Ronny BOCH, Christoph SPÖTL, Jürgen M. REITNER & Jan KRAMERS:
A Lateglacial travertine deposit in Eastern Tyrol (Austria)
1 Introduction

Travertine is an important group of freshwater carbonates forming locally extensive terrace-like deposits (Ford and Pedley, 1996; Pentecost, 2005). These deposits are typically well bedded—from outcrop scale down to thin section scale—and exhibit moderate to low primary porosity. Travertine consists of low-Mg calcite or, less abundantly, of aragonite (Guo and Riding, 1992; Fouke et al., 2000). The bulk of the world’s travertine deposits appears to have formed abiogenically, i.e., by rapid degassing of CO₂ and concomitant precipitation of calcium carbonate. The CO₂ required for the dissolution of the carbonate host rock is either derived from the soil zone, from a deep-seated source, or a combination of both. The latter two types of travertine are often associated with hot springs in tectonically active areas (e.g., Fouke et al., 2000; Brogi, 2004).

Travertine provides valuable information about palaeohydrological and palaeoenvironmental conditions, because it may form continuously over hundreds or thousands of years thereby recording changes in water availability and climate. Mineralogy and fabrics of travertine are strongly dependent on water temperature and composition and, locally, microbial activity (Turi, 1986; Fouke et al., 2000). Regular lamination often reflects a strong annual or even diurnal control (Guo and Riding, 1994). Stable isotopic and trace element studies can provide further insights into the physical and chemical conditions of the carbonate-precipitating waters (Fazdur et al., 1988; Garnett et al., 2004a; Smith et al., 2004) if the system is well understood (cf. Chafetz and Lawrence, 1994).

In contrast to travertine, tufa is a low-temperature, low-Mg calcite deposit associated with springs, streams or waterfalls, showing a highly porous fabric due to incrustation of plant material or microbial mats (Pedley, 1990; Ford and Pedley, 1996; Pentecost, 2005). Karstification driven by soil-derived CO₂ leads to the formation of Ca-HCO₃-waters which rapidly degas at springs and/or at zones of high water turbulence along streams.
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Figure 1: Geological sketch map of the southwestern part of the Schober Group showing the location of the travertine deposit near Ainet (compiled and simplified after Linner 1994, 1995b and Reitner, 2003).

(cascades, waterfalls). Carbonate precipitation is largely driven by thermodynamic supersaturation (as a result of degassing of CO₂), but plants and mosses growing at springs and in creeks provide large surfaces, thereby enhancing degassing (Arp et al., 2001). Microorganisms have a significant impact on crystal fabrics and rate of carbonate precipitation (Andrews et al., 1997; Merz-Preiß and Riding, 1999). Many tufa deposits are regularly bedded and locally also laminated (Kano et al., 2003). Some of these deposits faithfully record seasonal changes in temperature and/or rainfall variations (Matsuoka et al., 2001; Ihlenfeld et al., 2003). The potential for diagenetic alteration, however, is generally much higher in tufas than in travertine because of their generally high primary porosity and permeability.

An aspect which makes an investigation of Quaternary travertines and tufas particularly interesting is the possibility to absolutely date them using the U/Th method (Harmon et al., 1980; Sturchio et al., 1994; Eikenberg et al., 2001; Frank et al., 2000; Mallick and Frank, 2002; Garnett et al., 2004b; Wang et al., 2004). This permits palaeoenvironmental data obtained from these deposits to be tied into a chronostratigraphic frame with an upper age limit of approximately 400-500 kyr. Difficulties arise from contamination by detrital Th, low initial U concentrations and/or young sample ages (small ingrowth of radiogenic ²³⁰Th). Porous tufa deposits in general are more difficult to date than compact travertine (Garnett et al., 2004b), primarily because the system remained open with respect to the radionuclides long after sedimentation.

Tufa deposits of Quaternary age are numerous in the Alps and are particularly abundant during the Holocene (Hermann, 1957; Huckriede, 1975; Jerz and Mangelsdorf, 1989; Krois et al., 1993; Pentecost, 1995; Andrews et al., 1997). Dense and well laminated travertine, however, is largely absent. This paper reports an occurrence of such a laminated travertine deposit, albeit inactive, in Eastern Tyrol which is composed of both calcite and aragonite. Using a combined field and laboratory approach involving hydro- and geochemistry we examined this carbonate deposit in an attempt to reconstruct palaeohydrological and palaeoenvironmental conditions during its formation.

2. Geologic setting

The travertine deposit is located on a steep, woody SW facing slope near Ainet (Isel Valley, Eastern Tyrol, latitude 46.86179 N, longitude 12.70262 E) at the western edge of the Schober Group between 780 and 920 m a.s.l. (Fig. 1). The area belongs to the metamorphic basement of the Austroalpine unit south of the Tauern Window. The main part consists of the Schober basement.
which can be separated into a lower and an upper complex. A zone of imbrication showing extensive recrystallization constitutes the boundary between the two units (Troll et al., 1976). The lower Petzeck complex (Linner, 2005) — mainly present in the northern part of the Schober Group — consists of paragneiss, mica schist, quartzite, orthogneiss and amphibolite, whereas the upper Prijakt complex comprises amphibolite, eclogite-amphibolite, ortho- and paragneiss (Troll et al., 1976; Linner, 1995a). The tectonic position of the Prijakt complex is supposed to be the result of N-directed overthrusting (Troll et al., 1976; Behrmann, 1990). Marble is extremely rare within the Petzeck complex and only one outcrop of a 1 m thick marble bed intercalated with metapelites was mapped on the SW flank of the Schober Group (Linner 1995a; Fig. 1). The lower part of the Schober Group between Ainnet and Oberlenz consists of mica schist, gneiss and hornfels of the Deferegg Complex which belongs to the tectonic unit of the Defereggent Basement (Linner, 2005).

The NW-SE trending, dextral Isel fault running along the Isel Valley represents the morphologically dominant fault in the study area (Fig. 1). This fault is related to the Periadiatric dextral transpressive regime and, consequently, to the lateral extrusion around 17 Myr leading to the exhumation of the Tauern Window (Mancktelow et al., 2001). The Isel fault cuts the E-W trending Deferegg-Antholz-Valis (DAV) fault, which fades out W Ainnet (Linner, 2005). The ductile sinistral DAV fault separating the Defereggent from the Schober basement W Isel Valley was active until around 30 Myr ago (Mancktelow et al., 2001). During the following transpressive dextral regime a reactivation of this E-W fault zone occurred resulting in polyphase brittle structures. Between Ainnet and Oberlenz the Defereggent basement and the Schober basement are separated by a brittle dextral fault S Daberwald (Linner, 2005). Marbles as well as limestones are present, however, within and adjacent to the fault zone of the DAV ca. 2 km NW Ainnet and on the opposite flank of the Isel Valley (Linner, 2003).

Quaternary sediments are present in the Isel Valley and along the slopes of the Schober Group (Fig. 1). These sediments are predominantly till, mostly from the Last Glacial Maximum (LGM; 19-23 kyr BP according to Mix et al., 2001), when the Isel Valley was filled by an ice stream with a surface elevation of ca. 2300 m a.s.l. (Reitner, 2003). Crudely bedded, coarse grained, poorly sorted, and unconsolidated gravel is common from 1700 m a.s.l. down to the valley floor (ca. 720 m a.s.l.) (Reitner, 2003). Crude bedded, coarse grained, poorly sorted, and unconsolidated gravel is common from 1700 m a.s.l. during Greenland Stadial 2 and at ca. 2200 m a.s.l during the Greenland Stadial 1 (terminology according to Björk et al., 1998).

The travertine deposit stratigraphically overlies gravel of the above described kame terraces on the lower part of the mountain slope and appears to be at the toe of a deep-seated gravitational mass movement (Reitner, 2000). The SW-facing slope above the area of Ranach (1216 m a.s.l) is dissected by extensional graben structures and obsequent scarp margins giving rise to a stair-case morphology, typical of deep-seated toppling (Fig. 1). This slope failure along the SW facing flank of the Schober Group is the result of antithetic displacements along faults and joints striking parallel to the Isel fault and dipping steeply NE toward the slope (Reitner, 2000). This slope morphology suggests that the depth of rock disintegration may reach as deep as 150 m, as estimated for the slope near the Oberes Törl (Fig. 1). In analogy to other areas where this kind of mass movement was observed (Reitner et al., 1993) the toppling started as the slopes had been oversteepened by glacial erosion and had lost support during downwasting of the Isel glacier. It is important to note that the travertine deposit is disrupted by later gravitational slope movements.

3. Methods

Rock samples were obtained from both, carbonate cements within the underlying clastic ice-marginal sediments and the travertine above. Petrographical examinations included transmitted-light and epifluorescence microscopy on thin sections, as well as the determination of the mineralogical composition of the carbonate material using powder X-ray diffraction (XRD). Samples for stable C and O isotope analyses were microsampled from rock slabs at 0.1 mm increments using a semi-automated Micromill system (Merchantek) and measured using a continuous-flow isotope mass spectrometer in the isotope laboratory at Leopold-Franzens-Universität Innsbruck (see Spötl and Vennemann, 2003 for analytical details). Results are reported relative to the VPDB standard. Four samples were selected for U/Th age determination, including two samples of pore-filling calcite from the underlying clastic sediments (samples Ain1 and Ain9), one calcite sample from the travertine (sample Ain6) and one travertine sample almost exclusively consisting of aragonite (Ain4). Samples were dissolved in nitric acid after adding approximately 100 mg of a mixed 238Th-234U spike. Th and U were separated and purified in columns containing an ion exchange resin following standard techniques (Ivanovich and Harmon, 1992). Measurements were performed using a Nu Instruments multicollector inductively coupled plasma mass spectrometer at the University of Bern, Switzerland (see Burns et al, 2003 for details). Ages and 2-sigma uncertainties were calculated using the decay constants of Cheng et al. (2000).
To clarify the modern environmental conditions in the area of the travertine deposit, field studies, including the collection of spring water samples (Fig. 2), were carried out three times during the period of investigation (July and October 2003, May 2004). Analyses of the water samples included field measurements of electric conductivity, carbonate alkalinity and pH. Concentrations of cations (Na, K, Ca, Mg, Sr) and anions (F, Cl, NO₃, SO₄) as well as the concentrations of dissolved SiO₂ were measured in the laboratory using standard techniques (cations: University of Innsbruck; anions: Keele University/UK; dissolved SiO₂: Natural History Museum Vienna). Thermodynamic calculations were performed using PHREEQC. In addition, the C isotopic composition of dissolved inorganic carbon (δ¹³C_DIC) was determined using a gas evolution method based on continuous-flow technology and reported relative to VPDB (see Spötl, 2005 for analytical details). The O isotopic composition of the water samples was determined using the CO₂ equilibration method and results are reported relative to the VSMOW standard. Precision (1 sigma) is better than 0.1 ‰.

4. Results

4.1. Field studies

Field investigations show that the ice-marginal sediments of the kame terrace underlying and adjacent to the travertine deposit are strongly cemented (Fig. 3A). In addition, massively cemented patches of coarse grained clastic sediments (ice-marginal sediments probably intermixed with talus) are present higher up on the slope. Within the glacial sediments isopachous calcite rinds in porous gravel as well as flowstone-like layers of calcite are present in fractures (Fig. 3A). These calcite layers reach a thickness of up to 40 cm (typically a few centimetres) and caused localized consolidation of the otherwise unconsolidated ice-marginal sediments.

The travertine sharply overlies the consolidated gravels (Fig. 3B) and consists of a lower interval (ca. 2.5 m) of compact and regularly laminated carbonate, lacking siliciclastic inclusions. The travertine grades upward into progressively more porous and less distinctly laminated travertine. The uppermost 10 to 20 cm are highly porous tufa containing imprints of leaves and casts of grasses and needles. Although the travertine deposit has been fractured and partially disintegrated due to slope processes subsequent to its formation, there is clear field evidence of synsedimentary bending of the strata on metre-scale at the edge of the small terrace formed by slope movements (Fig. 3C). These primary sedimentary features resemble barrages commonly observed in modern tufa and travertine occurrences (e.g. Andrews et al., 2000).

The travertine body is clearly inactive today and covered by brown soil and vegetation (forest) and partially disintegrated into individual blocks (Fig. 3D). Hydrological activity in the vicinity of the travertine body is limited to streams which, although mildly supersaturated with respect to calcite (see Hydrochemistry, below), lack visible carbonate precipitation. Small, isolated occurrences of inactive spring tufa (Fig. 1) are also present in other places along the slope of the Schober Group (Reitner, 2003).

4.2 Mineralogy and Fabrics

The bulk of the travertine deposit consists of regularly laminated, dense carbonate material. White radiaxial, fibrous aragonite layers (confirmed by XRD analyses) alternate with typically thinner, light brown, fibrous calcite layers resulting in a macroscopically visible millimetre-scale rhythmite (Figs. 4A, B). Additionally, micrometre-thin micrite layers, which often pass laterally into the fibrous calcite layers, are present. Lamina thickness varies between 0.1 and 2 mm for both aragonite and calcite laminae, although aragonite laminae are typically thicker. Within the aragonite layers hemispherical aggregates are a common feature (Figs. 4B, C). These aggregates show a distinct, micrometre-scale lamination. Observations using epifluorescence suggests that this fine lamination is caused by a regular alternation of brightly fluorescent and dull fluorescent laminae (Fig. 4D). Up to 150 individual laminae are present within a ca.
1 mm thin layer. This fine lamination can also be observed in the fibrous calcite layers, albeit less distinct. Aragonite layers locally show evidence of partial dissolution (Figs. 4B and C). Shrub-like aggregates of a second generation of aragonite crystals are present in voids. Locally, fractures (both subhorizontal and obliquely oriented) within the calcite-aragonite succession are filled by isopachous, brown and dense calcite rinds showing bipolar growth textures and lamination. These fracture fills are identical to the isopachous calcite cement in the clastic sediments forming flowstone-like deposits locally up to 40 cm in thickness. Within the uppermost part (i.e. some tens of centimetres beneath the surface) the travertine changes from dense, well laminated into porous and less distinctly laminated (Fig. 4E). Thick, porous, mixed aragonite-calcite layers alternate with thinner, dense calcite layers. The abundance of siliciclastic material, plant casts and imprints increases up section within this interval, which then passes gradually into highly porous tufa (Fig. 4F). This topmost unit contains abundant sand- and silt-size detritus as well as encrusted plant material, and is composed of calcite only.

4.3 Carbonate stable isotope analysis

Stable C and O isotope analyses of aragonite range from +1 to +2 ‰ and -10.4 to -9.6 ‰, respectively, while those of calcite vary only between -1.8 to 0 ‰ and -11.2 to -10.5 ‰, respectively. C and O isotope values show strong covariance with a slope $\Delta^{13}C/\Delta^{18}O$ of 2.4 (Fig. 5). High-resolution isotope traverses across regularly laminated travertine show a near-rectangular pattern of low calcite values and high aragonite values (Fig. 6). Due to the slightly irregular boundaries between individual calcite-aragonite laminae micromilling resulted in variable admixing of calcite near aragonite boundaries giving rise to more gradual isotope shifts. Isotopic measurements of porous, calcitic tufa yielded values of -3 to -2 ‰ for $\delta^{13}C$ and -12 to -11 ‰ for $\delta^{18}O$.
(Fig. 5), which are clearly lower than those of the laminated (calcite) samples.

4.4. Hydrochemistry
Waters from five streams in the vicinity of the travertine deposit (Fig. 2) show elevated values of electrical conductivity (400-530 \( \mu \text{S/cm} \)) and carbonate alkalinity (9-13 °dH; Table 1). Cation analyses yielded elevated Mg and Sr concentrations (22-35 mg/l and 0.3-0.5 mg/l, respectively), as well as relatively high K/Na and Mg/Ca ratios (both 0.6 to 0.8). Anions show elevated SO$_4$ and...
with respect to calcite and even aragonite (Table 1). Small patches of tufa are present in the area (Fig. 1) and may have formed during the Early Holocene, but dating control is lacking. In summary, field evidence documents that the groundwater discharge that lead to the formation of bedded travertine near Ainet was a comparably short-lived event after deglaciation of the Isel Valley.

The most conspicuous aspect of the deposit are the calcite-aragonite couplets which constitute the main part of the succession (Figs. 4A, B). Both, the white aragonite and the light brown, fibrous calcite are of primary origin and we rarely found thin-section evidence of minor replacement of aragonite by calcite. The regular interlayering of these two polymorphs also

### 4.5. Age determination

Four carbonate samples dated using the U/Th method yielded Late-glacial ages (Table 2). A calcite sample from the top of the laminated succession (Ain6) and a predominantly aragonite sample from the central part (Ain4, containing minor amounts of calcite) show ages of 13.44 ± 0.16 kyr BP and 13.49 ± 0.17 kyr BP, respectively. Two samples of calcite cement (Ain1 and Ain9) from the underlying ice-marginal sediments show slightly older ages (13.69 ± 0.13 kyr BP and 13.96 ± 0.11 kyr BP). All samples exhibit very high U concentrations of approximately 200 ppm regardless of the mineralogical composition and the 232Th correction is therefore negligible.

### 5. Discussion

#### 5.1 Setting of the travertine

The travertine deposit located on a SW facing slope E Ainet is an isolated occurrence which was first discovered during routine geological mapping (Reitner, 2003). So far, it is the only such body in this area and we are unaware of comparable deposits in other regions of the Eastern Alps. The deposit is petrologically distinct from spring tufas and in fact gradually evolves into tufa up section. This suggests that the mode of formation of this travertine may not be directly comparable to (modern) tufa deposition. Although the majority of the deposit is hidden beneath forest soil, gravitational mass wasting and slope erosion provide local access to the internal structure of the travertine. These observations suggest that the waters first percolated through coarse-grained clastic sediments thereby precipitating isopachous calcite rinds. Subsequent carbonate precipitation occurred subaerially (and continued locally in the subsurface), giving rise to a travertine terrace forming on top of cemented clastic sediments. There is evidence of cascade- or barrage-like structures near the edge of the terrace (cf. Fouke et al., 2000), but the distal part of the deposit (further down the slope) is not preserved. Biological structures (e.g., casts of leaves) are not abundant within the main body of the travertine, unlike modern (and Holocene) tufa deposits which engulf trees and calcify mosses and grasses. The abundance of casts of grasses and imprint of needles in the top tufa layer, however, suggests an increase in local vegetation toward the end of travertine accretion.

No modern tufa or travertine formation occurs today, although streams in the vicinity of the deposit are mostly supersaturated with respect to calcite and even aragonite (Table 1). Small patches of tufa are present in the area (Fig. 1) and may have formed during the Early Holocene, but dating control is lacking. In summary, field evidence documents that the groundwater discharge that lead to the formation of bedded travertine near Ainet was a comparably short-lived event after deglaciation of the Isel Valley.

#### 5.2 Internal structure of the travertine

The most conspicuous aspect of the deposit are the calcite-aragonite couplets which constitute the main part of the succession (Figs. 4A, B). Both, the white aragonite and the light brown, fibrous calcite are of primary origin and we rarely found thin-section evidence of minor replacement of aragonite by calcite. The regular interlayering of these two polymorphs also

**Figure 5:** Stable isotopic analyses of travertine and tufa samples from Ainet. The two circles define the compositions of aragonite and calcite endmembers. For details see text.
argues in favour of a primary sedimentary origin, similar to calcite-aragonite preserved in speleothems (Railsback et al., 1994). While abundant in the rhythmite succession, aragonite is not present within the clastic sediments beneath and adjacent to the travertine body, which are cemented by vadose isopachous calcite rims only. The groundwater seeping through the clastic sediments apparently never reached the supersaturation required for aragonite to precipitate.

The highly regular alternation of the two CaCO$_3$ polymorphs on a scale of a few millimetres suggests a strong, high-frequency forcing, most likely of seasonal origin. Annual banding has commonly been reported from tufa and travertine deposits alike and is mostly attributed to seasonal variations in temperature and/or rainfall (Renaut and Jones, 1997; Kano et al., 2003; Ihlenfeld et al., 2003). The growth rates observed in Ainet are comparable to those from tufa occurrences (e.g., 4 mm/yr in SW Japan; Kano et al., 2003), and rather similar to the travertine deposit at Rapolano Terme, Italy (ca. 0.5 mm/yr – Guo and Riding, 1992). On the other hand, hot-spring travertine may show much faster growth rates. Chafetz and Guidry (2003) reported growth rates of more than 10 mm/yr from Mammoth Hot Springs, Yellowstone National Park, and Fouke et al. (2000) showed evidence of even higher rates from another section in the same region (several cm/yr).

As aragonite is favoured over calcite at higher temperatures (and higher Mg/Ca ratios in the water – Morse and Mackenzie, 1990) we attribute thick aragonite laminae to warm-season precipitation. Conversely, the typically much thinner low-Mg calcite laminae probably formed during the cold season, when the degree of supersaturation was lower, suppressing aragonite precipitation (e.g. Chafetz et al., 1991; Guo and Riding, 1992). Several studies conducted on travertines also suggest a possible biotic control on aragonite formation (e.g. Guo and Riding, 1992; Chafetz and Guidry, 2003). Photosynthetically active bacteria influence the degree of supersaturation by changing the CO$_2$ content of the water (Buczynski and Chafetz, 1991). However, both models are consistent with aragonite precipitation during the warm season and the lack of aragonite in the cemented clastic sediments beneath and lateral to the travertine body (lower temperatures in the vadose zone than at the surface).

An even finer-scale lamination is preserved in aragonite and many calcite layers (Figs. 4C, D). This lamination is not commonly seen in travertine and tufa deposits elsewhere. Given that the individual aragonite and calcite laminae are probably of seasonal origin, we regard the micrometre-scale lamination as most likely of diurnal origin. This interpretation is consistent with lamina counts (see above) and the presence of very thin fluorescent sublaminae (Fig. 4D). Folk et al. (1985) and Guo and Riding (1992) reported laminae from Italian travertine and attribute their origin to changes in the activity of photosynthetic bacteria due to diurnal variations in the intensity of sunlight and probably temperature (they did not report fluorescence properties, though).

The presence of rather regular lamination on millimetre and micrometre scales permits some first-order estimates of the duration of travertine formation. The average thickness of aragonite-calcite couplets is 1.5 mm, which suggests that the ca. 2.5 m thick bedded travertine terrace formed within less than ca. 1700 yr.
5.3 Stable isotopes as palaeoenvironmental proxies

The stable isotope values of C and O help to elucidate the processes involved in aragonite and calcite precipitation. The delicate interlayering of aragonite and calcite on millimetre scale demanded a spatially resolved sampling strategy. Despite applying high-resolution micromilling the measurements require careful evaluation prior to interpretation. The high-resolution isotope traverses show a steep rise in both isotope parameters at the bottom of each aragonite lamina followed by a short plateau-like feature and a steep drop near the boundary to the next calcite lamina (Fig. 6). Close inspection reveals, however, that this isotope pattern results from inevitable mechanical mixing due to the finite width of the milling trench. The more irregular the boundaries of the aragonite-calcite couplets (in three dimensions) the more gradual the apparent isotope shifts. We therefore regard only isotope values from the centre of each lamina as reliable and regard data from those few laminae that do not run strictly perpendicular to the direction of the sampling trench as mixtures. Within the central portions of the aragonite laminae there is little (<0.5 ‰) systematic change in δ¹⁸O (Fig. 6). This intra-lamina isotope variability is smaller than the inter-lamina variability.

When plotted on a standard scatter diagram the stable isotope data define a band showing a high degree of linear correlation (Fig. 5). This essentially reflects the covariance seen in the stable isotope traverses and therefore represents a binary (artificial) mixing line only.

At equilibrium conditions (25°C) aragonite is expected to be 18O enriched in O relative to coexisting low-Mg calcite by 0.6 ‰ (Tarutani et al., 1969). Frisia et al. (2002) reported a mean value of 1 ‰ (range 0.7 to 1.4 ‰) for aragonite-calcite speleothem samples from southern France. Pure aragonite layers from Ainet are on average ca. 0.8 ‰ higher in ¹⁸O compared to calcite layers, suggesting that both polymorphs formed from spring water of similar O isotopic composition.

This interpretation can be tested by comparing the stable C isotopic compositions of aragonite and calcite. According to equilibrium considerations aragonite is enriched in ¹³C relative to co-precipitating calcite at 25°C by 1.7 (±0.4) ‰ (Romanek et al., 1992). Speleothem samples studied by Frisia et al. (2002) showed a slightly higher ¹³C enrichment (2 to 3.4 ‰), attributed to additional kinetic fractionation during aragonite precipitation. Figure 5 shows that δ¹³C values of aragonite from Ainet are on average 2 to 2.5 ‰ higher than those of the calcite laminae, supporting our previous interpretation that no significant change in the isotopic composition of the water occurred during the seasonal shift from aragonite to calcite precipitation. Taking together, these data also argue against significant kinetic fractionation during carbonate precipitation. This is an important conclusion, as it rules out evaporation as a major driving force of aragonite precipitation. In addition, some quantitative constraints can be placed on the conditions of carbonate formation at Ainet. If we assume that the palaeowaters had a ¹⁸O value similar to today’s streams in the area (-12 ‰) the calculated equilibrium water temperature was <10°C for both aragonite and calcite. These values are sufficiently close to the mean annual air temperature (ca. 7°C) and to the measured water temperatures of streams in this area (see Table 1) to render a hydrothermal origin of the travertine-forming water unlikely.

A simple sensitivity test corroborates the robustness of these findings. Calculations of the ¹⁸O value of water in isotopic equilibrium with the observed aragonite isotope values at elevated temperatures (assuming 25-30°C) yield -6.7 to -5.6 ‰.
concentration of the solution as a means to promote aragonite over calcite precipitation. Seasonally changing pCO₂ of the isotope data, however, rule out significant evaporative through April resulted in thin laminae of calcite. The stable and partially freezing conditions during the months of November location) may have facilitated aragonite precipitation during the warm season, when both air temperatures and photosynthetic activity were high.

The C isotopic compositions of both the rhythmically bedded travertine and its tufa cap show elevated δ¹³C values (Fig. 5), significantly higher than those reported from most modern tufas in climatically comparable regions (see review in Andrews and Brasier, 2005), but consistent with a compilation of data from travertine deposits (Turi, 1986). These values indicate that DIC of the palaeowater was largely rock-buffered (there is only a small (~1 %) fractionation between DIC and calcite – Romanek et al., 1992). In contrast, δ¹³C values of streams in the area are significantly lower (~8 to -6 ‰) reflecting a higher proportion of soil-derived DIC in the present-day groundwater. In other words, the C isotope data suggest a change in groundwater composition between the time of travertine deposition and today.

What controlled the regular switching between aragonite and calcite precipitation? We argued above that these couplets are most likely of annual origin, an assumption that is largely consistent with the duration of travertine deposition as suggested by the U/Th data. The switch from metastable aragonite to low-Mg calcite precipitation is probably related to seasonal changes in air temperature, but the precise mechanism remains unclear. Solar heating of the water (SW exposed location) may have facilitated aragonite precipitation during summer (Morse and Mackenzie, 1990), whilst cold temperatures and partially freezing conditions during the months of November through April resulted in thin laminae of calcite. The stable isotope data, however, rule out significant evaporative concentration of the solution as a means to promote aragonite over calcite precipitation. Seasonally changing pCO₂ of the discharging groundwater could also influence the saturation state of groundwater as enhanced biological activity in the soil zone during summer gives rise to more CO₂ being dissolved in the groundwater (cf. Kano et al., 2003). Stable C isotope data, however, suggest that the proportion of the latter was low (see above), i.e. the C system was largely rock-buffered and insensitive to seasonally variable input of soil-CO₂. Bacteria may also influence crystal nucleation in travertine deposits, both actively and passively (Merz-Preiß and Riding, 1999; Fouke et al., 2000; Chafetz and Guidry, 2003; Kano et al., 2003) and it is conceivable that cyanobacterial activity during the warm season enhanced abiogenic degassing of CO₂, thereby favouring aragonite over calcite precipitation. Guo and Riding (1992) reported regularly alternating aragonite-calcite lamination from Italian travertines and suggest a biotic control on aragonite formation, whilst calcite is apparently of abiotic origin.

### 5.4. Origin of palaeofluid flow

The stable O isotope data of the travertine suggest that the palaeowaters were isotopically similar to present-day springs and streams on the flank of the Schober Group, i.e. they were recharged as meteoric precipitation higher up on the mountains. Hydrochemical data show that today’s streams contain an appreciable amount of total dissolved solids, expressed as electric conductivity values up to 530 µS/cm (Table 1), even exceeding values typical of aquifers in limestones of the Alps (e.g., Zötl and Goldbrunner, 1993). These high values in conjunction with high concentrations of dissolved silica and elevated concentrations of F and sulfate (Table 1) are fingerprints of rather extensive water-rock interactions in the aquifer of these metamorphic rocks even today. The very high U content of the travertine (both in aragonite and calcite – Table 2) as well as the high δ¹⁸O values underscore this conclusion. Geologic mapping revealed only a single small outcrop of a marble lens on the flank of the Schober Group (Linner, 1995a; Fig. 1). Present-day water compositions of the streams are also more consistent with extended leaching of carbonate-poor metamorphic rocks: the molar Ca(+Mg)/HCO₃ ratio is 0.81-0.66, inconsistent with simple stoichiometric dissolution of carbonate rocks. Elevated sulfate concentrations hint toward sulfide oxidation as a powerful process speeding up mineral dissolution. The most likely mechanism giving rise to such evolved water compositions in metamorphic rocks are water-rock interactions in a heavily fractured aquifer, providing large, fresh surfaces. An example of carbonate precipitation associated with metamorphic rocks are Lateglacial and Holocene calcitic and aragonitic

<table>
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<th>Sample</th>
<th>Description</th>
<th>U (ppm)</th>
<th>δ²³⁵U³⁷⁹U initial (activity)</th>
<th>δ³⁶⁸⁴⁹⁸U (activity)</th>
<th>δ³⁶⁸⁴⁹⁸Th³⁶⁸⁴⁹⁸Th (activity)</th>
<th>δ³⁶⁸⁴⁹⁸Th³⁶⁹¹⁶⁴⁹¹⁶⁴⁹¹ (activity)</th>
<th>Age (uncorr.) (years)</th>
<th>Age (corr.) (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ain 1</td>
<td>Calcite cement</td>
<td>208.9 ± 1.0</td>
<td>0.9771 ± 0.0012</td>
<td>0.9780 ± 0.0012</td>
<td>1484 ± 15</td>
<td>0.1178 ± 0.0000</td>
<td>13700 ± 130</td>
<td>13690 ± 130</td>
</tr>
<tr>
<td>Ain 9</td>
<td>Calcite cement</td>
<td>193.9 ± 0.8</td>
<td>0.9794 ± 0.0012</td>
<td>0.9802 ± 0.0012</td>
<td>2119 ± 21</td>
<td>0.1200 ± 0.0009</td>
<td>13960 ± 110</td>
<td>13960 ± 110</td>
</tr>
<tr>
<td>Ain 6</td>
<td>Travertine calcite</td>
<td>227.8 ± 1.0</td>
<td>0.9786 ± 0.0015</td>
<td>0.9794 ± 0.0015</td>
<td>70426 ± 1543</td>
<td>0.1158 ± 0.0013</td>
<td>13440 ± 160</td>
<td>13440 ± 160</td>
</tr>
<tr>
<td>Ain 4</td>
<td>Trav. aragonite</td>
<td>190.3 ± 0.9</td>
<td>0.9887 ± 0.0011</td>
<td>0.9891 ± 0.0011</td>
<td>1200 ± 21</td>
<td>0.1162 ± 0.0004</td>
<td>13490 ± 170</td>
<td>13490 ± 170</td>
</tr>
</tbody>
</table>

**Table 2: U/Th data**

Ronny BOCH, Christoph SPÖTL, Jürgen M. REITNER & Jan KRAMERS
A Late-glacial travertine deposit in Eastern Tyrol (Austria)

Flowstones in extensional joints of the heavily deformed Vinschgau schists, Southern Tyrol (Spötl et al., 2002). These speleothems are likewise very high in U and appear to be related to tufa mounds on the surface. In the case of Ainet there are two possible candidates of fractures, tectonic fractures, and fractures associated with deep-seated gravitational mass movements on the steep SW-facing flank of the Schober Group. Fractures of tectonic origin are undoubtedly present in the area (see Geologic setting) and may have facilitated fluid flow in the subsurface. The study area is situated southeast of the termination of one of the major faults in southern Austria, the DAV fault. Recent drilling for thermal waters in St. Jakob (Defreggen Valley), located 29 km WNW Ainet, encountered water of 29.5°C in strongly deformed metamorphic rocks of the DAV fault at a depth of 98 m (H. Mostler, pers. comm. 2005). Although the amount of water produced by this well was small, it proved that advective heat transport occurs along this fault zone. The chemical composition of this water, particular from a sample taken at a depth of 1.5 km, is very different from those near Ainet (electric conductivity 10.8 mS/cm, F-rich Na-Cl water type). No evidence of travertine deposition possibly associated with the DAV fault has been reported so far. The faults present in the immediate vicinity of Ainet are related to the Isel fault (Linner, 2005), but there is no clear relationship between these faults and the location of the travertine deposit.

In contrast, field studies have shown that the mountain slope above the travertine is dissected by extensional graben structures and NW-SE trending obsequent scarps (i.e., parallel to the Isel Valley; Fig. 1) leading to a stair-case like slope morphology. These features are the result of toppling due to antibiotic displacement of faults and joints oriented parallel to the Isel fault and dipping toward the slope. The location of the travertine body on one of these small stair-case terraces implies a connection between its formation and the presence of fractures resulting from slope movement, as suggested by Linner (2005) on the base of mapping. These fractures may have provided new pathways for groundwater to discharge near the foot of the mountain. U/Th data tightly constrain the formation of these carbonates to the Greenland Interstadial 1 (Allerod; Fig. 7), i.e. only a few thousand years subsequent to the completing of the downwasting of the ice masses that filled the Alpine valleys during the Last Glacial Maximum (van Husen, 2004). Both, the timing of the onset of travertine deposition and its short life span as indicated by the small size of the deposit and lamina counts are consistent with a model of slope movement initiated by the melting of the valley glacier and concomitant opening of new fluid pathways allowing groundwater to emerge and precipitate carbonate locally.

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