.2.4. Results

III.2.4.1. \(^{10}\text{Be}\) and \(^{26}\text{Al}\) data

Table III.2.1 summarizes the \(^{10}\text{Be}\) and \(^{26}\text{Al}\) nuclide concentrations of all analysed samples, the associated denudation rates, and the \(^{26}\text{Al}/^{10}\text{Be}\) ratios. Measured \(^{10}\text{Be}\) concentrations of the 19 samples taken from the Altiplano margin range from \((9.6 \pm 0.3) \times 10^5\) to \((78.5 \pm 2.4) \times 10^5\) at \(g_{\text{qtz}}^{-1}\) and yield single nuclide denudation rates of 3.2-29.0 mm ky\(^{-1}\) (Fig. III.2.4). Sample 123 taken farther SW on the Altiplano yields the lowest \(^{10}\text{Be}\) concentration of all samples \([(4.4 \pm 0.2) \times 10^5\) at \(g_{\text{qtz}}^{-1}\)] and the highest denudation rate of 57.2 mm ky\(^{-1}\). Concentrations of \(^{26}\text{Al}\) are between \((8.3 \pm 0.5)\) and \((45.7 \pm 2.1) \times 10^6\) at \(g_{\text{qtz}}^{-1}\), yielding denudation rates between 3.4 and 22.2 mm ky\(^{-1}\). Denudation rate estimates for both long-lived nuclides agree well within error, except for two samples (18-2 and 24-4, see below). Integration timescales (calculated with \(\Lambda = 160 \text{ g cm}^{-2}\) [Gosse and Phillips, 2001] and \(\rho = 2.6 \text{ g cm}^{-3}\)) are on the order of 11-194 ky for \(^{10}\text{Be}\) and 28-180 ky for \(^{26}\text{Al}\) (Table III.2.1). Most \(^{26}\text{Al}/^{10}\text{Be}\) ratios range between \(\sim 5.8\) and 7.3 and agree within 2\(\sigma\) with the production rate ratio of 6.8. Only samples 18-2 and 24-4 have much higher \(^{26}\text{Al}/^{10}\text{Be}\) ratios (10.3 and 8.7). In a two-isotope diagram (\(^{26}\text{Al}/^{10}\text{Be}\) vs. \(^{10}\text{Be}\)), most data points cluster around the erosion island defined by the lines of continuous exposure/no erosion and steady-state erosion (Fig. III.2.5). From these results a simple exposure/denudation history without long-term (\(10^5\)-\(10^6\) years) sediment storage can be inferred. Results for samples 18-2 and 24-4 that plot above the erosion island in the ‘forbidden field’ are most probably caused by a combination of analytical reasons.
Figure III.2.4. Catchment-wide denudation rates calculated from $^{10}$Be and $^{26}$Al concentrations. Sampling sites are given with their associated drainage basins (except for sample 123). Samples analysed additionally for in situ $^{14}$C are 18-7, 24-3, 24-6, and 25-4. Sediment gauging stations are named according to Guyot et al. (1990, 1992). Gauging-derived denudation rates were calculated from the mass flux (t km$^{-2}$ y$^{-1}$) of the suspended material. Note that the location of the northernmost gauging station SU is given in Fig. III.2.1 with the black diamond at the northeastern shore of the Lago Titicaca. Map source: ASTER GDEM Version 1, METI and NASA
III.2.4.2. In situ $^{14}$C data

In situ $^{14}$C concentrations in the four analysed samples range from $(2.54 \pm 0.04) \times 10^5$ at $g_{qtz}^{-1}$ (Table III.2.2). All in situ $^{14}$C concentrations are consistently lower than expected from the concentrations of $^{10}$Be and $^{26}$Al under the assumption of simple exposure and steady-state conditions. Thus, in a single nuclide approach these concentrations would correspond to comparatively high denudation rates of 152-264 mm ky$^{-1}$ with short integration times covering the late Holocene (2.3-4.1 ky).

Ratios of $^{10}$Be/$^{14}$C ratios range between 3.6-15.2, which is much higher than the production ratio of 0.31. In a two-nuclide diagram ($^{10}$Be/$^{14}$C vs. $^{14}$C) the data points therefore plot well within the field of complex exposure (Fig. III.2.6). This implies significant storage of the sampled sediment. The simplest case of deep burial with complete shielding of the sediment requires a minimum storage over the past 7.9-10.5 ky to reduce the in situ $^{14}$C concentrations from saturation to the measured...
values (Fig. III.2.6A). Combined $^{10}\text{Be} - ^{14}\text{C}$ paleodenudation rates (dotted lines) are in the same range as $^{10}\text{Be}$ or $^{26}\text{Al}$ denudation rates. The development of the \textit{in situ} $^{14}\text{C}$ concentration as a function of the thickness of a well-mixed soil layer is illustrated in a modified two-isotope diagram ($^{10}\text{Be}/^{14}\text{C}$ vs. $^{14}\text{C}$; Fig. III.2.6B). A long-term denudation rate of 4 mm ky$^{-1}$, which is the minimum value of the $^{10}\text{Be}$-derived denudation rates of the four samples analysed for \textit{in situ} $^{14}\text{C}$, was included into the calculations. This rate slightly influences the position of the constant exposure lines and defines the upper limit of the $^{10}\text{Be}/^{14}\text{C}$ ratio for each depth. Fig. III.2.6B shows that the measured \textit{in situ} $^{14}\text{C}$ data would correspond to mixing depths of as much as ~300-500 cm. In the discussion below, we will evaluate these results and present an interpretation that accounts for a combination of soil mixing and sediment storage (Figs. III.2.6C and D).

III.2.5. Discussion

Denudation on the eastern Altiplano is dominated by diffusive erosion processes on the hillslopes (e.g., soil creep, overland flow, gully erosion; cf. Simpson and Schlunegger, 2003) that are reflected in the $^{10}\text{Be}$ and $^{26}\text{Al}$ catchment-wide denudation rates. In the following, the spatial variability of these denudation rates will be discussed with regard to local changes in geomorphic parameters. Because precipitation is constant throughout the study area, we will concentrate on catchment morphology and lithology (Fig. III.2.7). Possible temporal variations in denudation rates will be evaluated by comparing results from the different cosmogenic nuclides with modern sediment load data (Guyot et al., 1990, 1992). \textit{In situ} $^{14}\text{C}$ will then be used to reconstruct complex sediment exposure and quantify sediment storage.

The $^{10}\text{Be}$ and $^{26}\text{Al}$ data imply consistently low denudation rates of ~ 3-29 mm ky$^{-1}$ for the eastern Altiplano. These overall low catchment-wide denudation rates are a common feature of low-relief landscapes worldwide (e.g., Bierman and Caffee, 2001; Hewawasam et al., 2003; Cox et al., 2009). However, our study area on the eastern Altiplano is situated at the geomorphic transition toward the adjacent Rio La Paz basin characterized by huge contrasts in denudation processes and topography (Fig. III.2.8). This setting probably has its nearest equivalent in passive continental margin escarpments that also exhibit strong morphologic contrasts between the escarpment and the higher-elevated plateau area (e.g., Ollier, 1985; Kooi and Beaumont, 1994; Seidl et al., 1996). In the Rio La Paz basin, geomorphology is strongly affected by tectonic forcing (Zeilinger and Schlunegger, 2007). Landslides and other mass wasting processes are prevalent (Blodgett and Isacks, 2007) and control headward expansion of the drainage basin into the Altiplano (Zeilinger and Schlunegger, 2007). With ~ 200-600 mm ky$^{-1}$ (Safran et al., 2005) and ~ 100-600
Figure III.2.6. Results from the four samples analysed for in situ $^{14}$C plotted in different two-nuclide diagrams showing the $^{10}$Be/$^{14}$C ratio vs. the $^{14}$C concentration. Error bars represent 1σ analytical uncertainty including errors on the subtracted blank. (A) Diagram calculated equivalent to Fig. III.2.5. In situ $^{14}$C concentrations of all samples plot consistently left in the field of complex exposure suggesting one or more episodes of sediment storage, i.e., deep burial with complete shielding (solid lines left of the steady-state line). (B) In situ $^{14}$C concentrations as a function of deep soil mixing. Instead of burial lines, the shift of the erosion island with increasing mixing depth is illustrated. Calculations are based on Eq. (12) in the Appendix using a substrate density of 2.0 g cm$^{-3}$ for the mixed layer. About 300-500 cm deep mixing would be necessary to generate the measured low in situ $^{14}$C concentrations. (C and D) Recalculations of (A) including a realistic mixing depth (30 cm) and an estimate of a possible maximum depth (100 cm), respectively. For both diagrams, burial lines are given for deep burial with complete shielding (black dashed lines) and shallow burial at ~ 2 m depth (red solid lines). Note that there is no drastic change in burial times between the 30-cm and the 100-cm mixing depth model.
mm ky$^{-1}$ (Zeilinger et al., 2009), respectively, cosmogenic nuclide-derived denudation rates reported for the Rio La Paz basin and the Eastern Cordillera are more than two orders of magnitude higher than $^{10}$Be and $^{26}$Al denudation rates presented here for the eastern Altiplano. These data illustrate a remarkable shift in denudation processes and rates with changing geomorphology within a distance of only a few kilometres. Furthermore, these contrasts exceed by far differences in denudation rates reported for comparable plateau-escarpment settings (Heimsath et al., 2006; Vanacker et al., 2007).

Interestingly, sample 123 indicates that the average large-scale denudation rate on the northern Altiplano is somewhat higher (~ 57 mm ky$^{-1}$) than the rates on the eastern Altiplano margin. As part of the sediment in the Rio Desaguadero is derived from the Western Cordillera, this result might indicate that denudation rates in the Western Cordillera are higher. In fact, a study on denudation in the Chilean Andes has presented cosmogenic nuclide-derived denudation rates of up to 46 mm ky$^{-1}$ for the Western Cordillera, close to the Altiplano (Kober et al., 2007).

### III.2.5.1. Geomorphic parameters and spatial variability of denudation rates

To assess the importance of basin topography on the denudation rates of the individual catchments, surface parameters such as catchment area, elevation, mean hillslope angle, and mean relief were extracted from a DEM. We will discuss denudation rates based on the $^{10}$Be data only, but results presented here are equally applicable for the $^{26}$Al data. In situ $^{14}$C data are not included here because we do not consider the concentration of that nuclide to be primarily controlled by denudation (see discussion below).

The catchments investigated for this study on the eastern Altiplano vary in size by up to two orders of magnitude. However, no influence of catchment area on the denudation rates can be observed (Fig. III.2.7A). The smallest (18-7, 14 km²) and the largest (18-5, 1420 km²) catchments yield similarly low denudation rates (Fig. III.2.3). This shows that as long as mass wasting is absent adequate denudation estimates can be gained even from small basins.

For the majority of catchments that are between 3900-4300 m asl, no correlation between denudation rates and mean basin altitude (Fig. III.2.7B) is indicated. However, overall highest denudation rates were derived from basins at high mean altitudes above ~4300 m asl. Interestingly, the overall lowest denudation rate was obtained for a high elevation catchment (18-4). This is the only catchment that shows a clear glacial modification of the headwaters with glacial valley morphology and moraine deposits ~ 10 km from the drainage divide. Although fluvial-glacial deposits have also been mapped within the upstream areas of catchments 18-2, 18-6, and 25-2 (Fig. 2; GEOBOL, 1991-1994), no obvious trend in the denudation rates of those catchments is observed in our data. Thus, the actual
impact of glaciation on the measured $^{10}$Be or $^{26}$Al concentrations is difficult to evaluate, but seems to be minor.

Mean basin slope is correlated with catchment lithology, more precisely with the percentage of Palaeozoic rocks within a catchment (Fig. III.2.7C, Tab. III.2.1). This indicates a stronger resistance of Palaeozoic formations to weathering and erosion processes resulting in an increase in topography. However, no clear correlation is given between denudation rates and the amount of Palaeozoic rocks. Interestingly, the two highest denudation rates are from catchments with the highest mean basin slopes (24-3 and 24-4; Fig. III.2.7D) implying a more efficient removal of sediment from steeper slopes. On the other hand, for the majority of catchments with mean slopes < 12° there is no obvious correlation between mean basin slope and denudation rates. This suggests that most slope angles are too low to exert a distinct control on denudation rates. These results are supported by similar observations reported from the high-elevation plateau at the Sri Lankan escarpment (Vanacker et al., 2007). Several studies have proposed a linear correlation between denudation rates and mean slope (or local relief) in low-relief, low-gradient settings (e.g., Ahnert, 1970; Montgomery and Brandon, 2002; Ouimet et al., 2009). But this correlation is in most cases defined over a wide range of basins slope or mean relief, which by far exceed the gradients on the Altiplano. From the data presented here, we suppose that only when a certain threshold slope angle is exceeded can an explicit increase in denudation rates be expected. This might be the case for catchments 24-3 and 24-4 whose steeper slopes allow a more efficient transport from the hillslopes. Because the relation between basin mean local relief (calculated over a 1-km-diameter circle) and denudation rate is nearly identical to the one shown for mean basin slope and denudation rate, it is not separately discussed here.

In conclusion, our results show that individual denudation rates are not coupled to interbasin variations in geomorphic parameters because these variations are altogether small. However, the low geomorphic gradients essentially influence sediment routing by limiting sediment transport capacity and facilitate sediment storage.

**III.2.5.2. Temporal stability – cosmogenic nuclide data vs. sediment yield**

To evaluate recent changes of denudation rates on the eastern Altiplano, the cosmogenic nuclide-derived denudation rates are compared with denudation rates inferred from annual sediment discharge measurements. The mass flux (t km$^{-2}$ y$^{-1}$) of suspended material collected at five hydrometrical stations (Fig. III.2.4) in the northern Altiplano and published by Guyot et al. (1990, 1992) was converted into denudation rates assuming a substrate density of 2.6 g cm$^{-3}$ (thus, 2.6 t km$^{-2}$ y$^{-1}$ correspond to 1 mm ky$^{-1}$). The integration time over which these data have been collected is 1-6 years.
Two gauging stations (SU and JJ; Fig. III.2.2) on streams directly draining the eastern Altiplano margin yield denudation rates of 1.9 and 7.8 mm ky\(^{-1}\), respectively. These data are in good agreement with similarly low \(^{10}\)Be and \(^{26}\)Al denudation rates obtained for many of the investigated catchments along the Altiplano margin (Fig. III.2.4). A comparatively high sediment gauging-derived denudation rate of 40.7 mm ky\(^{-1}\) has been recorded for the small Rio Tiwanaku (TI, ~50 km NW of our study area) whose catchment is comparable to most catchments studied here in terms of area, elevation, relief, slope and lithology. Guyot et al. (1992) attributed the high amount of suspended material in the Rio Tiwanaku to the presence of unconsolidated Quaternary sediments, which are easily eroded during floods.
Several catchments investigated in this study are also dominated by Quaternary deposits (e.g., 18-2, 19-1, 25-3) but do not yield higher denudation rates than catchments comprising mainly Palaeozoic rocks (e.g., 24-4, 25-2; Fig. III.2.2). We therefore propose that the increased sediment load observed at Rio Tiwanaku might rather reflect a short episode of larger sediment flux during the time of gauging.

Sediment discharge data from two gauging stations at the Rio Desaguadero yield denudation rates of 21.9 mm ky\(^{-1}\) (CA) north of the inflow of the Rio Mauri and 107.4 mm ky\(^{-1}\) (UL) south of the confluence (Guyot et al., 1990, 1992), respectively. In comparison, the \(^{10}\)Be denudation rate of 57.2 mm ky\(^{-1}\) from sampling point 123 farther downstream lies in-between the two gauging station values.

Altogether, the few available sediment discharge data are in relatively good agreement with the long-term cosmogenic denudation rates, despite the short integration time for sediment gauging and the methodological differences. This supports the assumption that the erosional regime on the eastern Altiplano did not undergo substantial changes since the late Pleistocene. These results further support to our interpretation that the \textit{in situ} \(^{14}\)C concentrations from the Altiplano do not record denudation rates. Single nuclide \textit{in situ} \(^{14}\)C data would suggest a period of strongly increased (~ 20-40 fold) denudation rates starting in the late Holocene. Pollen and sediment records provide evidence for various late Quaternary and Holocene climate changes (Blodgett et al., 1997 and references therein; Baker et al., 2001; Rigsby et al., 2005; Placzek et al., 2006) that could possibly be related to changes in denudation rates. In view of the smooth topography and the transport-limited conditions on the Altiplano, which were probably overall constant during the Holocene, we argue against such a drastic increase in denudation rates during the last few thousand years. Most importantly, if denudation rates in the late Holocene were as high as indicated from a straightforward interpretation of the \textit{in situ} \(^{14}\)C concentrations, rates would have had to decrease rapidly in the last decades to few centuries in order to match the lower modern sediment fluxes again. As we find no evidence supporting this scenario, we propose that the measured \textit{in situ} \(^{14}\)C concentrations actually do not reflect a denudation signal but rather provide information on sediment storage or soil mixing.

\textit{III.2.5.3. Sediment storage and soil mixing}

Fluvial sediment transport on the eastern Altiplano is dominated by episodic events that strongly depend on rainfall. Gravel terraces document episodes of high fluvial capacity (Fig. III.2.3), probably related to periods of increased precipitation. During these events of high discharge, material is removed from the hillslopes and deposited in the flat, floodplain areas commencing some kilometres downstream of the Altiplano margin (Fig. III.2.8). Channels incise the floodplain deposits during
periods of low sediment transport and form an ephemeral fluvial network with temporarily active channels migrating laterally over the floodplain area.

Usually, sediment transfer or floodplain storage times, respectively, cannot be inferred from the concentrations of $^{10}$Be and $^{26}$Al because in most settings residence times are too short to be resolvable by this nuclide pair (cf. Wittmann and von Blanckenburg, 2009). This is also the case for the eastern Altiplano where a simple and continuous exposure/denudation history is suggested from the $^{10}$Be and $^{26}$Al concentrations (Fig. 5). Because the results for *in situ* $^{14}$C do not agree with steady exposure, the *in situ* $^{14}$C concentrations are used as indicators for floodplain storage or soil mixing depth. Two end-member models are illustrated in Fig. III.2.6. The first model (Fig. III.2.6A) ignores soil mixing and interprets the low $^{14}$C concentrations to be entirely caused by sediment storage. Suggested storage times cover the interval from 7.9-10.5 ky until today (complete shielding) and have to be considered minimum estimates. With repeated episodes of sediment storage and reworking and/or burial at shallow depths, i.e. incomplete shielding, calculated storage times would further increase. Importantly, these results are well consistent with the geomorphic and climatic setting of the eastern Altiplano (floodplains, episodic rainfall).

Because denudation on the Altiplano occurs mainly on soil covered hillslopes, the impact of soil mixing on the *in situ* $^{14}$C concentration has to be taken into account as discussed in section III.2.4.2. In the simplest case of no sediment storage, *in situ* $^{14}$C concentrations can be directly converted into soil mixing depths that, for samples studied here, would correspond to depths of 300-500 cm (Fig. III.2.6B). This seems unreasonably large compared to field observations that indicate typical soil depths in the range of 20-30 cm or less. These estimates are similar to soil depths reported from comparable settings in central Peru and northern Chile (Wilcox et al., 1988; Owen et al., 2010). Because a 30-cm-deep, well-mixed soil is not sufficient to produce such low *in situ* $^{14}$C concentrations (Fig. III.2.6B) a combination of soil mixing and sediment storage is most likely. Including a 30-cm-deep mixed layer on the hillslopes into the sediment storage model results in only slightly shorter floodplain storages times compared to the no-mixing scenario (7.0-9.8 ky vs. 7.9-10.5 ky; Fig. III.2.6C). For comparison, a mixing depth of 100 cm, which we consider a maximum estimate for the eastern Altiplano, still yields sediment storage for 4.6-7.4 ky (Fig. III.2.6D). These models assume complete shielding, i.e., deep burial, of the sediment during residence on the floodplain. However, channels in the study area do not incise deeply and usually do not excavate sediment from more than ~ 2-m depth. Such shallow storage would increase the residence time by ~ 40-50% (assuming a single storage episode; Figs. III.2.6C and D) because of further low *in situ* $^{14}$C production during storage.
Altogether, we suppose that the solution given in Fig. III.2.6C, i.e., 30-cm mixed soil on the hillslopes and shallow sediment storage on the floodplain, is the most realistic reflection of the environmental conditions on the eastern Altiplano. Comparing Fig. III.2.6C to Fig. III.2.6A shows that, in this case, nuclide decay during sediment storage is the critical element controlling the in situ $^{14}$C concentrations. Although soil mixing has only a minor influence on the samples studied here, the discussion above illustrates that in other settings in situ $^{14}$C could be applied to investigate the actual degree of mixing within soils.

While all storage times presented here are minimum estimates assuming a single, recent sediment cycle, several periods of sediment storage and reexposure may be more likely and would lead to even longer residence times. Notably, sediment storage does not have to be restricted to the floodplain or alluvial fan area surrounding the sampling site. As shown on the example of catchment 24-6, gently sloping channel reaches in the upstream area provide further potential sites for sediment deposition (Fig. III.2.8).

### III.2.6. Summary and conclusions

Geomorphology and climate define denudation on the Bolivian eastern Altiplano by controlling the dynamics of erosional processes and the transport capacity of the fluvial system. Our analyses of cosmogenic $^{10}$Be and $^{26}$Al in fluvial sediments show consistently low denudation rates on the order of $\sim 3$-$29$ mm ky$^{-1}$ that reflect slow sediment production on the hillslopes along the Altiplano margin (Fig. III.2.8). These denudation rates are one to two orders of magnitude lower than in the adjacent Rio La Paz basin and the Eastern Cordillera and coincide with a sharp contrast in geomorphology and denudation processes. Although the formation of topographic highs along the Altiplano–Rio La Paz drainage divide might result from isostatic compensation centered in the Rio La Paz basin (Zeilinger and Schlunegger, 2007), denudation processes on the eastern Altiplano appear to be largely disconnected from the rapid, tectonically controlled processes in the Rio La Paz basin.

Denudation rates in the individual catchments studied here vary by more than one order of magnitude. However, no clear correlation between local denudation rates and variations in geomorphic basin parameters (relief/slope/basin area) can be observed. This might result from the overall low topographic gradients in the study area. There is a good agreement between cosmogenic nuclide-derived denudation rates obtained from the long-lived nuclides $^{10}$Be and $^{26}$Al and modern sediment discharge data. These data suggest that the rate at which sediment is removed from the eastern Altiplano today is of the same order as the rate of sediment production by hillslope denudation since the latest Pleistocene. While for the central Andean fold-thrust belt a significant increase in denudation rates during the Holocene was
Figure III.2.8. Relief map (ASTER GDEM Version 1, METI and NASA) of the southern part of the study area illustrating local topography and geomorphic processes on the eastern Altiplano (top) as well as the topographic contrasts between the Altiplano and the Rio La Paz drainage basin (bottom). The catchment of sample 24-6, for which all three cosmogenic nuclides were analysed, is highlighted. The colour coding allows to differentiate between sediment-producing hillslopes along the Altiplano–Rio La Paz drainage divide and the flat, low elevation areas at the transition to the floodplain. The small inset gives channel profiles for the eastern and western main reaches within that catchment. Vertical, red dashed lines mark channel segments with very low channel slope angles (< 2°), which could present possible domains for sediment storage. Note that the eastern reach of catchment 24-6 exhibits such low slopes also along an upstream channel segment, proposing that sediment storage does not necessarily have to be restricted to the area close to the sampling site. With crossing the drainage divide toward the Rio La Paz watershed, relief and local slope strongly increase.
suggested (Insel et al., 2010), data from the eastern Altiplano do not record any temporal variation in denudation rates. Altogether, our results point at a long-term (~$10^5$ y) geomorphic and isotopic ($^{10}$Be, $^{26}$Al) steady-state for the eastern Altiplano.

Concentrations of in situ cosmogenic $^{14}$C do not give information about catchment-wide denudation rates but provide evidence for sediment storage on the eastern Altiplano. The low in situ $^{14}$C concentrations are in agreement with at least one episode of sediment storage and partial shielding lasting through most of the Holocene or even up to ~20 ky (Fig. III.2.6C). However, several periods of storage and reworking during sediment routing through a catchment are even more likely. Most importantly, results are consistent with the geomorphic setting of the eastern Altiplano and the episodically occurring fluvial processes. This study proves that over comparatively short distances (several kilometres, see Fig. III.2.8) sediment storage can be an important element in low gradient landscapes. Moreover, it illustrates that in situ $^{14}$C is a valuable tool to investigate sediment routing within fluvial systems as it gives fundamental information on the sediment flux and residence time.

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Appendix

Determining the cosmogenic nuclide concentration in an eroding, well-mixed soil layer

The development of the cosmogenic nuclide concentration within a bioturbated, well-mixed soil or regolith layer of constant thickness has been described in detail by Brown et al. (1995), Lal and Chen (2005), and Granger and Riebe (2007) and is given by:

$$\frac{d\langle N \rangle}{dt} = \langle P \rangle - \langle N \rangle \lambda - \langle N \rangle \frac{e}{\rho x} + N(x) \frac{e}{\rho x}$$

(9)

where $\langle N \rangle$ is the mean nuclide concentration within the mixed layer and is a function of the average production rate $\langle P \rangle$ over the entire mixing depth $x$. Nuclides are lost from the mixed layer by denudation $(\epsilon)$ and radioactive decay $(\lambda)$ but also added by the incorporation of material from below with a concentration $N(x)$ and with a rate $(\epsilon)$ equal to the denudation rate. Moreover, mixing is assumed to be rapid so that the nuclide concentration is uniform over the entire mixed layer.

The mean production rate $\langle P \rangle$ and the nuclide concentration $N(x)$ at the top of the unmixed parent material can be derived from the local surface production rate $P(0)$ by (Brown et al., 1995):

$$\langle P \rangle = \sum_i P_i(0) \frac{A_i}{\rho x} \left(1 - e^{-\rho x/A_i}\right)$$

(10)

and

$$N(x) = \sum_i \frac{P_i(0)}{\lambda + \rho \rho A_i} e^{-\rho x/A_i} \left(1 - e^{-t(\lambda + \rho \rho A_i)}\right)$$

(11)

The subscript $i$ denotes the different production pathways of nucleonic and muonic nuclide production. Coefficients given in Schaller et al. (2002) were used for depth scaling of the surface production rate. Solving Eq. (9) for $\langle N \rangle$ yields the expression below (Eq. 12), which has been modified after Brown et al. (1997) and Schaller et al. (2009):

$$\langle N \rangle = \sum_i \left(\frac{A_i \rho x/A_i}{A_i - \rho x}\right) \left[P_i(0) \frac{1}{\lambda + \rho \rho A_i} \left(1 - e^{-t(\lambda + \rho \rho A_i)}\right)\right]$$

$$+ \sum_i \left(1 - \frac{A_i \rho x/A_i}{A_i - \rho x}\right) \left[P_i(0) \frac{1}{\lambda \rho x/A_i + \rho \rho A_i} \left(1 - e^{-t(\lambda + \epsilon x)}\right)\right]$$

(12)

Eq. (12) was used in this study for all calculations involving in situ $^{14}$C and for the modelling of Fig. III.2.6 (A-D).
IV. Applications
Part 2 – Surface exposure dating in the Swiss Alps

IV.1. An introduction into the Quaternary glaciation of the Alps

This chapter provides an introduction into the second application study of this dissertation that deals with surface exposure dating in the Swiss Alps. It gives a review of the Alpine glacial history with focus on the Last Glacial Maximum (LGM) and the Lateglacial period. This chapter is intended to summarize the geochronological work that has been done in the Alps and present a wider chronological framework for the interpretation of the exposure ages obtained from the Gotthard Pass (Section IV.2).

* All cosmogenic \(^{10}\)Be data shown in the following are quoted as given in the original publication.

For comparison with the data presented in Section IV.2 and in view of the current re-evaluation of the \(^{10}\)Be production rate, published \(^{10}\)Be ages were recalculated using a \(^{10}\)Be spallogenic production rate of 3.93 ± 0.19 at g\(^{-1}\)yr\(^{-1}\) (Northeast North America calibration data of the CRONUS-Earth online calculator; Balco et al., 2008). Recalculated exposure ages (Lal, 1991; Stone, 2000, scaling scheme) are given in parentheses and do not include corrections for erosion or snow, even if these were applied for the original ages. For \(^{10}\)Be results measured at ETH data were renormalized to the S2007N standard used today (calibrated to 07KNSTD; Kubik and Christl, 2010). The \(^{10}\)Be half-life of 1.387 ± 0.012 My was used (Chmeleff et al., 2010; Korschinek et al., 2010).

If not stated otherwise, radiocarbon ages have been recalibrated using the OxCal online program (OxCal 4.1, IntCal 09 curve; Bronk Ramsey, 2009; Reimer et al., 2009).

IV.1.1. The global glacial record

The Quaternary period spanning the last 2.6 My has often been considered a synonym for the last glacial phase of the Cenozoic. However, already in the Late Eocene glaciation began in eastern Antarctica (Ingólfsson, 2004; Trapati et al., 2005). In the Miocene/Pliocene ice caps expanded on both hemispheres and covered the mountain areas in the southern and northern high latitudes (Fig. IV.1.1) (Ehlers and Gibbard, 2007). By the early Pleistocene extensive ice sheets existed on the North American continent, Greenland and Northern Europe/Asia. Glaciers reached their maximum extent by the Middle Pleistocene expanding southward beyond 40\(^\circ\)N latitude. At that time extensive mountain ice and large piedmont glaciers also expanded in the Alpine region (Ehlers and Gibbard, 2007).

Polar ice cores and marine sediment cores have provided a continuous and global climate dataset dating back into the Lower Pleistocene (e.g. Emiliani, 1955; Shackleton, 1967; GRIP members, 1993; EPICA community members, 2004;
Rasmussen et al., 2008). Based on the δ^{18}O from benthic foraminifera, that records changes in ice volume and identifies cycles of warm and cold temperature in the Earth's paleoclimate, the global stratigraphic scheme of Marine Isotopic Stages (MIS) was developed (Emiliani, 1955; Shackleton, 1967; Shackleton and Opdyke, 1977). It could be shown that the pattern of Pleistocene glacial-interglacial climate changes is caused by cyclic variations in the Earth’s orbit (‘Milankovitch cycles’) (Milankovitch, 1941; Hays et al., 1976; Imbrie and Imbrie, 1980).

Figure IV.1.1. Climate development from the early Cenozoic warm climate to the Quaternary cold climate, documented by changes in deep-sea oxygen isotope records based the analyses of benthic foraminifera. Figure from Zachos et al. (2001).
IV.1.2. Alpine glaciations

At the beginning of the 20th century, Penck and Brückner (1901/1909) divided the Pleistocene glacial advances in the Alps into four main stages: Günz, Mindel, Riss, and Würm (in chronological order). This division was based on field relations of distinct foreland deposits in Bavaria, southern Germany, including gravel deposits (‘Deckenschotter’) interpreted as glacial outwash, moraine remnants and till deposits (Penck and Brückner, 1901/1909; van Husen, 2000; Preusser et al., 2011). According to this fourfold scheme, the most extensive Pleistocene glaciation (sometimes termed ‘MEG’; Schlüchter, 2004) is most commonly assigned to the Rissian glacial (van Husen, 2000, 2004; Dehnert et al. 2010). However, the timing of the maximum glacial extent into the Alpine foreland might have differed locally. For example, in some areas of the Bavarian Alpine foreland the maximum glacial advance during Mindel and Günz is thought to have outreached the maximum Rissian extent by some kilometres (Doppler et al., 2011 and references therein).

After one century of intensive research on the glacial history of the Alps the original classification of Penck and Brückner (1901/1909) has been significantly refined and modified. Based on lithostratigraphic units established for the northern foreland of the Swiss Alps Schlüchter (1988) proposed at least 15 Quaternary glaciations reaching into the Alpine foreland. Summarizing field evidence and chronological data, Preusser et al. (2011) reported evidence for at least eight lowland glaciations during the Quaternary in northern Switzerland.

During the Pleistocene maximum glaciation glacial outlets are recorded from 5°E in the western Alpine foreland (Campy, 1992; Buoncristiani and Campy, 2004) to beyond 15°E in the eastern Austrian Alps (van Husen, 2004) (Fig. IV.1.2). Terminal moraines that are associated with the maximum (Rissian) glacial advance were identified in most regions of the Alpine foreland (Campy, 1992; Muttoni et al., 2003; Castiglioni et al., 2004; Schlüchter, 2004; van Husen, 2004; Doppler et al., 2011). Substantial glacial erosion is recorded by the occurrence of overdeepened main Alpine valleys (van Husen, 2004 and references therein). These have usually been correlated to the Rissian glaciation but sedimentary deposits point at a formation during even older glacial events (Schlüchter, 1986).

The Rissian glacial stage was followed by the Eemian interglacial (Fig. IV.1.3) that is considered equivalent to the marine isotope stage (MIS) 5e (Mangerud et al., 1979; Shackleton et al., 2003 and references therein). Starting about 130 ky BP and culminating by 125 ky BP (Imbrie et al., 1984) the Eemian was characterized by up to 5°C warmer temperatures and a several metres higher sea level than at present (e.g. Cuffey and Marshall, 2000; Kukla, 2000; NGRIP members, 2004). There are diverging records on the climatic stability, and the possibility of strong regional variations has been proposed (e.g. Dansgaard et al.
1984, Anderson et al. 1991, GRIP members 1993, Johnsen et al. 1995). With rapid cooling events a sharp shift in the Earth’s climate towards a cool glacial environment began around 116 ky BP (Kukla et al., 2002). In the Alps, a dramatic change in vegetation with the replacement of deciduous forests by a tundra-like vegetation marked the beginning of the Würmian glacial stage (MIS 5d; equivalent to the term ‘Weichselian’ stage of northern Europe) (Welten, 1981; Drescher-Schneider, 2000; Müller et al., 2003). Optically stimulated luminescence (OSL) dating of delta sediments and of glaciofluvial deposits in northern Switzerland documents an early advance of glaciers down into the Swiss Alpine foreland already during the early Würmian (Preusser et al., 2003; Preusser and Schlüchter, 2004). This is in agreement with vegetation reconstruction from pollen analyses that indicate cold but humid conditions (Welten, 1981; Wegmüller, 1992). However, there is no evidence for a similar early Würmian glacial advance into the eastern Alpine valleys (van Husen, 2004; Spötl and Mangini, 2006).

Based on pollen records at least two major interstadial phases (Brørup, Odderade) are documented for the Early Würmian (cf. Preusser, 2004). The subsequent switch to cold conditions after the second interstadial is by definition of the Subcommission on European Quaternary Stratigraphy (SEQS) the transition to the Middle Würmian stage (MIS 4/3) (Chaline and Jerz, 1984). Glacier readvance down into the Alpine lowlands was suggested for the Western Alps (Schlüchter, 1991; Keller and Krayss, 1998; Preusser et al., 2007) but no such evidence is found for the Eastern Alps (van Husen, 2004). The cold climate of the early Middle Würmian was replaced by mild conditions during the third Würmian interstadial (Dürnten) (Spötl and Mangini, 2002; Preusser, 2004). The stratigraphic position of the Dürnten interstadial is, however, debated and some palynologists prefer a placement into the Early Würmian (e.g. Welten, 1982, 1988; Wegmüller, 1992; Müller et al., 2003). Similar to the two first interstadials, the vegetation was characterized by coniferous forests but the overall climate was probably less temperate than during the Early Würmian interstadials (Welten, 1982; Wegmüller, 1992; Grüger and Schreiner, 1993). Maximum summer temperatures of up to 13°C and minimum winter temperatures of -10°C were reconstructed based on the interpretation of beetle fauna (Coleoptera) from the Swiss foreland (Jost-Stauffer, 2001, 2005; Coope, 2007). Palynological and paleontological evidence as well as radiocarbon, U/Th, and luminescence dating suggest an overall unstable climate during the Middle Würmian (MIS 3) with cool to temperate conditions but no glacial advances into the Alpine lowlands until the Late Würmian (e.g. Schlüchter et al., 1987; Jost-Stauffer, 2001; Müller et al., 2003; Preusser et al., 2003, Coope, 2007). Greenland ice-cores document large climate fluctuations during MIS3 characterized by cycles of slow cooling and rapid warming (Dansgaard-Oeschger-
Comparable climate fluctuations are seen in the oxygen isotope record of high-elevation speleothems from the central Austrian Alps (Spötl et al., 2006). From U/Th-dating it was suggested that speleothems grew around ~56-48 ky BP during the presence of warm-based glaciers (Spötl and Mangini, 2002; Spötl et al., 2006).

**IV.1.3. The Last Glacial Maximum**

The Late Würmian (MIS 2) is the time of maximum ice extent during the last glacial cycle and is therefore commonly referred to as the ‘LGM’ (Last Glacial Maximum). Globally, a rapid drop in sea level is associated with the build-up of ice volumes at the onset of the LGM (Lambeck et al., 2002a). Sea level remained low (~120-130 m lower than today) from ~30-19 ky BP followed by a rapid sea level rise (Yokoyama et al., 2000; Mix et al., 2001 and references therein; Lambeck et al., 2002b). In Greenland, LGM minimum temperatures inferred from ice cores were about 20°C colder than at present (Dahl-Jensen et al., 1998; Johnsen et al., 2001;
Masson-Delmotte et al., 2006). Regional differences have been reported for the timing at which the large northern hemisphere ice sheets reached their maximum extent. A rapid advance to the maximum LGM position by ~27-24 14C ky BP (~31-29 cal. ky BP) has been proposed for the Laurentide Ice Sheet (Dyke et al., 2002) while the British and Scandinavian ice sheets reached their maximum extent between ~27-23 cal. ky BP (Bowen et al., 2002; Marks, 2002; Olsen, 2002). In general, the size of the LGM ice sheets in the northern hemisphere was similar as during the mid-Pleistocene glacial maximum (Ehlers and Gibbard, 2007), although in some regions of Europe ice sheets remained smaller during the LGM (e.g. Giraudi, 2004; Woodward et al., 2004).

In the high Alps large precipitation-controlled ice domes were proposed to have formed during the LGM (Florineth and Schlüchter, 1998, 2000). These domes provided the source for the ice streams flowing into the main valleys and the foreland and controlled the transfluent ice flows over the high Alpine passes (Florineth and Schlüchter, 1998, 2000; Schlüchter, 2004). Trimlines and glacial erosional markers have been mapped in the Central Alps to reconstruct LGM ice elevations and broad ice flow patterns (Florineth and Schlüchter, 1998, 2000). In the foreland, glacial advances are indicated from sequences of glacial outwash and the deposition of moraine ridges and erratic boulders (cf. Schlüchter, 2004).

Various dating methods have been applied to obtain a temporal record of the last glacial cycle in the Alps. Sediment sequences were chronostratigraphically classified by radiocarbon dating of organic material, e.g. bones or peat, embedded in the sediment profile (e.g. Schlüchter et al., 1987; Keller and Krayss, 1998; Hajdas et al., 2007) and/or OSL dating (e.g. Preusser et al., 2003; Preusser and Schlüchter, 2004). Furthermore, compressed peat deposits (‘Schieferkohle’) formed during interglacial times in the northern Alpine foreland have been dated with the U/Th method (Wegmüller, 1992). In the last two decades, cosmogenic nuclide surface exposure dating has been used increasingly to date moraine deposits, erratic boulders and bedrock surfaces. Obtained data provided age information on the stabilization of moraine crests and the downwasting of glaciers in the Alpine foreland (Ivy-Ochs et al., 2004, 2006b; Reuther, 2007; Federici et al., 2011) as well as on the deglaciation of the high Alps (Kelly et al., 2006; Böhlert et al., 2011).

Radiocarbon ages from the Eastern Alps and their foreland valleys show ice free conditions until no later than ~ 29-30 cal. ky BP (summarized by Starnberger et al., 2011). This is consistent with results from radiocarbon and luminescence dating suggesting that the LGM started by ~ 29 cal. ky BP (Fliri, 1989; de Graaff, 1992; Starnberger et al., 2011). For the southern Alpine foreland (Italy) two pulses of
LGM glacial expansion have been suggested (Monegato et al., 2007). The beginning of glacial advance was dated to $27.1 \pm 0.4 \text{^14C\,ky\,BP}$ ($32.4-30.9$ cal. ky BP). The first maximum was reached by $~ 22-21 \text{^14C\,ky\,BP}$ ($~ 26.5-25$ cal. ky BP) followed by a readvance at $~ 20-17.5 \text{^14C\,ky\,BP}$ ($~ 24-21$ cal. ky BP) (Monegato et al., 2007). In the Inn Valley of the Eastern Alps the beginning glacial advance recorded by fluvioglacial aggradation was dated to $31.6 \pm 1.3 \text{^14C\,ky\,BP}$ ($40.2-34.0$ to $34.8-29.4$ cal. ky BP) (Fliri et al., 1970; Fliri, 1973). An age of $22.0 \pm 1.1 \text{^14C\,ky\,BP}$ ($29.3-24.0$ cal. ky BP) is associated with the maximum extent of the Inn Glacier (Habbe et al., 1996). Further radiocarbon data for the Austrian Alps yielded comparable ages indicating that glaciers had reached the main longitudinal valley by $~ 25-24 \text{^14C\,ky\,BP}$ ($~ 30-28.5$ cal. ky BP) and approached maximum extent around $21 \text{^14C\,ky\,BP}$ ($~ 25$ cal. ky BP) (van Husen, 2004).

In the Swiss Alps, dating of a cave bear provides evidence for ice free conditions at an elevation of $1800$ m at $~ 32 \text{^14C\,ky\,BP}$ ($~ 36.5$ cal. ky BP) (Morel et al., 1997). In the Rhone valley, glacial expansion is dated at $25.4 \pm 0.2 \text{^14C\,ky\,BP}$ ($30.6-29.6$ cal. ky BP) from a mammoth tusk retrieved from fluvioglacial sediments deposited by the advancing Rhone Glacier (Schlüchter, 2004). This timing is also supported by luminescence dating (Preusser et al., 2007). A chronology for the Rhine-Linth glacier compiled (and calibrated) by Keller and Krass (2005) marks the timing of glacier advance from the inner Alpine valleys at $~ 28$ cal. ky BP and defines a maximum extent at $~ 24$ cal. ky BP. An age of $28.1 \pm 0.3 \text{^14C\,ky\,BP}$ ($33.2-31.5$ cal. ky BP) was obtained from ‘Schieferkohle’ found below basal till of the Linth/Rhein Glacier in Zürich area (Schlüchter and Röthlisberger, 1995).

The LGM climate in the northern Alpine foreland was cold and dry with low mean annual temperatures about $10-12^\circ\mathrm{C}$ colder than at present (Frenzel et al. 1992). From the chronology above it is shown that the LGM in the Alps occurred contemporaneously with the global LGM as recorded by low sea levels (e.g. Yokoyama et al., 2000; Mix et al., 2001; Lambeck et al., 2002a) and Greenland temperatures (Stuiver and Grootes, 2000; Johnsen et al., 2001; Masson-Delmotte et al., 2006).

IV.1.4. The Alpine Lateglacial

The Alpine Lateglacial is defined as the time period between deglaciation of the Alpine foreland and the beginning of the Holocene. It was a phase of gradual warming and glacial downwasting but climate was fluctuating and short cold phases repeatedly interrupted the general warming trend (e.g. Dansgaard et al., 1993; Reitner, 2007; Vescovi et al., 2007). In the Alps, the Lateglacial is divided into a number of stadials first specified by Penck and Brückner (1901/1909) but repeatedly revised later on (Maisch, 1982, 1987; Kerschner, 1978, 2009; Reitner, 2007). These
stadials reflect episodes of glacier halt or readvance and moraine deposition that interrupt the stepwise deglaciation (Ivy-Ochs et al. 2006a, 2008; Reitner, 2007). From investigations in the area of the former Inn Glacier tongue, Reitner (2007) proposed to abandon the concept of the early Lateglacial stadials (‘Bühl’ and ‘Steinach’) and define the period after the LGM as ‘phase of early Lateglacial ice decay’. The chronology from the LGM until today is illustrated in Figure IV.1.3.

Deglaciation of the Alps has probably occurred rapidly with the glacial retreat from the foreland closely followed by the downwasting of ice in the Central Alps (Schlüchter, 1988 and references therein; van Husen, 2000). Cosmogenic nuclide ages from a terminal moraine in northern Switzerland suggest that the maximum extent of the Rhône Glacier was reached just prior or at 21.1 ky (23.5 ky*) and that deglaciation in the foreland began by that time. By 19.1 ky (21.5 ky*) the outermost position was completely abandoned (mean ages; Ivy-Ochs et al., 2004). This correlates well with the global timing of sea level rise triggered by the rapid decay of the continental ice sheets (Yokoyama et al., 2000; Clark and Mix, 2000; Mix et al., 2001; Lambeck et al., 2002a). Lacustrine sediments from the Northern Alpine foreland suggest ice-free conditions by 14.6 ± 0.3 14C ky BP (18.5-17.2 cal. ky BP) (Lister, 1988; Wessels, 1998). Ice-free lowlands during the Oldest Dryas are further confirmed by a number of Palynological studies (Welten, 1982; Ammann et al., 1994 and references therein; Wohlfarth et al., 1994). An age of 14.0 ± 0.3 14C ky BP (17.8-16.6 cal. ky BP) reported from the Inn Valley (Bortenschlager, 1984) is interpreted as a minimum age for deglaciation. Further studies from the Austrian Alps propose a complete deglaciation of the inneralpine valleys already by 15.5 ± 0.2 14C ky BP (19.3-18.5 cal. ky BP) (Schmidt et al., 2002; Reitner, 2007 and references therein). OSL dating of Eastern Alpine delta sediments associated with the early Lateglacial ice decay provided an age of 18.7 ± 1.7 ky BP (Klasen et al., 2007).

Numerous radiocarbon, fossil and pollen data from the Southern Alps propose climate warming at ~ 18.0-17.5 cal. ky BP (summarized and calibrated by Vescovi et al., 2007). A warm episode at ~ 14.7 14C ky BP (~ 18.5-17.5 cal. ky BP) is also recorded in the GRIP Greenland ice core (Björk et al., 1998) and might have immediately preceded glacier readvances of the Gschnitz stadial (Ivy-Ochs et al., 2008). In the Austrian Alps, early glacier readvances are constrained by a maximum radiocarbon age of 15.4 ± 0.5 14C ky BP (19.6-17.6 cal. ky BP) (Draxler, 1977) and a minimum 10Be age of 15.4 ± 1.4 ky (17.3 ky*) (Ivy-Ochs et al., 2006a). Following major downwasting after the Gschnitz stadial, several readvances were observed from a series of moraine deposits at different locations in Switzerland and Austria (Kerschner and Berktold, 1982; Maisch, 1982). These are attributed to the Clavadel/Senders stadial and the subsequent Daun stadial (Fig. IV.1.3).
At about 14.7-14.5 ky BP the Bølling/Allerød interstadial commenced with a significant increase in temperature (4-6°C in Europe) and distinct changes in the biosphere (Vescovi et al., 2007 and references therein). Oscillations in the isotope record of Greenland ice cores and of Swiss lake sediments as well as lake level fluctuations recorded in the Alpine foreland reflect the variability in climate conditions during the Bølling/Allerød interstadial (Magny, 2001 and references therein). An abrupt vegetational change at 10.8 ± 0.2 14C ky BP (13.1-12.2 cal. ky BP) is attributed to the beginning of the cold Younger Dryas period in the Alps (cf. Vescovi et al., 2007). Younger Dryas temperature estimates derived from relict rock glaciers suggest a lowering of the mean annual air temperature by 3-4°C and a 30-40% reduction of precipitation in the south-eastern Swiss Alps (Frauenfelder et al., 2001). A radiocarbon-varve chronology established at the Lake Soppensee in the Northern Alpine foreland places the Younger Dryas at 12.1-11 cal ky BP (Hajdas et al., 1993; calibrated by these authors). The Younger Dryas cold phase lasted about 1100-1300 years (Muscheler et al., 2008 and references therein) and led to glacier advance and build-up of Egesen stadial moraines throughout the Alpine valleys (Kerschner et al., 2000; Frauenfelder et al., 2001).

Cosmogenic nuclide dating of Egesen stadial moraine complexes in the Central, Eastern and Maritime Alps have provided similar 10Be mean dates of ~ 12.3-11.2-ky (~ 14.1-12.8 ky*) which are interpreted as moraine stabilization ages (Ivy-Ochs et al., 1996, 1999, 2006b; Kelly et al., 2004a; Federici et al., 2007; Hormes et al., 2008). These are in good agreement with pollen analyses and radiocarbon data of peat bogs in the Austrian Alps that suggest a minimum age of 10.2 ± 0.2 14C ky BP (12.1-11.3 cal. ky BP) for the Egesen advance of the Ötztal Glacier (Bortenschlager, 1984). Final downwasting of Egesen glaciers is suggested by ~ 11 ky BP (Ivy-Ochs et al., 2008 and references therein).
Figure IV.1.3. Chronology and climate variability of the last glacial cycle in the Alps and the correlation to global climate evidence.

Left: Changes of the mean annual temperature in the Swiss Alpine foreland compared to present temperatures (second half of 20th century), modified from Keller and Krayss (2005). Alpine glacial chronology from Ivy-Ochs et al. (2008 and references therein), marine isotope stages from Martinson et al. (1987) and Shackleton et al. (2002).

Middle: Global climate changes as recorded from oxygen isotopes in benthic foraminifera preserved in deep sea sediment cores. Chronostratigraphy developed by Martinson et al. (1987).

Right: A more detailed chronology for the Lateglacial stage plotted together with the oxygen isotope curve from Greenland ice cores as another proxy for global climate changes. Glacial stadials after Ivy-Ochs et al. (2009). δ¹⁸O data from Rasmussen et al. (2006), Andersen et al. (2006), Vinther et al. (2006).
Moraines found in the Ferwall Group, Austria, define the ‘Kartell stadial’ (Fraedrich, 1979). $^{10}$Be ages from boulders at the Kartell site provide minimum ages for moraine deposition of $11.2 \pm 0.8$ to $10.4 \pm 0.5$ ky (12.3-11.6 ky*) placing the glacial advance into the earliest Holocene (Ivy-Ochs et al., 2006b). Contemporaneously, a short readvance of the Palü Glacier in Central Switzerland occurred during mid-Preboreal after $9.5 \pm 0.1$ $^{14}$C ky BP (11.7-10.3 cal. ky BP) (Zoller et al., 1998). $^{10}$Be ages of $10.4 \pm 0.8$ to $10.0 \pm 0.8$ ky (12.0-11.5 ky*) obtained for rock glaciers in the Austrian Alps are another indicator for a still cold earliest Holocene (Kerschner and Ivy-Ochs, 2008; Ivy-Ochs et al., 2009).

Around 10.5 ky a rapid downwasting of the Alpine glaciers marks the beginning of the pronounced Holocene warming (cf. Ivy-Ochs et al., 2009). The overall warm Holocene climate was repeatedly interrupted by rapid climate changes that are recognized from various proxies in the Alpine region and globally (e.g. Denton and Karlén, 1973; Haas et al., 1998; von Grafenstein et al., 1999; Maisch et al., 1999; Heiri et al., 2003; Tinner and Theurillat, 2003; Mayewski et al., 2004; Joerin et al., 2005). Glaciers remained generally small during the early and middle Holocene although some minor advances of short duration have been identified (Patzelt, 1972; Maisch et al., 1999; Ivy-Ochs et al., 2009 and references therein). Surface exposure dating of boulders from the Kromer valley in the Austrian Alps suggest a pronounced middle Holocene glacier advance (Kerschner et al. 2006) that might have occurred simultaneously to a rapid global cooling event around 8.2 ky BP (Alley et al., 1997; Tinner and Lotter, 2001; Rohling and Pälike, 2005).

Climate started getting colder around 4 ky BP and glaciers readvanced frequently. Between the 16th and the mid-19th century a cold period known as the ‘Little Ice Age’ (LIA) caused the most extensive recent glacial expansion (Mann, 2002). The European continent and other regions around the North Atlantic were most strongly affected by climate cooling (Dahl-Jensen et al., 1998; Broecker, 2001). In the Alps, where the LIA has been studied in most detail, at least three main periods of maximum glacier advance are recorded from moraines and rock glaciers (Grove, 2001; Zasadni, 2007, and references therein). Most Alpine glaciers reached their latest maximum during the first half or by the middle of the 19th century and retreated shortly afterwards with a progressively warming climate (e.g. Holzhauser, 1982; Holzhauser et al. 2005; Joerin et al., 2006).
IV.2. Chronology of Lateglacial ice flow reorganization and deglaciation in the Gotthard Pass area, Central Swiss Alps, based on cosmogenic $^{10}$Be and in situ $^{14}$C

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ABSTRACT

We reconstruct the timing of ice flow reconfiguration and deglaciation of the Central Alpine Gotthard Pass, Switzerland, using surface exposure dating with $^{10}$Be and in situ $^{14}$C. Combined with detailed mapping of glacial erosional markers, exposure ages of bedrock surfaces reveal a progressive glacier downwasting from the maximum LGM ice volume and a gradual reorganization of the paleoflow pattern with a southward migration of the ice divide. Exposure ages of ~16-14 ky (snow corrected) give evidence for continuous early Lateglacial ice cover and indicate that the first deglaciation was contemporaneous with the decay of the large Gschnitz glacier system. In agreement with published ages from other Alpine passes, these data support the concept of large transection glaciers that persisted in the high Alps after the breakdown of the LGM ice masses in the foreland and possibly decayed as late as the onset of the Bølling warming. A younger group of ages around ~12-13 ky records the timing of deglaciation following local glacier readvance during the Egesen stadial. Glacial erosional features and the distribution of exposure ages consistently imply that Egesen glaciers were of comparatively small volume and were following a topographically controlled paleoflow pattern. Dating of a boulder close to the pass elevation gives a minimum age of 11.2 ± 0.5 ky for final deglaciation by the end of the Younger Dryas. In situ $^{14}$C data are overall in good agreement with the $^{10}$Be ages and confirm continuous exposure throughout the Holocene. However, in situ $^{14}$C demonstrates that partial surface shielding, e.g. by snow or till, has to be incorporated in the exposure age calculations and the model of deglaciation.

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IV.2.1. Introduction

Reconstructing the extent and dynamics of past glaciers provides valuable information on paleoclimate conditions. The extent of a glacier is determined by the mass balance, which is largely controlled by climate. Variations in the ice volume and glacial expansion therefore give evidence for paleoclimate changes (Oerlemans et al., 1998; Oerlemans, 2001). Being comparatively small ice bodies, Alpine glaciers are particularly sensitive paleoclimate indicators that respond rapidly to changes in temperature and/or precipitation (Kerschner, 2005).

The onset of the Alpine Lateglacial is defined as the time of massive downwasting of the large valley glaciers built up during the Last Glacial Maximum (LGM; late Würmian) (Penck and Brückner, 1901/1909; Reitner, 2007). Deglaciation of the Alps is thought to have occurred rapidly with retreat of the foreland piedmont glaciers closely followed by the disintegration of the Central Alpine ice cap (Florineth and Schlüchter, 1998; Schlüchter, 2004). Although climate was warming gradually, short climatic fluctuations and cold phases repeatedly interrupted the general trend of ice decay (e.g. Reitner, 2007; Schmidt et al., 2011). These fluctuations are associated with several Lateglacial stadials determined by glacier stillstands and readvances before the beginning of the Holocene warming (Ivy-Ochs et al., 2008 and references therein).

Classically, former extents of Alpine glaciers and related climate changes have been dated by radiocarbon from organic material, mainly retrieved from glacial deposits in the Alpine foreland (e.g. Heuberger, 1966; Patzelt, 1972; Fliri, 1973; Draxler, 1977; Bortenschlager, 1984; Geyh and Schreiner, 1984; Kerschner, 1986; Hajdas et al., 1993; Schlüchter and Röthlisberger, 1995; van Husen, 2004; Keller and Krayss, 2005; Reitner, 2007 and references therein). These data are synchronized with relative chronologies constructed from morpho- and lithostratigraphic observations and fossil and pollen evidence (e.g. Penck and Brückner, 1901/1909; Keller and Krayss, 1987; Ammann et al., 1994; Wohlfarth et al. 1994; van Husen, 2000; Vescovi et al., 2007; Preusser et al. 2011; van Husen and Reitner, 2011). In the last two decades, direct dating of glacial surfaces and moraine deposits by cosmogenic nuclides has provided further valuable information on the chronology of past glacial extents and the timing of glacier retreat (Ivy-Ochs et al., 1996, 2006b, 2007, 2008; Kelly et al., 2006; Hormes et al., 2008; Böhlert et al., 2011; Federici et al., 2011; Reuther et al., 2011). From these data a detailed chronology for the early recession of the LGM ice and the Lateglacial readvances (‘stadials’) in the Alpine foreland and the inner Alpine valleys was established.

In the high Alps, however, the timing of the breakdown of the LGM ice cap and the extent of Lateglacial local ice is less well constrained. From mapping of glacial trimlines and further glacial erosional features the presence of large, precipitation-controlled ice domes during the LGM has been proposed (Florineth
and Schlüchter, 1998, 2000; Kelly et al., 2004a). From the inner Alpine accumulation areas, ice streams expanded into the valleys and glacier transfluences developed at several high Alpine passes (Florineth, 1998; Florineth and Schlüchter, 1998). It is assumed that this ice flow configuration persisted until the piedmont glaciers in the Alpine forelands retreated from their maximum extent (Florineth and Schlüchter, 1998; Kelly et al. 2006). Thus, major downwasting of the inner Alpine ice masses and the termination of glacier transfluence over the high passes were thought to be roughly synchronous to the onset of ice-free conditions in the foreland valleys. However, there is evidence that the high Alps did not deglaciate by that time but that ice persisted locally at high elevations until the beginning of the Bolling/Allerød interstadial (~15-14 ky BP) or even longer (Kelly et al., 2006; Böhlert et al., 2011).

To improve the knowledge about the Lateglacial ice decay in the high Alps and better understand the effect of climate changes on the high Alpine mountain glaciers and ice caps, we performed surface exposure dating of glacially modified bedrock on the Gotthard Pass, central Swiss Alps, using cosmogenic $^{10}$Be and in situ $^{14}$C. Combining $^{10}$Be dating with in situ $^{14}$C analyses takes advantage of the short half-life of $^{14}$C (5730 y) which allows to recognize episodes of surface burial as well as constant surface shielding. In situ $^{14}$C can therefore provide information on the extent of Holocene ice on the Gotthard Pass and can be used to evaluate the necessity of snow shielding corrections for exposure dating in an Alpine environment.

To reconstruct the paleoflow pattern, we combine surface exposure dating with detailed mapping of glacial erosional features in the Gotthard pass area. This yields a detailed chronology of the LGM ice surface lowering and local glacier readvances in conjunction with a progressive reorganization of the glacial ice flow pattern from the LGM until the Holocene.

**IV.2.2. Chronology of the Lateglacial ice decay in the Alps**

By ~21 ky the Alpine foreland piedmont glaciers had started to retreat from their maximum position (Schlüchter, 1988 and references therein, 2004; Ivy-Ochs et al., 2004; Preusser, 2004; Keller and Krayss, 2005; Preusser et al., 2011). Deglaciation of the foreland and the inner Alpine valleys by ~19-18 ky marks the beginning of the Alpine Lateglacial (Lister, 1988; Wessels, 1998; van Husen, 2004; Reitner, 2007). According to the work of Reitner (2007) there is no evidence for a climate-driven glacier readvance during the early Lateglacial and therefore the concept of early Lateglacial stadials (‘Bühl’ and ‘Steinach’) should be abandoned and replaced by the expression ‘phase of early Lateglacial ice decay’. An early Lateglacial phase of warming at ~18.0-17.5 cal. ky BP was recorded regionally from southern Alpine macrofossil and pollen data (cf. Vescovi et al., 2007), and by
the δ^{18}O in Greenland ice cores (Björk et al., 1998). In the following, a series of prominent moraines were deposited throughout the Lateglacial until the beginning of the Holocene within the Central and Eastern Alps (Maisch, 1981, 1982; Kerschner and Berktold, 1982; Kerschner, 1986).

The first pronounced glacier readvance occurred during the Gschnitz stadial. A maximum age for Gschnitz advances is given by a radiocarbon age of 15.4 ± 0.5^{14}C ky BP (19.6-17.6 cal. ky BP) from the Eastern Alps (Draxler, 1977). Consistently, exposure ages obtained by ^{10}Be dating of moraine boulders at the type locality in Trins (Gschnitz Valley, Tyrol, Austria) as well as from a Gschnitz terminal moraine deposit from the Maritime Alps (Italy) have provided mean ages around 17 ky (Ivy-Ochs et al., 2006a; Federici et al., 2011). Note, that these ages and all published ^{10}Be exposure ages discussed below have been recalculated using a ^{10}Be spallogenic production rate of 3.93 at g^{-1}y^{-1} (see section 4.3). The Gschnitz advance was followed by pronounced glacier downwasting before smaller readvances of the Clavadel/Senders and Daun stadials (Maisch et al., 1999; Ivy-Ochs et al., 2006b; Kerschner, 2009). These readvances were followed by marked ice decay during the Bolling/Allerød interstadial (~ 14.7-12.9; Björk et al, 1998; Vescovi et al., 2007; Ivy-Ochs et al., 2008) which ended abruptly with the beginning of the Younger Dryas cold period (Mangerud et al., 1974). Widespread glacier readvance during the Younger Dryas is documented by series of Egesen stadial moraine complexes deposited throughout the Alpine valleys (Kerschner et al., 2000 and references therein). Several surface exposure ages have been obtained from different moraine complexes in Switzerland and Italy. ^{10}Be ages range between ~13.9-10.6 ky and are interpreted to give the timing of moraine stabilization during various glacier readvances of the Egesen stadial (Ivy-Ochs et al., 1996, 1999, 2006b; Kelly et al., 2004b; Federici et al., 2007; Hormes et al., 2008). Several radiocarbon ages of ~ 11 cal. ky BP (summarized and calibrated in Ivy-Ochs et al., 2008) as well as consistent ^{10}Be ages (Kelly et al., 2006) trace the final downwasting of Egesen glaciers. Continued glacier activity into the earliest Holocene is suggested from moraine deposition and rock glacier activity (Fraedrich, 1979; Frauenfelder et al., 2001; Ivy-Ochs et al., 2006b, 2009 and references therein; Kerschner and Ivy-Ochs, 2008).

IV.2.3. Study Area

The Gotthard pass is located in Central Switzerland with a pass elevation of 2106 m a.s.l. (Fig. IV.2.1). Since the historic past, it has been one of the most important routes traversing the Alps in north-south direction. The Gotthard region comprises crystalline rocks of the Gotthard Massif that forms a part of the crystalline basement of the Swiss Alps. Granitic rocks in the study area are associated with the Fibbia granite gneiss, which is separated by paragneisses from
the Gamsboden granite gneiss further north (Labhart, 2009). The Fibbia granite gneiss exhibits a porphyritic texture and syenogranitic composition (Sergeev et al., 1995; Debon and Lemmet, 1999). Plutonic rocks of the Gotthard massif are of Variscan age and were deformed during Alpine orogeny at greenschist to amphibolite facies conditions (Frey et al., 1980; Labhart, 1999).

The pass area shows a typical U-shaped cross section and is characterized by highly polished granitic surfaces and abundant glacial erosional features (Fig. IV.2.2). Trimlines at 2640 m a.s.l. on the Pizzo d’Orsino (Fig. IV.2.1; Florineth and Schlüchter, 1998) and at ~ 2500 m a.s.l. at the pass are evidence for the presence of massive ice during the LGM reaching up to 500 m above the pass elevation (Fig. IV.2.3). In the northern part of the study area, Lateglacial moraine deposits have been mapped by Renner (1982) and were assigned to the Egesen and Daun stadials (see discussion). Several Holocene rock glaciers are located in the upper part of the cirque north of Monte Prosa.

**IV.2.4. Methods**

**IV.2.4.1. Reconstruction of the LGM and Lateglacial ice flow pattern**

Two approaches were used to reconstruct the glacier geometry and ice flow pattern in the Gotthard Pass area during and since the LGM: Glacial erosional features were mapped in order to trace the directions of former ice flow, and the LGM ice surface geometry was reconstructed with a GIS-based analysis of glacial trimlines.
In the study area, abundant crescentic fractures and gouges, glacial striae, roches moutonnées and lunate fractures show the direction of past glacier flow (Glasser and Bennett, 2004; Benn and Evans, 2010). During mapping of these features and their interpretation, rows of crescentic gouges were considered most important because their axis of symmetry allows the most accurate reconstruction of the paleoflow direction. Crescentic gouges vary largely in size, depth and state of weathering. At some sites, larger crescentic gouges (up to 1 m wide and several cm deep) appear more strongly weathered than smaller ones of different direction and were therefore assigned to an older generation that has been overrun by later glacier readvance. Because most glacial striae in the study area are thin and shallow features that often cross-cut comparatively deep crescentic gouges, they are considered to have formed during the last glacier readvance. An example of weathered crescentic gouges cross-cut by younger striae and weakly developed crescentic gouges is given in Fig. IV.2.4.

The glacial trimline represents the boundary between an ice-moulded downslope area and a frost-affected upslope zone (Ballantyne, 1990; Florineth, 1998). In high relief mountains as the Alps, this boundary is well visible in the morphology of valley-side spurs separating glacial cirques. The maximum extent of ice in main valleys is recorded as a spur truncation showing a more or less sharp

![Figure IV.2.2. Glacial erosional features at Gotthard Pass. White arrows indicate the ice flow direction. (A) Glacial striae; yellow scale bar is ~ 1 m. (B) Row of crescentic gouges (chatter marks). (C) Crescentic fractures. (D) Lunate fractures.](image-url)
Figure IV.2.3. LGM ice cover of the Gotthard Pass area as reconstructed from trimline mapping. (A) N-S cross-section illustrating the different position of the LGM ice divide in comparison to today’s water divide. Red numbers are trimline point elevations. (B) Block diagram showing the ice configuration in the larger pass area. Blue numbers indicate ice surface elevations; white arrows give the direction of ice flow from the ice divide (dashed white line). The grey line represents the thalweg with today’s water divide (grey dashed line) and water flow direction (grey arrows) and corresponds to the line of cross-section (A). The vertical black numbers give the thickness of ice at the positions of the LGM ice divide and today’s water divide. Sampling sites for exposure dating closely follow the line of the water divide.
transition between the frost-weathered arête zone above the trimline and the gentle ice-moulded ridges and trough shoulders below. In the study area, 19 trimline points were recognized in the field and their detailed position and altitude was extracted from digital elevation models (DEMs) and orthophotomaps. Ice-surface contours with intervals of 25-50 m were drawn for the main valleys with respect to the elevation of the trimline points and considering a concave shape of the ice surface within the accumulation zone. Additionally, ice contour lines directly above the pass were drawn perpendicularly to the direction of the oldest generation of glacial erosional features.

![Figure IV.2.4. Cross-cutting glacial erosional features. Photograph was taken close to sampling site got-08 (see Fig. IV.2.4). Two weathered crescentic gouges (next to the compass) indicate southward ice flow and are cross-cut by ENE-WSW-striking glacial striae/polish (direction indicated by the pencil). Two small and weakly developed crescentic gouges (white circle) give the same flow direction as the striae. Another single crescentic gouge (left of the pencil) also points into WSW-direction.](image)

### IV.2.4.2. Sampling and sample preparation

Samples for cosmogenic nuclide dating were taken along an altitude transect ranging from 2270 m a.s.l. southwest of Gotthard pass down to pass elevation and up to 2336 m a.s.l. northeast of the pass (Tab. IV.2.1). All samples except one (got-05) are from the topmost few centimetres of bedrock surfaces. Sample got-05 was taken from the edge of a ~5x4 m large and ~1-1.5 m high erratic boulder. Glacial polish is most pervasive at bedrock surfaces in the lowermost pass area (around samples got-06, got-07, got-11, got-12). All other surfaces are weakly weathered to slightly pitted with quartz grains standing out a few millimetres. Some surfaces are
partially covered by lichens. One glacially polished quartz vein was sampled (got-11).

All samples were crushed and sieved to a grain size range of 0.25-1 mm. Quartz mineral separates were prepared and purified by leaching in HCl and weak HF following the methods described in Kohl & Nishizumi (1992) and Ivy-Ochs (1996). Samples were spiked with 0.3 g $^{9}$Be and dissolved in concentrated HF. $^{10}$Be was separated from ~30-70 g quartz using ion exchange column chemistry according to Ivy-Ochs (1996). The $^{10}$Be/$^{9}$Be ratio was measured at the ETH Zürich 6 MV Tandem accelerator mass spectrometry (AMS) facility (Synal et al., 1997; Kubik and Christl, 2010). Subtracted $^{10}$Be/$^{9}$Be blank ratios were on the order of $3 \times 10^{-15}$. In situ $^{14}$C was extracted from ~5 g quartz by heating at 1550-1600°C as described in Hippe et al. (2009; in review). Extraction was initially performed in two subsequent, high-T heating steps. For both steps, concentrations were measured separately and then added to a total $^{14}$C concentration for the sample (Tab. IV.2.2). Later, $^{14}$C was extracted in one single heating step (cf. Hippe et al., in review). Subtracted long-term processing blanks were $(2.81 \pm 1.02) \times 10^4$ $^{14}$C atoms ($\pm 1$ stdev, n=11) for the first and $(1.48 \pm 0.66) \times 10^4$ $^{14}$C atoms ($\pm 1$ stdev, n=10) for the second extraction step, respectively, and $(4.55 \pm 2.19) \times 10^1$ $^{14}$C ($\pm 1$ stdev, n = 9) for the modified extraction method. Samples were measured at ETH Zürich with the MICADAS AMS system using a gas ion source (Ruff et al., 2007; Synal et al., 2007; Wacker et al., 2010). To check for analytical reproducibility, two aliquots of sample got-04 were analysed. Independent extractions (separated by six months) gave identical results within 2%. For the exposure age calculation the mean of the total concentrations from both aliquots was taken (Tab. IV.2.2).

### Table IV.2.1. Sample information and the measured $^{10}$Be concentrations.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Latitude (°N)</th>
<th>Longitude (°E)</th>
<th>Elevation (m a.s.l.)</th>
<th>Sample thickness (cm)</th>
<th>Topographic shielding factor</th>
<th>$^{10}$Be concentration ($10^4$ at g$^{-1}$)$^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>got-01</td>
<td>46.5539</td>
<td>8.5539</td>
<td>2270</td>
<td>3</td>
<td>0.821</td>
<td>27.35 ± 1.35</td>
</tr>
<tr>
<td>got-02</td>
<td>46.5541</td>
<td>8.5546</td>
<td>2252</td>
<td>1</td>
<td>0.986</td>
<td>26.13 ± 1.14</td>
</tr>
<tr>
<td>got-03</td>
<td>46.5553</td>
<td>8.5556</td>
<td>2195</td>
<td>4</td>
<td>0.986</td>
<td>27.28 ± 1.30</td>
</tr>
<tr>
<td>got-04</td>
<td>46.5557</td>
<td>8.5579</td>
<td>2166</td>
<td>4</td>
<td>0.987</td>
<td>25.55 ± 1.20</td>
</tr>
<tr>
<td>got-05</td>
<td>46.5564</td>
<td>8.5587</td>
<td>2140</td>
<td>4</td>
<td>0.993</td>
<td>23.93 ± 0.96</td>
</tr>
<tr>
<td>got-06</td>
<td>46.5572</td>
<td>8.5601</td>
<td>2120</td>
<td>4</td>
<td>0.993</td>
<td>30.79 ± 1.02</td>
</tr>
<tr>
<td>got-07</td>
<td>46.5582</td>
<td>8.5611</td>
<td>2116</td>
<td>3</td>
<td>0.992</td>
<td>24.50 ± 1.09</td>
</tr>
<tr>
<td>got-08</td>
<td>46.5641</td>
<td>8.5670</td>
<td>2336</td>
<td>2</td>
<td>0.980</td>
<td>33.23 ± 1.14</td>
</tr>
<tr>
<td>got-09</td>
<td>46.5637</td>
<td>8.5664</td>
<td>2324</td>
<td>4</td>
<td>0.992</td>
<td>31.64 ± 1.37</td>
</tr>
<tr>
<td>got-10</td>
<td>46.5628</td>
<td>8.5658</td>
<td>2250</td>
<td>2</td>
<td>0.936</td>
<td>29.76 ± 1.26</td>
</tr>
<tr>
<td>got-11</td>
<td>46.5619</td>
<td>8.5653</td>
<td>2197</td>
<td>2</td>
<td>0.972</td>
<td>23.75 ± 1.11</td>
</tr>
<tr>
<td>got-12</td>
<td>46.5605</td>
<td>8.5628</td>
<td>2135</td>
<td>3</td>
<td>0.987</td>
<td>24.23 ± 1.08</td>
</tr>
</tbody>
</table>

$^{a}$ Correction factor calculated according to Dunne et al. (1999) including shielding due to the dip of the sampled surface and the shielding by the surrounding topography.

$^{b}$ Errors are at the 1σ level and include the AMS analytical uncertainties and the error of the subtracted blank. Measured ratios were normalized to the S2007N standard (calibrated to 07KNSTD) using a half-life of 1.387 ± 0.012 (Chmeleff et al., 2010; Korschinek et al., 2010).
IV.2.4.3. Exposure age calculation

To calculate $^{10}$Be exposure ages a sea level-high latitude (SLHL) pallogenic production rate of $3.93 \pm 0.19$ at g$^{-1}$y$^{-1}$ was applied, based on the Northeast North America calibration data of the CRONUS-Earth online calculator (Balco et al., 2008). This value was chosen in view of a number of recently published production rate data from various calibration sites worldwide that suggest a $^{10}$Be production rate for spallation on the order of 3.7-4.3 (Lal, 1991; Stone, 2000 scaling; Balco et al., 2009; Lifton et al., 2009; Putnam et al., 2010; Fenton et al., 2011; Goehring et al., 2011; Kaplan et al., 2011; Briner et al., 2012). Notably at most northern hemisphere sites the $^{10}$Be production rate seem to converge to a value between 3.9-4.0 at g$^{-1}$y$^{-1}$ (Balco et al., 2009; Fenton et al., 2011; Briner et al., 2012). 

In situ $^{14}$C exposure ages were calculated with a SLHL pallogenic production rate of $12.29 \pm 0.99$ at g$^{-1}$y$^{-1}$ (Lifton, pers. comm.), which is based on a re-evaluation of the published in situ $^{14}$C...
calibration data (Lifton et al., 2001; Miller et al., 2006; Dugan, 2008) using the total muonic production rates as given in Heisinger et al. (2002b). The contribution due to muon production was calculated independently using the freely accessible MATLAB code of the CRONUS-Earth online calculator (Balco et al., 2008), which implements the method of Heisinger et al. (2002a, b) for altitude and depth scaling. Parameters were adjusted to allow muon scaling for $^{10}$Be and in situ $^{14}$C using the revised muon interaction cross sections for $^{10}$Be as specified in Balco (2009) and cross sections for $^{14}$C as published in Heisinger et al. (2002a, b).

Spallogenic production rates were scaled to altitude and latitude according to the scaling scheme of Lal (1991)/Stone (2000). No correction was done for geomagnetic field intensity variations because their effect on the production rates is assumed negligible at latitudes $>40^\circ$ (Masarik et al., 2001). Corrections for sample thickness were applied on spallogenic production only assuming an exponential decrease of production with depth and using an effective attenuation length $\Lambda_{sp}$ of 160 g cm$^{-2}$ and a rock density of 2.65 g cm$^{-3}$. The attenuation of muons within the uppermost few centimetres below the surface is small and can be reasonably ignored. Correction factors for topographic shielding and sample geometry were derived according to Dunne et al. (1999).

Exposure ages were calculated with an erosion rate of 1 mm ky$^{-1}$ estimated from the slightly weathered appearance of the rock surfaces. An additional correction for snow cover was performed for some samples and will be discussed in detail in section IV.2.5.3. Any snow shielding corrections were applied on the spallogenic production only because of the comparatively small attenuation effect of snow on the muonic production (cf. Schildgen et al., 2005).

IV.2.5. Results

Sample information and measured concentrations are given in Table IV.2.1 for $^{10}$Be and Table IV.2.2 for in situ $^{14}$C. Exposure ages are summarized in Table IV.2.3 and displayed in Fig. IV.2.5. For the following discussion we use exposure ages corrected for erosion as described above. However, the effect of the erosion correction on the exposure ages is small (at most 1% for $^{10}$Be and 2% for in situ $^{14}$C) and well within the uncertainties. Given errors are at the 1σ level including the AMS counting error and the error associated with the subtracted blank. For in situ $^{14}$C, an additional uncertainty of 3% was included to account for analytical variability in the in situ $^{14}$C extraction procedure (Hippe et al., 2012).

Exposure ages obtained from $^{10}$Be range from 10.8 ± 0.5 ky to 14.7 ± 0.5 ky (Fig. IV.2.5). Consistently, ages of eight samples analysed for in situ $^{14}$C vary from 9.3 ± 0.3 ky to 15.0 ± 0.5 ky and cover about the same age range as obtained from $^{10}$Be. These ages represent minimum estimates for deglaciation of the Gotthard Pass area suggesting that at latest by the beginning of the Holocene the Gotthard Pass
area was completely ice free. The overall agreement between $^{10}$Be and \textit{in situ} $^{14}$C ages is illustrated in the two-isotope diagram (Fig. IV.2.6) in which all data points cluster around the line of constant exposure suggesting a simple exposure history throughout the Holocene. For individual samples, differences between $^{10}$Be and \textit{in situ} $^{14}$C ages are between ~ 1-3 ky but show no clear trend, i.e. some $^{14}$C ages are younger, some are slightly older than the corresponding $^{10}$Be ages. Including production rate uncertainties (~ 5 and 8% for $^{10}$Be and $^{14}$C, respectively), ages from both nuclides are equal for each sample (Fig. IV.2.6A). However, we suppose that the small differences between $^{10}$Be and \textit{in situ} $^{14}$C results can provide important information about snow (or sediment) cover and should be discussed independently of the intrinsic uncertainties for the production rates. In the following, we will discuss the observed spread in exposure ages and evaluate the information on snow shielding gained from the combined $^{10}$Be-$^{14}$C data.

Table IV.2.3. Calculated exposure ages for the Gotthard samples. All

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Snow * (cm in 6 month)</th>
<th>$^{10}$Be exposure ages (years)</th>
<th>$^{14}$C exposure ages (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>uncorrected</td>
<td>corr. for erosion</td>
<td>corr. for erosion, snow</td>
</tr>
<tr>
<td>got-01</td>
<td>115</td>
<td>13920 ± 690</td>
<td>14080 ± 700</td>
</tr>
<tr>
<td>got-02</td>
<td>100</td>
<td>11100 ± 480</td>
<td>11160 ± 490</td>
</tr>
<tr>
<td>got-03</td>
<td>100</td>
<td>12310 ± 580</td>
<td>12440 ± 590</td>
</tr>
<tr>
<td>got-04</td>
<td>0</td>
<td>11750 ± 550</td>
<td>11870 ± 560</td>
</tr>
<tr>
<td>got-05</td>
<td>0</td>
<td>11140 ± 450</td>
<td>11240 ± 450</td>
</tr>
<tr>
<td>got-06</td>
<td>175</td>
<td>14540 ± 480</td>
<td>14720 ± 490</td>
</tr>
<tr>
<td>got-07</td>
<td>115</td>
<td>11510 ± 510</td>
<td>11620 ± 520</td>
</tr>
<tr>
<td>got-08</td>
<td>70</td>
<td>13470 ± 460</td>
<td>13630 ± 470</td>
</tr>
<tr>
<td>got-09</td>
<td>100</td>
<td>12990 ± 560</td>
<td>13130 ± 570</td>
</tr>
<tr>
<td>got-10</td>
<td>0</td>
<td>13390 ± 570</td>
<td>13530 ± 570</td>
</tr>
<tr>
<td>got-11</td>
<td>190</td>
<td>10670 ± 500</td>
<td>10770 ± 500</td>
</tr>
<tr>
<td>got-12</td>
<td>100</td>
<td>11290 ± 500</td>
<td>11400 ± 510</td>
</tr>
</tbody>
</table>

* Snow thickness was deduced from the combined $^{10}$Be-$^{14}$C data (Fig. IV.2.6B). For samples without \textit{in situ} $^{14}$C data, a minimum estimate of 100 cm during 6 month per year was taken.

b boulder

**IV.2.6. Discussion**

**IV.2.6.1. Overall trends in the exposure ages**

As illustrated in Fig. IV.2.5, there is a trend towards older exposure ages at higher elevations along the north-eastern pass side with oldest ages recorded from locations above 2250 m (got-08, got-09, got-10). Nuclide inheritance has been proposed as one possible interpretation for such a pattern (Fabel et al., 2004). This means that the LGM ice would not have eroded the bedrock deeply enough at these sites to completely remove cosmogenic nuclides that have accumulated during pre-
LGM surface exposure. Different studies have shown that the spatial pattern and rate of glacial erosion can vary significantly within a landscape depending, e.g., on the thermal regime of the ice (Fabel et al., 2002; Stroeven et al., 2002), the position within the valley (Fabel et al., 2004), or the bedrock type and fracturing (Dünnforth et al., 2010). Erosion rates beneath modern temperate glaciers are estimated to be at least 1 mm y\(^{-1}\) for mid-latitude regions (e.g. Small, 1987; Nesje et al., 1992; Hallet et al., 1996 and references therein; Riihimaki et al., 2005). This would be sufficient to remove several meters of bedrock during the LGM and erase the pre-glacial nuclide inventory. From trimline elevations in the Gotthard Pass area we estimate that even the highest sampling sites were at least 100 m below the LGM ice surface. Furthermore, the fact that the oldest exposure age was obtained from a sampling site

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**Figure IV.2.5.** Detailed map of the Gotthard Pass area with sampling locations and corresponding \(^{10}\)Be exposure ages (in ky; \(P_{R} = 3.93 \pm 0.19\) at g y\(^{-1}\)). Upper values are exposure ages corrected for erosion only (1 mm ky\(^{-1}\)); lower values have additionally been corrected for snow as specified in Table IV.2.3. For samples marked with an asterisk, snow corrections were directly inferred from the \textit{in situ} \(^{14}\)C data. Note that the snow corrected ages are identical for \(^{10}\)Be and \textit{in situ} \(^{14}\)C (Tab. IV.2.3). Samples with a slightly older \textit{in situ} \(^{14}\)C age compared to \(^{10}\)Be were not corrected for snow cover. For the chronology of Lateglacial deglaciation, the \(^{10}\)Be ages (bold) of these samples were used.
close to pass elevations (got-06) strongly argues against nuclide inheritance. This site in the central pass area was covered by about 400 m of ice (Fig. IV.2.3) and is situated in between two sampling sites that yielded about 3 ky younger ages (got-04, got-07). Field evidence does not suggest markedly variable glacial erosion for these sampling sites or generally within the entire study area. Also, there is no obvious trend in the age distribution on the south-western pass side. We therefore propose that the observed spread in exposure ages does not result from nuclide inheritance but reflects more than one episode of ice surface lowering and deglaciation in the Gotthard Pass area. This will be presented in detail in Section IV.2.6.

IV.2.6.2. Combined \( ^{10}\text{Be} \)–\( ^{14}\text{C} \) data

In mountainous regions, the recognition of surface shielding by snow and an appropriate snow correction can be crucial for the calculation of accurate surface exposure ages (cf. Schildgen et al., 2005; Böhlert et al., 2011; Fenton et al., 2011). As snow cover reduces the cosmogenic nuclide production rate, ignoring the presence of snow can cause a systematic underestimation of exposure ages. However, a correction for snow shielding usually involves large uncertainties because no direct information on past snow depths is available and any assumptions have to rely on historic climate data (e.g., Gosse and Phillips, 2001). Here, the combination of \( ^{10}\text{Be} \) with \textit{in situ} \( ^{14}\text{C} \) provides the opportunity to check on the necessity and extent of a shielding correction for exposure dating of the Gotthard Pass. Because of its short half-life, the \textit{in situ} \( ^{14}\text{C} \) concentration approaches secular equilibrium much faster compared to the long-lived \( ^{10}\text{Be} \). Also the contribution by muons to the total production rate is significantly higher for \textit{in situ} \( ^{14}\text{C} \). Therefore, snow cover and the correction of exposure ages for snow shielding has a much stronger effect on calculated \textit{in situ} \( ^{14}\text{C} \) ages compared to \( ^{10}\text{Be} \).

As shown in the two-isotope diagram (Fig. IV.2.6), data points for 5 of 8 samples plot above the line of constant exposure/no erosion (no shielding by snow or sediment). For those samples that yielded slightly lower \textit{in situ} \( ^{14}\text{C} \) than \( ^{10}\text{Be} \) ages (got-01, got-06, got-07, got-08, got-11), partial surface shielding is indicated. Assuming constant snow depths throughout the Holocene, measured concentrations of both nuclides can be brought into agreement for a variable amount of snow cover of ~ 70-190 cm during 6 months per year (Fig. IV.2.6B). Two samples (got-06, got-11) agree with the modern snow depth of ~ 180 cm during 6 months per year as deduced from the mean Nov-April snow depths recorded from 1983-2002 at climate stations nearby (data from the Institute for Snow and Avalanche Research and MeteoSwiss; Auer, 2003). The other three samples indicate only about half the amount of snow throughout the Holocene. Consistently, some authors have suggested a somewhat warmer climate during the middle Holocene (Hormes et al., 2001; Davis et al., 2003 and references therein; Joerin et al., 2006). Finally, data
points for three other samples (got-04, got-05, got-10) do not plot above line of constant exposure/no erosion implying that no further shielding correction is needed for these sites. With sample got-05 taken from the edge of a boulder and sample got-10 from a 30° dipping surface, these results are very reasonable. For sample got-04, however, there is no obvious reason why this sampling site should not be affected by snow shielding in a similar way as the neighbouring sites. We exclude analytical reasons, because for both nuclides two quartz aliquots of got-04 were measured independently and results of both $^{10}$Be analyses and both in situ $^{14}$C analyses, respectively, are identical within 1 $\sigma$.

In addition to snow cover, surface shielding by glacial sediment (till) can be considered. Although no sediment cover exists at the sampling sites at present, it cannot be excluded that patches of till covered the now exposed bedrock during an unknown time interval right after deglaciation. Shielding by sediment could explain some differences observed for adjacent sites on the pass (e.g., got-06 and got-07). It may also be possible that the well-preserved glacial polish around the low-elevation sites results from surfaces being protected by an initial sediment layer now eroded. Assuming shielding by sediment only (no snow), about ~ 5-17 cm thick till is required to explain the measured differences in the $^{10}$Be and in situ $^{14}$C concentrations (Fig. IV.2.6C). However, we assume snow to be the main shielding element and till to be of minor influence, if any.

Furthermore, the fact that data points for samples got-04, got-05, and got-10 plot below the line of constant exposure/no erosion could imply that the in situ $^{14}$C production rate might be slightly underestimated. A production rate determined from the combined $^{10}$Be and $^{14}$C data of samples got-04, got-05, and got-10 would be around 13 at g$^{-1}$y$^{-1}$, which is well within the uncertainty of the current production rate of 12.29 ± 0.99 at g$^{-1}$y$^{-1}$. However, a higher production rate would also implicate increased snow shielding corrections for the other samples.

Altogether, combining $^{10}$Be with in situ $^{14}$C analyses may yield more accurate surface exposure ages as it provides a tool to identify surface shielding and to estimate the amount of snow correction. We have corrected all exposure ages individually for snow cover as suggested from the combined $^{10}$Be-$^{14}$C data. For those samples that have no in situ $^{14}$C data, a minimum estimate of 100 cm in 6 months was applied (Tab. IV.2.3). Overall, these corrections increase the $^{10}$Be ages by ~ 1-3 ky and in situ $^{14}$C ages by ~ 2-6 ky (Tab. IV.2.3).
Figure IV.2.6. Results for samples analysed for $^{10}$Be and in situ $^{14}$C plotted in different two nuclide-diagrams. Error bars represent 1σ analytical uncertainty including errors on the subtracted blank and 3% uncertainty for in situ $^{14}$C to account for reproducibility. All samples plot close to the line of simple exposure and show a general agreement between $^{10}$Be and in situ $^{14}$C data. (A) Including the current production rate uncertainties, marked with grey dashed lines, $^{10}$Be and in situ $^{14}$C exposure ages would be identical within 1σ. (B) Considering only the analytical uncertainties, in situ $^{14}$C exposure ages that are slightly younger than the $^{10}$Be ages, i.e. samples plotting left of the constant exposure line, could be explained by Holocene snow cover. Dotted lines are lines of constant exposure that include permanent shielding due to snow cover ($\rho = 0.3$ g cm$^{-3}$). (C) Alternatively to (B), slightly younger in situ $^{14}$C ages can also be caused by shielding due to a thin sediment (till) layer ($\rho = 2.0$ g cm$^{-3}$).
IV.2.7. Surface exposure ages in the context of paleoflow reconstruction

Snow corrected exposure ages from the Gotthard Pass cover most of the Lateglacial and suggest a successive deglaciation of the pass area. Deglaciation started at ~ 16-15 ky and the pass became completely ice-free at the beginning of the Holocene by ~ 11 ky. Although an exposure age of 17.3 ky from sample got-06 suggests that some sites might have become ice-free slightly earlier, our interpretation that major deglaciation started at ~ 16-15 ky is based on results from the higher elevation sites. Using field observations of glacial erosional features, exposure age data will be linked in the following to changes of ice volume and paleoflow directions throughout the period of Lateglacial ice decay. Results from the mapping of erosional markers are presented in Fig. IV.2.7A and IV.2.7B, which summarize our interpretation of these markers and illustrate the conclusions on the glacial flow pattern. At most sites on the pass two generations of erosional features occur in a cross-cutting pattern. We interpret these to correspond altogether to three generations of erosional markers and, thus, to document three different paleoflow patterns.

IV.2.7.1. LGM

Landscape geometry and strongly abraded bedrock surfaces on the Gotthard Pass record an intensive glacial imprint by highly erosive ice masses. Within the central pass area up to 1 m large, deep and often weathered crescentic gouges are superimposed on the erosional bedforms. These features are consistent with the proposed LGM flow pattern into SSE direction (Fig. IV.2.3; cf. Florineth and Schlüchter, 1998) but could also have formed during later glacial stages. The only site where the first generation of erosional markers can be clearly identified is on the ridge south of the Alpe di Fortinéi, where SSE to SSW-directed crescentic gouges are cross-cut by SW to WSW-pointing crescentic gouges and parallel running glacial striae (Fig. IV.2.4, IV.2.7A). The older generation of erosional features implies a roughly S-directed ice flow, which does not follow local topography and agrees with the LGM flow pattern. As suggested by our reconstruction of the LGM glacial cover illustrated in Fig. IV.2.3, the LGM ice divide was about two kilometres north of today’s water divide on the Gotthard Pass. Glacier transfluence over the pass was imposed by the dynamics of the enormous ice masses originating from the cirques north of the Monte Prosa and at the Lago di Lucendro that served as main accumulation areas. Although a lowering of the LGM ice surface is suggested from field evidence (see below), our exposure ages do not record ice-free conditions at the end of the LGM.
**IV.2.7.2. Early Lateglacial**

Small and shallow crescentic gouges that are less weathered, fine glacial striae and glacial polish represent a younger generation of erosional features that show variable directions of ice flow deviating from the main LGM flow direction. This second generation of erosional markers (SW to WSW-directed) imply a change in the ice flow configuration, most likely after a significant decrease of the ice elevation, and suggests the presence of a local glacier at the Monte Prosa. However, because the glacial ice from the Monte Prosa cirque is continuously flowing opposite to topography, the persistence of a large ice mass on the pass is required to force local glaciers into the predominant southward direction. The termination of the ice flow over the ridge south of the Alpe di Fortünéi represents the timing of severe glacier downwasting and is constrained by the exposure ages of got-08 and got-09 that give a mean age of $14.5 \pm 0.8$ ky. Based on the large volume of ice implied by the pattern of the glacial erosional features these exposure ages are interpreted to portray the downwasting of Gschnitz stadial glaciers. These are envisioned as a large system of transection glaciers with a pattern similar to the LGM but limited to the high elevation inner Alpine valleys. Crescentic gouges east of the Lago di Lucendro (Fig. IV.2.7A) suggest that local ice coming out of the lake depression was forced to flow towards SE opposite to topography. Thus, erosional markers are considered to have formed at the same time as the ones assigned to the second generation on the ridge south of the Alpe di Fortünéi. Erosional features in the SW of the pass agree with this flow pattern. Approaching pass elevation, the ice flow direction recorded by the erosional markers gradually changes from the initial E-ENE direction into a SSE-ward flow. However, as this pattern follows the general topography, these markers must not necessarily have formed contemporaneously with the second generation of erosional features further north. Nevertheless, abundant deep crescentic gouges point to a quite large volume of ice that caused strong glacial erosion (cf. Glasser and Bennett, 2004). Within this configuration the ice divide was still situated north of the Gotthard Pass.

An exposure age of $15.7 \pm 0.8$ ky obtained from the highest sampling site at the south-eastern pass side (got-01) suggests an overall synchronous deglaciation of the pass area. Altogether, these ages propose that glacier transfluence persisted in the Gotthard Pass area throughout the Oldest Dryas and that the large system of local transection glaciers decayed even as late as the onset of the Bølling/Allerød interstadial.

**IV.2.7.3. Younger Dryas**

An apparent third generation of erosional features is well defined east of the Lago di Lucendro by ~E-W-striking glacial polish cross-cutting the second
generation of crescentic gouges (SE-directed). These features clearly show a major reorganization of the paleoflow pattern into a nearly completely topographically controlled system and a shift of the ice divide towards south close to today’s water divide. During this phase of glacier readvance local ice from the Lago di Lucendro moved down-valley towards the north as well as eastwards across the pass. Consistently, a single but not very well developed crescentic gouge at the Alpe di Fortünéi is indicating northwards glacial flow out of the cirque according to local topography. A left lateral moraine within the Alpe di Fortünéi, which may correspond to this readvance, was mapped by Renner (1982) and attributed to the Daun stadial (Fig. IV.2.7).

Rows of comparatively small and shallow crescentic gouges around sampling site got-12 suggest a much smaller glacier system with little erosional potential but also indicate that ice from the Lago di Lucendro valley spread over a large part of the northern pass area. In agreement to field observations, samples got-12 and got-11, that were located within the lower pass area below 2200 m a.s.l., yielded younger $^{10}$Be ages of 12.5 ± 0.6 ky and 12.9 ± 0.6 ky, respectively. These suggest an attribution of the third generation of erosional markers with the Younger Dryas cold phase and to a readvance of Egesen stadial glaciers. This supports the interpretation of Renner (1982) that the right lateral moraine east of the Lago di Lucendro (Fig. IV.2.7) was deposited during the Egesen stadial. Consistently, readvance of local ice at the southwestern pass side was dated to 11.9 ± 0.6 ky to 12.9 ± 0.6 ky (got-02, got-04, got-07). Finally, a minimum age of 11.2 ± 0.5 ky for the final deglaciation of the Gotthard Pass is given from the boulder (got-05) and is consistent with deposition during Egesen advance and ice free conditions by the end of the Younger Dryas. This age is also in good agreement with radiocarbon dates from the Central Alps indicating ice free conditions at elevations of ~ 2150 m by ~11.2-12.6 cal. ky BP (Renner, 1982).

Glacial striae (E-W to SE-NW-striking) that are cross-cutting older crescentic gouges in the central pass area clearly demonstrate that local ice was expanding from the cirque north of the Piz Lucendro (Fig. IV.2.7B) at some time after the breakdown of the large Oldest Dryas glacier system. This pattern of striae right at the pass documents the dominance of local glaciers and indicates the absence of a large, south-flowing glacier in that area. Although all sampling sites in the southwestern study area are located below the cirque basin north of the Piz Lucendro, not all samples yielded Egesen stadial ages. We propose that the spread in ages documented on this side of the pass results from a first exposure of all sites starting at ~ 16 ky and only a partial coverage by readvancing Egesen glaciers. The Younger Dryas was ~ 1.1-1.3 ky long, climatically unstable period (Alley, 2000; Muscheler et al., 2008). In some regions of the Alps up to seven Egesen moraines
with intervening periods of ice recession have been identified (Maisch, 1982, 1987; Kerschner et al., 2000 and references therein). Because of the flat topography of the pass area, during each advance the glacier may have followed a slightly different path leading to some areas being covered and others not.

Figure IV.2.7. Reconstructions of generalized ice flow pattern for the LGM and Gschnitz stadial (A), and for the Egesen stadial (B), based on glacial erosional markers.
IV.2.8. Conclusions

In this study $^{10}$Be and \textit{in situ} $^{14}$C exposure dating were combined with mapping of glacial erosional features to elucidate the pattern of deglaciation of the Gotthard Pass after the LGM. Erosional markers suggest a progressive glacier downwasting from the maximum LGM ice volume and a gradual re-organization of the ice flow pattern with a southward migration of the ice divide. Glacial trimlines record the enormous ice volume that accumulated during the LGM and that forced glaciers into an exclusively SSE-directed flow. With downwasting of the LGM ice the glacial regime changed into a system of large interconnected dendritic glaciers.
that seems to have continuously followed the general LGM paleoflow direction. This phase of early ice decay can be clearly identified from field evidence but is not recorded by the exposure ages. The oldest obtained $^{10}$Be exposure ages from samples above 2250 m a.s.l. indicate first deglaciation as early as ~ 15.7 ky and no later than ~ 14.5 ky. These ages can be attributed to the decay of the large Gschnitz glacier system by the end of the Oldest Dryas. From these data it is suggested that although the ice volume was decreasing by the end of the LGM, large transection glaciers persisted in the Gotthard region throughout the Oldest Dryas allowing glacier transfluence over the pass. These results are in good agreement with bedrock exposure ages reported from the high Alpine Grimsel and Albula passes (Kelly et al., 2006; Böhlert et al., 2011) proposing that the scenario of rapid deglaciation by the end of the LGM, as recorded for the Alpine foreland, does not reflect the conditions in the high Alps. Local glaciers remained large in high elevation areas for several thousand years after the downwasting of the valley glaciers and possibly decayed as late as the onset of the Bølling warming.

After drastic downwasting of the ice volume during the Bølling/Allerød interstadial, local glaciers readvanced during the Younger Dryas cold phase forming an entirely topographically controlled ice flow pattern with ice flowing out of the cirques. $^{10}$Be exposure ages of ~ 12-13 ky give the timing of Egesen glacier readvance. Egesen glaciers expanding from the higher elevated accumulation areas covered most of the pass area. However, glacial erosion was negligible. From the recorded spread in $^{10}$Be exposure ages we assume that the Egesen readvance was preceded by an episode of ice free conditions during a part or all of the Bølling/Allerød interstadial. Thus, some sites have been pre-exposed during that time. Egesen glaciers may not have equally covered the entire area due to local variations in tongue geometry. The timing of final deglaciation by the end of the Younger Dryas is constrained by the $^{10}$Be minimum exposure age of 11.2 ± 0.5 ky from the only analysed boulder (got-05) that was deposited during the last glacier readvance.

From the combination of $^{10}$Be and in situ $^{14}$C data, we were able to evaluate the necessity of a snow shielding correction. Detailed constraints on the amount of such a correction were gained for each sampling site. The overall consistency between the in situ $^{14}$C and the $^{10}$Be data excludes the presence of significant glacial ice (including non-erosive ice patches) for any time on Gotthard Pass during the Holocene and points to a continuous exposure of the pass area since the end of the Younger Dryas.
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V. Synthesis and outlook

The work done during this PhD was intended to achieve two main goals:

i) to establish the method of in situ $^{14}$C analysis at ETH Zürich, and

ii) to apply in situ $^{14}$C analysis to questions in Earth surface sciences.

i) In situ $^{14}$C analysis at ETH

Achievements and current status

The in situ $^{14}$C extraction system at ETH has proven that in situ produced $^{14}$C can be quantitatively and reproducibly extracted from quartz samples. With stepped heating experiments the separation of atmospheric $^{14}$C contamination from the quartz surface at temperatures ~500°C followed by the release of in situ-produced component above 900°C was demonstrated. From these, a temperature of 700°C for the removal of atmospheric $^{14}$C was chosen. Our extraction system uses an electron bombardment furnace capable of heating the quartz (5 g) to temperatures of 1550-1600°C for several hours which allows in situ $^{14}$C extraction without the addition of a fluxing agent and, thus, without melting the quartz. With the omission of a flux agent a potential component of contamination could be excluded. The reliability of extraction furnace was constantly improved by minor yet important technical modifications.

Sample outgassing is performed under a flow of ultra-high-purity O$_2$ and followed by a rigorous gas cleaning system through a series of cryogenic traps and passage through hot Ag and Cu wool/mesh. Tests simulating the extraction procedure show a consistently high CO$_2$ recovery rate of >99.8%, confirming that virtually no CO$_2$ is lost during heating or gas cleaning. The clean CO$_2$ gas is taken off to be directly measured with the gas ion source MICADAS AMS system. This system allows the measurement of few µg of carbon and does not require additional graphitization. Therefore, sample dilution by $^{14}$C-free CO$_2$ is usually not needed which further reduces potential contamination. Typical quartz samples ($^{14}$C concentrations of $>10^5$ at g$^{-1}$) are measured at AMS with a precision of better than 2% while for samples with low $^{14}$C concentrations (few $10^4$ at g$^{-1}$) a precision of <6% is usually achieved. The initial extraction procedure included two high-temperature extraction steps performed on two days to ensure complete sample outgassing. With a shorting of the extraction protocol by integrating both steps into one long extraction step now accomplished on one day, the procedural efficiency was greatly increased.
Analyses of the quartzite sample (PP-4) used as an internal standard at the University of Arizona, have shown a good reproducibility of <5% that was confirmed by repeated analyses of other samples measured during the studies in samples from the Altiplano (Bolivia) and the Gotthard Pass (Switzerland). Although concentrations measured for PP-4 are in reasonable agreement with published data, our results are slightly higher (up to 10%). It is possible that the difference in the in situ $^{14}$C extraction process, i.e. the fact that our system is the only one that does not fuse the quartz sample, could give one explanation. Extraction blanks are about one order of magnitude lower than those reported for other in situ $^{14}$C extraction systems. The weighted mean extraction blanks for the two subsequent high-temperature steps of the initial extraction procedure are $(2.80 \pm 1.02) \times 10^4$ $^{14}$C atoms ($\pm$ 1 stdev, n=11), and $(1.48 \pm 0.66) \times 10^4$ $^{14}$C (weighted mean $\pm$1 stdev, n=10), respectively. Preliminary blank data for the modified extraction procedure are $(3.84 \pm 1.17) \times 10^4$ $^{14}$C atoms (n=4). On the example of the historically documented rock avalanche in Val Ferret, Italy, it was shown that due to these low blank levels quartz samples can be analysed that have been exposed as short as a few hundred years.

Additionally, we have suggested to re-evaluate the current approach for in situ $^{14}$C data reduction and proposed a revised approach that (i) omits the conventionally used, but for in situ $^{14}$C inappropriate, $\delta^{13}$C correction, (ii) corrects for the year of measurement instead of AD 1950, and (iii) accounts for the natural isotopic composition of carbon, i.e. accounts for $^{13}$C in the conversion of the $^{14}$C/$^{12}$C ratio $^{14}$C atoms.

Potential technical and methodological improvements

The main difficulty with our in situ $^{14}$C extraction system is the stability and reliability of the extraction furnace. During sample processing the furnace is heated many hours each day to high temperatures so that it is constantly operating at the limits of its physical stability. Repairing of comparatively simple failures (as bending filaments or control grid bars) has to be done every few months. With the current setup of the extraction furnace, each repairing requires that the furnace is completely vented and partially disassembled. Although this usually does not (any more) take longer than half a day, it means that the sample that has been processed at the time of failure is lost for further analysis. Moreover, as higher system blanks have been observed after repairing thorough heating followed by a blank analysis is required before another sample can be processed. Therefore, often a few days are lost altogether.

This disadvantage will hopefully be resolved soon with a new mounting of the furnace which is currently built (design A. Süsli, ETH, 2011). The changed design
will allow the removal of the outer cover of the extraction furnace and repairing of the heating elements without removing the sapphire tube that holds the internal vacuum. In that way, the inside of the sapphire tube does not have to be exposed to atmosphere and the down-time of the extraction system should be significantly reduced.

Currently, complete in situ $^{14}$C extraction from a quartz sample can be achieved within two days. This time cannot be significantly shortened with the present setup of the extraction system. Nevertheless there is potential to reduce the time in between the extraction of two samples. Presently, about 1-2 days are needed for cleaning the Pt crucible by HF leaching and heating at high temperatures. The latter is done in the extraction furnace. An additional device to bake-out the Pt crucible outside the extraction system, would allow using two Pt crucibles alternately so that a new sample could be placed into the extraction furnace at the same time when the previous one is removed.

From the comparison of the in situ $^{14}$C and $^{10}$Be data obtained from the Gotthard Pass it is suggested that the currently used in situ $^{14}$C spallogenic production rate might be underestimated. This has already been indicated from the slightly higher concentrations measured for the PP-4 ‘standard’ compared to other laboratories (see above). However, results from the Gotthard Pass have also illustrated that small changes in the production rate can significantly affect the in situ $^{14}$C exposure ages. To fully exploit potential of in situ $^{14}$C for surface exposure dating it is therefore crucial to determine the in situ $^{14}$C production rate more accurately. This also implies a better knowledge of the contribution by muonic production which is has not been constrained by any field data, yet. Future work at the ETH in situ $^{14}$C extraction system should therefore also include a methodological aspect to improve the basis for the application of in situ $^{14}$C in Earth surface science.

The first step to gain a better understanding of the in situ $^{14}$C production systematics has to include detailed inter-lab comparison and requires that all laboratories publishing in situ $^{14}$C data (the few that there are at the moment) also publish the results from the analysis of standard material. The PP-4 sample that we have used so far for comparison other laboratories will be replaced by two quartz standards distributed by the CRONUS-Earth project. Analyses of these standards are planned to start soon at ETH and should help to evaluate the differences observed for PP-4.
ii) Applying \textit{in situ} $^{14}\text{C}$ in Earth surface sciences

\textit{Denudation rates and sediment storage on the Bolivian eastern Altiplano}

Studying $^{10}\text{Be}$, $^{26}\text{Al}$ and \textit{in situ} $^{14}\text{C}$ in the high-elevation, low relief landscape of the eastern Altiplano, Bolivia, has illustrated how geomorphology and climate control the dynamics of erosional processes and define the transport capacity of the fluvial system. Low catchment-wide denudation rates (4-32 mm ky$^{-1}$) obtained consistently from analyses of $^{10}\text{Be}$ and $^{26}\text{Al}$ in sediment samples, reflect the slow sediment production on the hillslopes along the Altiplano margin. Denudation rates are one to two orders of magnitude lower than in the adjacent Rio La Paz basin indicating that denudation processes on the eastern Altiplano are largely disconnected from the rapid, tectonically-controlled processes in the Rio La Paz basin. From the remarkable agreement between cosmogenic nuclide-derived denudation rates and modern sediment discharge data long-term geomorphic and isotopic steady-state over the late Pleistocene and Holocene is suggested for the eastern Altiplano.

The analysis of cosmogenic \textit{in situ} $^{14}\text{C}$ provided important evidence for sediment storage on the eastern Altiplano, which has not been recorded by the long-lived cosmogenic nuclides ($^{10}\text{Be}$ and $^{26}\text{Al}$). The low concentrations measured for \textit{in situ} $^{14}\text{C}$ imply at least one episode of sediment storage with partial shielding lasting through most of the Holocene or even up to \~{}20 ky. These results reflect well the geomorphic setting of the eastern Altiplano and the episodically occurring fluvial processes. They further emphasize that even over comparatively short distances sediment storage can be an important element in low-gradient landscapes. This study has shown that \textit{in situ} $^{14}\text{C}$ can give fundamental information on the sediment flux and residence time within a fluvial system. Furthermore, the potential application of \textit{in situ} $^{14}\text{C}$ as a proxy for soil mixing was introduced.

\textit{Surface exposure dating at Gotthard Pass, Swiss Alps}

In this study $^{10}\text{Be}$ and \textit{in situ} $^{14}\text{C}$ bedrock exposure dating were combined to reconstruct the pattern of deglaciation on the Gotthard Pass. From mapping of glacial erosional markers a progressive downwasting of ice from the maximum LGM ice volume and a gradual re-organization of the ice flow pattern with a southward migration of the ice divide were shown. Although the decay of the LGM ice was identified from field evidence it was not recorded by the bedrock exposure ages because of constant ice coverage. The oldest obtained $^{10}\text{Be}$ exposure ages indicate first deglaciation between \~{}16-15 ky and were correlated with the decay of the large Gschnitz glacier system by the end of the Oldest Dryas. These data support the idea that large interconnected dendritic glaciers persisted on the passes of the high Alps throughout the Oldest Dryas possibly decayed as late as the onset of the
Bølling warming. $^{10}$Be exposure ages of ~ 12-13 ky were interpreted to give the timing deglaciation following local glacier readvance during the Egesen stadial. The spread in exposure ages and erosional features suggest a comparatively small Egesen ice volume that was following an entirely topographically controlled ice flow pattern.

The in situ $^{14}$C results presented here are consistent with the $^{10}$Be ages and verify continuous exposure since the end of the Younger Dryas. Moreover, in situ $^{14}$C provides important constraints on the amount of Holocene snow cover and on the depth of snow that should be included in the exposure age corrections. Further in situ $^{14}$C analyses on are planned to confirm these initial results.
Detailed laboratory procedure for the chemical extraction of $^{10}$Be and $^{26}$Al

Before chemical purification all samples were crushed and sieved (for bedrock) or just sieved (for sediment) to the desired grain sizes. For all analyses presented in this work, a grain size fraction of 0.25-1 mm was used. For catchment-wide denudation rates about 4-6 kg of sediment was sampled, for surface exposure dating about 1-2 kg of bedrock.

The procedure given here is based on the protocol described by Ivy-Ochs (1996) with modifications presented in Norton (2008).

1. Quartz purification
   - Put ~100 g of crushed rock or sediment into a 1 L PE bottle
   - If the sample contains many carbonates or metal oxides, start purification by carefully adding ~10% HCl and let sample sit at room temperature until it the reaction is finished
   - Repeat or increase acid strength if necessary
   - Rinse the sample several times with ultrapure 18Ω Milli-Q water (in the following referred to as MQ water)
   - Fill bottle with 500 ml of MQ water and 5 ml of 40 % HF (extra pure)
   - Leave sample on the shaker table overnight and in the ultrasonic bath at 80°C during daytime
   - Wash/rinse sample with MQ water when the acid solution is cloudy (usually every day at the beginning and every few days when the sample gets cleaner)
   - Repeat the HF and washing steps until the acid stays clear
   - If the sample contains many resistant heavy minerals (e.g. zircon or sphene) or if feldspars do not completely dissolve in the weak HF solution, use heavy liquid separation to get rid of these components
   - This step has to be followed by another leaching with weak HF before the sample is rinsed thoroughly and dried on a hot plate or under an infrared lamp

2. Adding the carrier
   - Clean and prepare 300 ml Savillex beaker
   - Take the weight of the beaker, add 0.3 g of the $^{9}$Be carrier (Be sulphate 1 mg/ml) without taking the beaker off the balance and take the weight again
   - Weight in the sample (usually between 20-50 g quartz)
   - In cases where a very low $^{9}$Be/$^{10}$Be is expected, the sample size can be increased and/or the amount of $^{9}$Be carrier decreased
3. Sample dissolution

- Add HF (40%, suprapur) so that the quartz is fully covered plus 0.5 cm above it
- Put the samples on a hot plate (without lids) but do not heat for one hour
- Then heat to ~80-85°C
- Careful: exothermic reaction, check repeatedly, if sample fumes to strong take it off the hot plate and wait until reaction lessens
- Heat to 110-120°C after another hour and let evaporate to dryness
- Add few splashes of HNO₃ before another addition of HF on the dry sample
- Overnight always reduce temperature to max. 85°C and add HF to 1 cm above sample height
- Repeat until the quartz is dissolved
- Fume the HF by adding 1-2 ml of HNO₃ (4x), HNO₃+HCl (2x) and HCl
- Dissolve sample in 2 ml 9 M HCl
- If sample is not clean centrifuge (cleaned 15 ml centrifuge tube, 10 min)
- Evaporate again and dissolve in 2 ml 9 M HCl (evaporation not necessary when Al aliquot is taken)

4. Optional: Al aliquot

- Transfer sample solution into cleaned 100 ml volumetric glass flasks
- Fill up flasks to exactly 100 ml
- Shake well and pipette 3 ml of sample solution from the flasks into cryovials
- Close tightly and mark filling level on the cryovials
- Pour sample solution back into beaker and let it evaporate to dryness
- Dissolve in 2 ml 9 M HCl

5. Anion columns (removal of Fe)

- Fill columns (20 ml) with 4 ml resin AG 1-8X 100-200 mesh, chloride form
- Use 6 ml resin for samples with high Fe-content (very dark yellow)
- Clean resin with: 20 ml MQ water + 20 ml 1 M HCl + 20 ml 4.5 M HCl + 20 ml 9 M HCl
- Place 50 ml PE bottle under column to collect sample
- Load sample (in 2 ml 9 M HCl)
- Elute sample: 2 ml + 2 ml + 20 ml 9 M HCl (for 4 ml resin)
  2 ml + 2 ml + 32 ml 9 M HCl (for 6 ml resin)
- Pour sample solution back into Savillex beakers and evaporate to dryness
- Keep sample stored in ~1 ml MQ water before the next step
- Fe columns are not re-used

6. Optional: Cation columns (Al separation)

- Fill columns (7.5 ml) with 2 ml resin AG 50W-X8 resin 200-400 mesh
- Clean resin with: 10 ml MQ water + 10 ml 4.5 M HCl + 10 ml 9 M HCl + 3 ml 4.5 M HCl + 10 ml 1 M HCl
- Dissolve dry samples in 2 ml exact 1 M HCl
- Check if sample is completely dissolved, if not add another 2 ml of 1 M HCl
- Optionally heat sample carefully on hot plate (repeatedly add 1 ml of 1 M HCl to not dry down the sample)
- Place 50 ml PE bottle (same as before) under column to collect sample
- Load sample (only 2 ml at once)
- Elute Be (and others, e.g. Mg, Ca) with: 2 ml + 2 ml + 16 ml 1 M HCl (use only exact 1 M HCl)
- Place clean 20 ml PE bottle under column
- Elute Al with 10 ml 5 M HCl
- Clean resin with: 10 ml 9 M HCl + 3 ml 4.5 M HCl + 10 ml 1 M HCl
- Seal and store column in MQ water for re-use
- Evaporate sample to dryness
- Keep sample stored in ~1 ml MQ water before the next step

7. Cation columns (Be separation)

a) Sample preparation
- Dissolve sample in MQ water and some drops of HCl
- Transfer sample solution into clean 15 ml centrifuge tube
- Add NH₄OH (25 %, suprapur) drop by drop until pH~8-9 (usually 10-20 drops), shake as NH₄OH is added
- Centrifuge sample (10 min), decant supernate
- Rinse precipitate with ~6 ml MQ water, centrifuge again and decant supernate
- Add 4 ml 0.4 M oxalic acid, shake well to loosen precipitate and wait 1 hour
- If sample is not dissolved, add another 2-4 ml of 0.4 M oxalic acid
- Optionally heat sample in hot water bath (~80°C)

b) Columns
- Fill columns (7.5 ml) with 1 ml resin AG 50W-X8 resin 200-400 mesh
- Clean resin with: 5 ml MQ water and 2 ml + 3 ml 5 M HNO₃
- Remove HNO₃ with: 2 ml + 3 ml + 1 ml MQ water
- Condition resin with: 2 ml + 3 ml 0.4 M oxalic acid
- Place clean 30 ml PE bottle under column
- Load sample
- Wash in with: 1 ml + 1 ml + 10 ml 0.4 M oxalic acid and 1 ml + 2 ml MQ water
- Place clean 22 ml Savillex vial under column
- Elute Be with: 2 ml + 2 ml + 4 ml exact 0.5 M HNO₃ and 3 ml + 3 ml + 5 ml + 2 ml exact 1 M HNO₃
- Evaporate sample solution to dryness and add 1-2 drops of MQ water
- Clean resin with: 1 ml + 2 ml 5 M HNO₃ and 2 ml MQ water
- Seal and store column in MQ water for re-use

The resin volume has to be adjusted to sample size. 1 ml resin is suitable for up to 1 ml of sample precipitate (before dissolution in oxalic acid). For 1-2 ml of sample precipitate use 2 ml resin. For larger samples use 5 ml resin and 11.5 ml column sizes. Adapt the quantity of acids accordingly.
8. Be precipitation

- Transfer samples (dissolved in MQ water and 1-2 drops of HNO3) into clean 15 ml centrifuge tubes
- Precipitate Be by adding NH\textsubscript{4}OH (25 %, suprapur) drop by drop until pH~9, shake as NH\textsubscript{4}OH is added
- Add 150-200 µl of Fe solution per 0.1 g \textsuperscript{9}Be carrier (here 450 µl) and wait 1 hour
- Centrifuge sample and decant supernate
- Rinse precipitate with MQ water, centrifuge again and decant supernate
- Add 150-200 µl of Fe solution per 0.1 g \textsuperscript{9}Be carrier (here 450 µl)
- Place clean quartz crucible into a metal or ceramic holder
- Centrifuge sample and decant supernate
- Dry samples on a hot plate (80-90°C for 1-2 hours, then ~50°C over night)
- Put lids on and transfer crucible into a quartz sled
- Oxidize sample in a muffle furnace at 650°C

9. Optional: Al precipitation

- Transfer samples (dissolved in MQ water and 1-2 drops of HNO3) into clean 15 ml centrifuge tubes
- Precipitate Al by adding NH\textsubscript{4}OH (25 %, suprapur) drop by drop until pH max. 8, shake as NH\textsubscript{4}OH is added
- Centrifuge sample and decant supernate
- Rinse precipitate with MQ water, centrifuge again and decant supernate
- Place clean quartz crucible into a metal or ceramic holder
- Transfer sample into crucible (not more than half-full)
- Dry samples on a hot plate (80-90°C for 1-2 hours, then ~50°C over night)

AMS target were pressed at PSI/ETH AMS facility.


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