Deformation induced quartz-fluid oxygen isotope exchange during low-grade metomorphism : an example from the Glarus thrust, E Switzerland

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Deformation induced quartz-fluid oxygen isotope exchange during low-grade metamorphism: an example from the Glarus thrust, E Switzerland

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Abstract

The Glarus overthrust is a large thrust fault in the Helvetic Alps of eastern Switzerland, where Helvetic decollement nappes were thrust northwards over Infrahelvetic units at subgreenschist (in the north) to greenschist (in the south) facies conditions during the Miocene. In the northern section of the thrust, a minimum of 35 kilometers of displacement was largely accommodated by deformation of a calc-mylonite layer (about one to three meter thick) between the Tertiary flysch in the footwall and the siliciclastic Verrucano formation in the hangingwall of the thrust and by deformation of the lowermost two to five meters of the Verrucano formation. Pressure solution, cataclastic flow and limited dynamic recrystallization were the prime deformation mechanisms in the siliciclastic rocks. Oxygen isotope exchange between quartz and a pore fluid that ascended from the dewatering flysch in the footwall was effective only in the highly strained portions at the base of the Verrucano. In contrast, quartz was largely inreactive with respect to oxygen isotope exchange at distances of more than about 2 meters above the thrust, where thrust related deformation is practically absent. The correlation between deformation intensity and the extent of quartz oxygen isotope alteration suggests that deformation was the prime control for quartz-fluid oxygen isotope exchange. Fracturing during cataclastic flow probably generated permeability, which allowed fluids to migrate from the flysch in the footwall into the Verrucano in the hangingwall of the thrust. Dissolution-reprecipitation, grain size reduction by fracturing and limited grain boundary migration associated with bulging recrystallization were the mechanisms that allowed for significant quartz-fluid oxygen isotope exchange at the base of the Verrucano.

Keywords: Glarus thrust, subgreenschist facies, deformation, cathodoluminescence, oxygen isotope exchange.

Introduction

Oxygen is a major component of fluids in the earth crust. Depending on their provenance fluids may have characteristic oxygen isotope signatures (e.g. SHEPPARD, 1986). During migration through the crust, fluids can exchange isotopically with the rocks. This will, in general, lead to a change in the isotopic compositions of both, the minerals and the fluid. Abnormal isotopic compositions of rocks and minerals are a robust indication of fluid rock interaction. The systematics of oxygen isotope alteration has become a cornerstone in the investigation of fluid-rock interaction (e.g. NABELECK, 1991). In this context an understanding of mineral-fluid oxygen isotope exchange is of crucial interest. The rate at which a mineral exchanges its oxygen with the pore fluid decides upon the degree of equilibration that is attained during fluid-rock interaction. Knowledge about the equilibration state is in turn important for the interpretation of fluid induced oxygen isotope alteration (e.g. CRISS et al., 1987; BAKER and SPIEGELMAN, 1995; ABART and SPERB, 1997).

If no growth or dissolution of mineral grains is involved in oxygen isotope exchange, then the exchange rate is most probably controlled by oxygen diffusion within mineral grains. Oxygen volume diffusion is a relatively slow process, particularly at low temperatures. Experimentally determined oxygen diffusivities in quartz are too slow to allow for significant oxygen isotope exchange of millimeter sized quartz grains during

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low-grade metamorphism (FARVER and YUND, 1991a). The fact that oxygen isotope alteration is, nevertheless, documented for quartz from low-grade environments (e.g. GREGORY et al., 1989; EPPEL and ABART, 1997) suggests that in natural systems isotopic exchange may be significantly enhanced by alternative processes such as grain size reduction during fracturing or dynamic re-crystallization. Quartz-fluid oxygen isotope exchange may also be controlled by dissolution-re-precipitation (COLE, 1983; COLE and OHMOTO, 1986; KIRSCHNER et al. 1995a). It has been shown experimentally, that quartz dissolution-reprecipitation is a particularly viable mechanism for quartz-fluid oxygen isotope exchange (CLAYTON et al., 1972; MATHEWS et al., 1983). Dissolution-reprecipitation may be induced by deformation. Quartz may be mobilized in the course of pressure solution, which has been recognized as an important deformation mechanism at greenschist and sub-greenschist facies conditions (e.g. PASS-CHIER and TROUW, 1998). Quartz is precipitated from dissolved silica preferably in pressure shadows of rigid objects, and it may seal fractures to form veins (KIRSCHNER et al. 1995b)

Here we report on observations pertaining to the interplay between deformation during low-grade metamorphism and quartz-fluid oxygen isotope exchange in the northern section of the Glarus thrust, a crustal scale thrust fault in the Helvetic Alps of eastern Switzerland. New petro-graphic data including cathodoluminescence ob-servations are presented from a sampling profile through the lowermost eight meters of the Verru-cano formation in the hangingwall of the Glarus thrust at the Lochseiten locality. These data are correlated with published oxygen isotope data on quartz and calcite from the same locality. We focus on the influence of thrust related deforma-tion upon quartz-fluid oxygen isotope exchange. The significance of quartz dissolution reprecipita-tion, deformation-induced grain size reduction and limited grain-boundary migration as well as the effectivity of oxygen diffusion in quartz and quartz aggregates are discussed.

Geologic Setting

The Glarus thrust is a prominent thrust fault ex-posed over an area of about 600 square kilo-meters in the eastern Helvetic Alps (Fig. 1). The hangingwall of the thrust is represented by the Helvetic nappes, which comprise a pile of décolle-ment nappes composed of Permian to Eocene sediments. The Infrahelvetic units in the footwall of the thrust consist of a crystalline basement and a parautochthonous Mesozoic to Tertiary sedi-mentary cover. In addition the Infrahelvetic in-cludes allochthonous slices of south-Helvetic (Blattengrat) and Penninic (Sardona) flysch. The allochthonous flysch units were emplaced on the parautochthonous N-Helvetic flysch during the Oligocene "Pizol" phase of deformation (PFIF-FNER, 1977). The major penetrative deformation occurred during the Upper Oligocene "Calanda" phase, which produced large scale folding of the Infrahelvetic complex. Thrusting along the Glarus
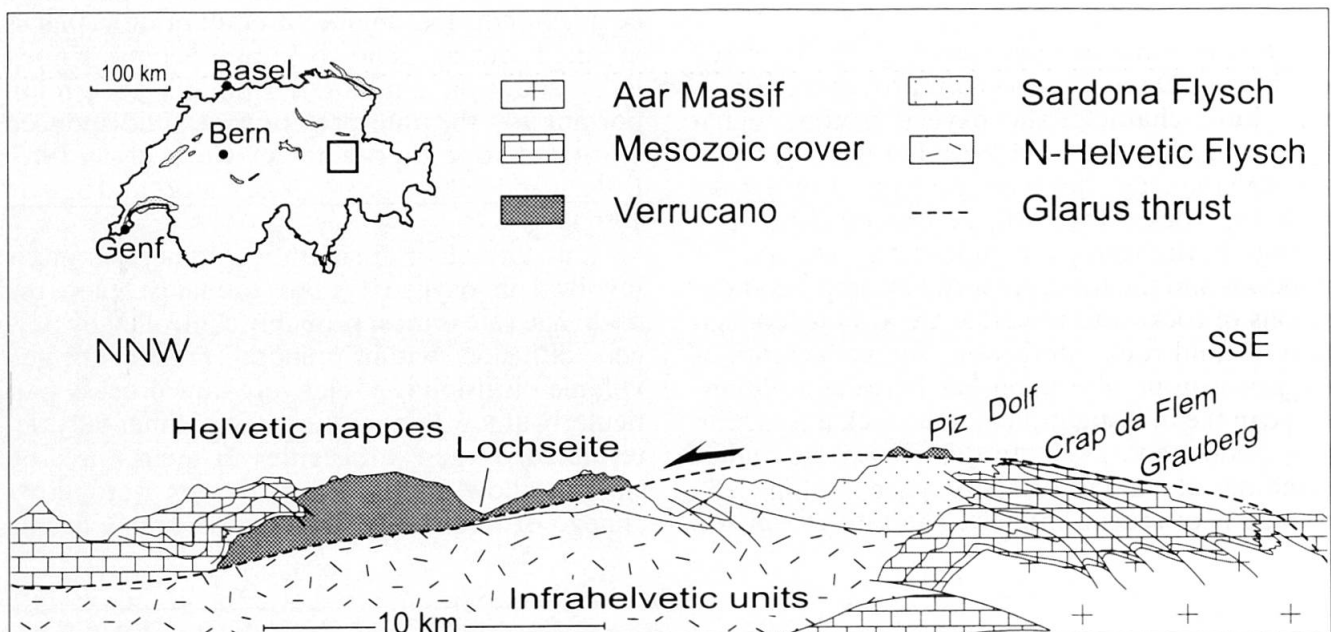

Fig. 1 Simplified cross section of the Glarus thrust, modified from BADERTSCHER et al. (2002).

thrust occurred during the Early Miocene (MILNES and PFIFFNER, 1980) and is referred to as the "Ruchi" phase. Subsequent shortening in the Infrahelvetic basement occurred during the Miocene "Grindelwald" phase (SCHMID et al., 1996). It caused up-doming of the Helvetic realm and produced the present day geometry of the thrust.

The Glarus thrust is exposed as an exceptionally sharp horizon. The thrust surface is characterized by the presence of a thin (<1 to 5 meters thick) continuous layer of calc-mylonite, the "Lochseiten calc-mylonite". The hangingwall is represented by the Permian Verrucano formation, a clastic series of predominantly siltstones, sandstones and shales with minor intercalations of conglomerates and volcanoclastic horizons. In the southernmost exposures of the Glarus thrust Verrucano is thrust over parautochthonous Late Jurassic to Early Cretaceous limestones. In the north, the footwall of the thrust is represented by flysch primarily comprised of marly slates, sandstones and conglomerates.

Metamorphic grade ranges from "anchizonal" (i.e. ≥200 °C) in the north and in the footwall flysch to lower greenschist facies (i.e. ≅ 350 °C) in the south and in the hangingwall Verrucano (FREY, 1988; RAHN et al., 1995). The "anchi/epi zone" boundary is offset along the Glarus thrust by about two kilometers (RAHN et al., 1995), and an inverse metamorphic gradient is documented across the thrust (FREY, 1988). This indicates that displacement along the thrust occurred at least in part after the thermal peak of metamorphism. The Glarus thrust probably developed at a depth of 10 to 15 kilometers corresponding to lithostatic pressures of about 300 to 450 MPa. Metamorphism in the Verrucano was dated by HUNZIKER et al. (1986) and by HUNZIKER (1987) at 30 Ma based on K/Ar data. Concordant K/Ar and Rb/Sr ages of "illite" (< 2μm) from the Lochseiten locality indicate that thrusting was active untill at least 23 Ma.

The thrust contact at Lochseiten

The Lochseiten locality is situated about two kilometers east of the village of Schwanden at Swiss coordinates 725.860/206.400. A vertical section of about one meter of footwall flysch, 50 centimeters of Lochseiten calc-mylonite and 20 meters of the hangingwall Verrucano is exposed. The flysch is composed of marly slates and shale layers alternating with impure sandstone layers on a millimeter scale. The metamorphic mineral assemblage comprises illite, chlorite, albite, quartz, calcite, and organic material. The Lochseiten calc-

mylonite is characterized by abundant millimeter-thick folded and disrupted calcite veins. It shows evidence of both ductile and brittle deformation (SCHMID, 1975; BADERTSCHER and BURKHARD, 2000). The mesoscopic structure of the calc-mylonite was referred to as "knead structure" by HEIM (1921). The Verrucano formation in the hangingwall is primarily comprised of massive siltstones and sandstones with conglomerate horizons. The main constituents of Verrucano are quartz and albite, which are either present as detrital grains or as lithic fragments. Muscovite, calcite, and chlorite are present in a fine-grained matrix. In the lowermost one to two meters above the thrust the Verrucano is intensely deformed and has obtained a green colour. Macroscopically it exhibits features that are transitional between those of a mylonite and a cataclasite, respectively. Because of its close spatial association with the Glarus thrust, intense deformation in the lowermost Verrucano is ascribed to the "Ruchi" phase. Further away from the thrust the intensity of thrust-related deformation quickly decreases, and the rocks have a reddish colour, which is characteristic for unaltered Verrucano in the northern section of the Glarus Alps. At distances of more than about 10 meters above the thrust, the schistosity is probably due primarily to the pre-thrusting deformation of the "Calanda" phase (SIDDANS, 1979). Detrital grains of quartz and albite of up to five millimeter diameter are abundant in the rock. Towards the thrust, the detrital grains are progressively transformed into fine-grained polycrystalline aggregates, and albite shows progressive alteration to sericite. An increase of the phyllosilicate content in the lowermost few meters of the Verrucano is also reflected by an increase in the bulk rock water content from background values of about 2 wt% at more than 10 meters above the thrust to about 4 wt% at the base of the Verrucano (ABART et al., 2002). Ankerite and calcite are present in micro-fractures and as alteration products of feldspars. The carbonates were precipitated or at least remobilized during thrusting.

Analytical methods

All samples were cut normal to the foliation and parallel to a N–S stretching lineation. Polished thin sections were examined under a high-sensitivity cathodoluminescence microscope (RAMSEYER et al., 1989) with an energy of 25 keV and a beam current density of 0.3 μA/mm². Luminescence photomicrographs were recorded on Ectachrome 400 ASA colour transparency film and developed at 800 ASA.
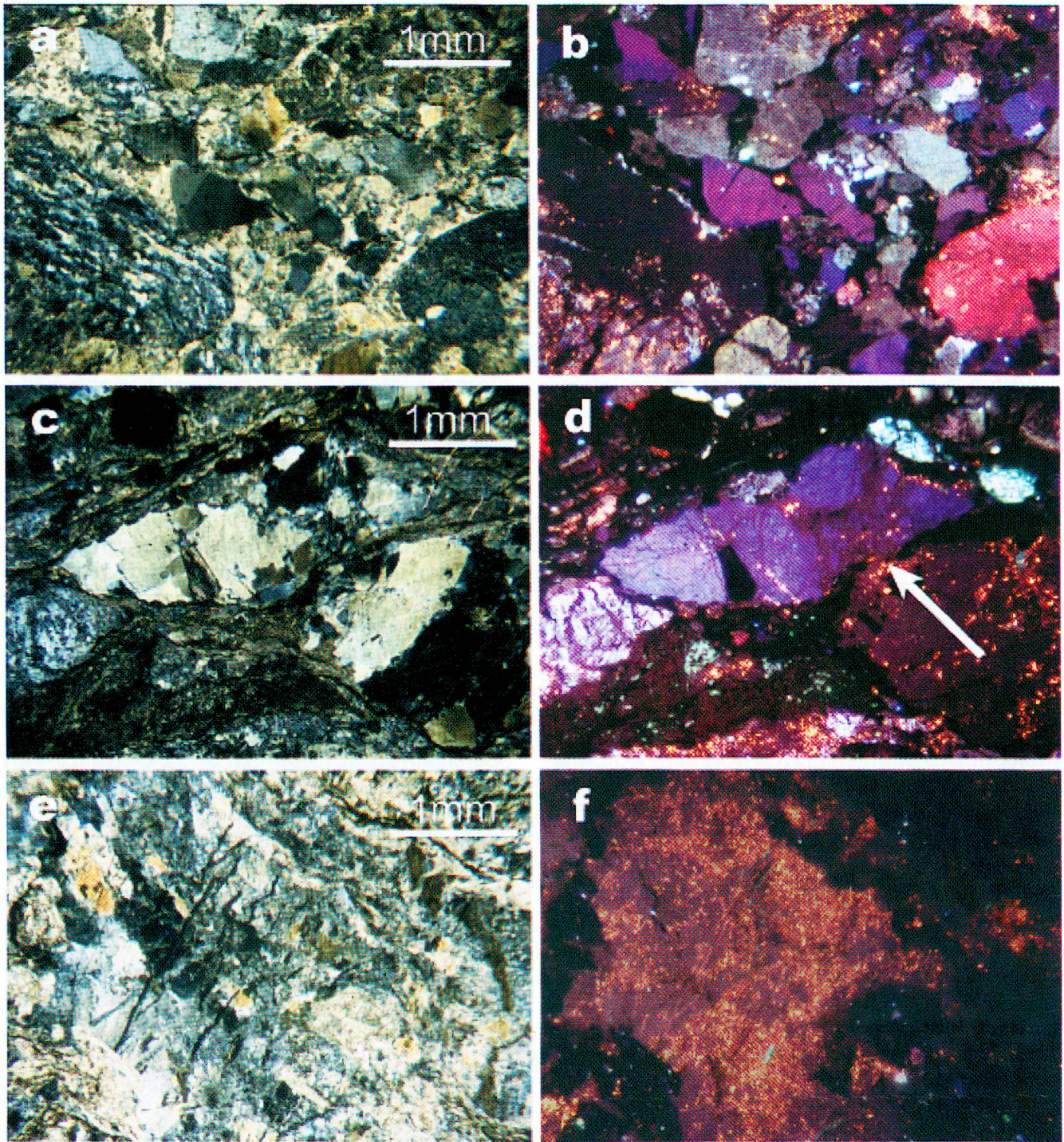
Fig. 2

Oxygen isotope analyses of quartz were made on mineral separates obtained through combined physical and chemical separation techniques from sample aliquots of about 40 grams. Analyses of calcite were made from bulk rock powders of the same samples. The preparation and analytical techniques employed were described in detail by ABART et al. (2002). All isotope compositions are given in the conventional δ-notation relative to the V-SMOW standard.

Quartz microstructures

A series of samples was taken in a sub-vertical profile through the lowermost 8 meters of the Verrucano formation. In the following, the micro-structures from four samples taken at 6.4, 1.0, 0.3 and 0.1 meters above the base of the Verrucano (Fig. 4) are described. These samples represent a transition from essentially absent to intense pene-trative thrust related deformation. An increase in

←*Fig. 2*   Photomicrographs taken from petrographic thin sections under cross polarized light and under cathodoluminescence; the positions of the respective samples are indicated in Fig. 4.

(a) and (b): Conglomeratic variety of Permian Verrucano (sample LS016) taken from 6.4 meters above the Glarus thrust under cross polarized light and under cathodoluminescence; densely packed millimeter sized detrital quartz (undulose extinction) and albite (poly-synthetic twinning) grains in a sericitic matrix; quartz shows blue and violet (detrital components of igneous provenance) to pink (detrital grains of volcanic provenance) luminescence, the luminescence of albite is gray to brown, small grains with intense orange to yellow luminescence are apatite; locally tight quartz-albite grain contacts indicate pressure solution, which probably already occurred during burial diagenesis and during nappe stacking in an early deformation phase; no evidence for thrust related deformation and quartz recrystallization is observed in this sample except for undulose extinction of quartz.

(c) and (d) moderately deformed conglomeratic Verrucano variety (sample LS07) taken from one meter above the thrust under cross polarized light and under cathodoluminescence; large albite and quartz grains in a sericite matrix; quartz shows evidence of incipient recrystallization by grain boundary bulging, which is particularly intense where a large albite grain impinges on the quartz grain (arrow); subgrains show sutured grain boundaries; in large parts quartz has preserved its original, typical detrital blue to violet luminescence, more brownish luminescence colors in the apparently most heavily deformed and most intensely recrystallized portions of the grain adjacent to the albite "indenter" reflect low temperature recrystallization during thrust related deformation.

(e) and (f): intensely deformed quartz grain in a fine-grained quartz sericite matrix (sample LS03) taken from 0.3 meters above the thrust under cross polarized light and under cathodoluminescence; the quartz grain has a brown, still somewhat brighter luminescence than the finely recrystallized matrix quartz, but it has lost almost all of its original detrital luminescence signature; the small grains with bright yellow to orange luminescence are small calcite inclusions within the quartz aggregate, which could not be removed by acid treatment during sample preparation, this calcite impregnation is probably also related to fluid-rock interaction during thrusting.

Fig. 3   (a) millimeter sized detrital quartz grain in fine grained recrystallized matrix, sample LS07 taken from one meter above the thrust under cross polarized light; the large quartz grain shows patchy extinction, fractures serve as nucleation sites for bulging recrystallization (white arrow); (b) ankerite (dark) and quartz sealed fractures in an intensely deformed and recrystallized quartz aggregate (sample LS03, taken 0.3 meters above the thrust), cross polarized light; authigenic quartz typically grows as fibrous crystals from the fracture walls into the void space, which is filled by ankerite and/or calcite in a late stage. (c) fibrous authigenic quartz in pressure fringes parallel to the main foliation around pyrite (sample LS01, taken 0.1 meter above the thrust), cross polarized light.

strain intensity towards the thrust is manifest macroscopically from the development of a successively more pronounced sub-horizontal foliation. The foliation is defined by stylolitic bands rich in sheet silicates suggesting a considerable contribution of pressure solution to strain accommodation.

The sample from the Verrucano taken at 6.4 meters above the thrust (sample LS016, Figs. 2a–b) is characterized by abundant relatively densely packed quartz and feldspar grains and lithic fragments in a fine grained sericitic matrix. Macro-
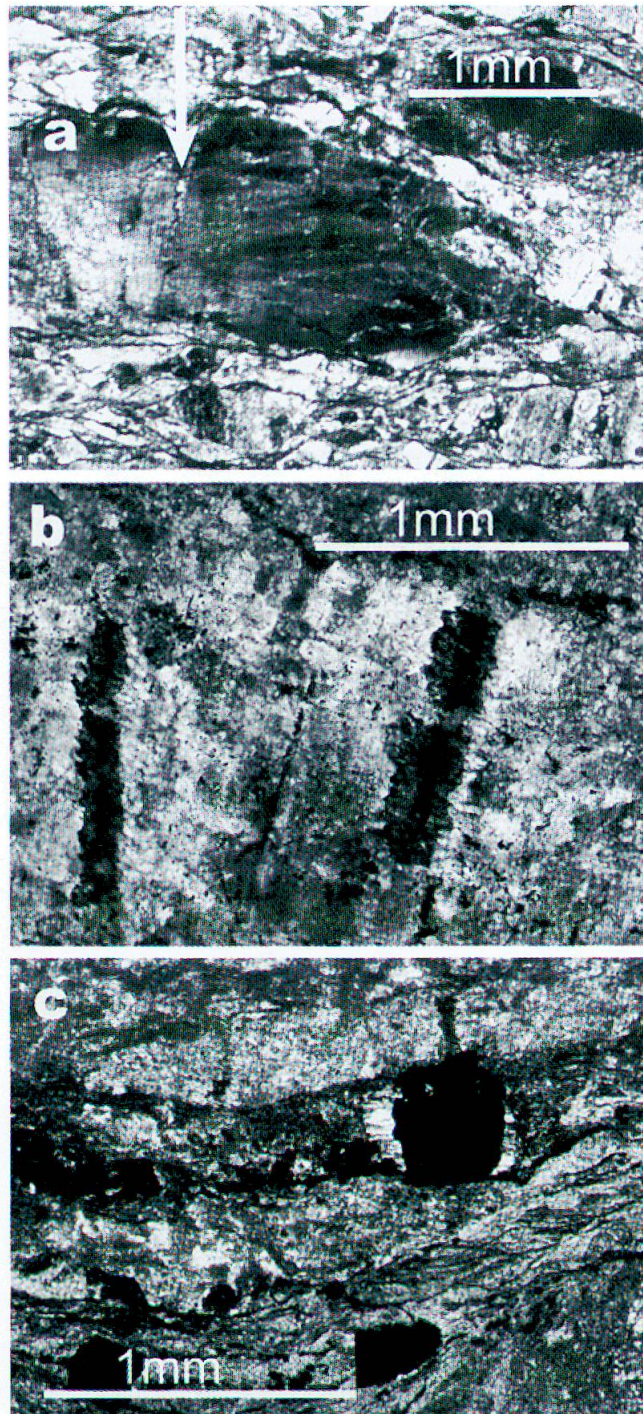
scopically this sample is devoid of any foliation. On a microscopic scale quartz does not show evidence of neither thrust related deformation nor recrystallization. The blue, violet and pink luminescence colours are typical of detrital quartz grains of igneous and volcanic provenance and of medium to high grade metamorphic rocks (MATTER and RAMSEYER, 1985) and indicate that these grains did not recrystallize during low-grade metamorphism. Pressure solution as evident from locally tight quartz albite-grain contacts and brittle features such as healed cracks within quartz grains and patchy extinction along such cracks are ascribed to burial diagenesis and/or to the effect of the tectonic load during nappe stacking.

The domain of incipient thrust related deformation is represented by sample LS07, which was taken about one meter above the thrust (Fig. 2c,d,

3a). In this sample evidence of both, grain size reduction by fracturing and limited crystal plastic deformation is identified. Several millimeter-sized detrital quartz grains show pronounced patchy extinction associated with microfractures, which can usually be identified from fluid-inclusion trails. The grains are locally also penetrated by larger fractures oriented approximately perpendicular to the stretching lineation (Fig. 3a). These fractures seem to be preferred sites of nucleation of grain boundary bulges (compare also STIPP et al., 2002). Incipient bulging recrystallization also occurs along "old" grain boundaries in lithic components. In domains of high fracture density grain boundary bulging may lead to local recrystallization of detrital quartz grains, which are transformed to quartz aggregates with a grain size on the order of 1 to 10 μm. It is interesting to
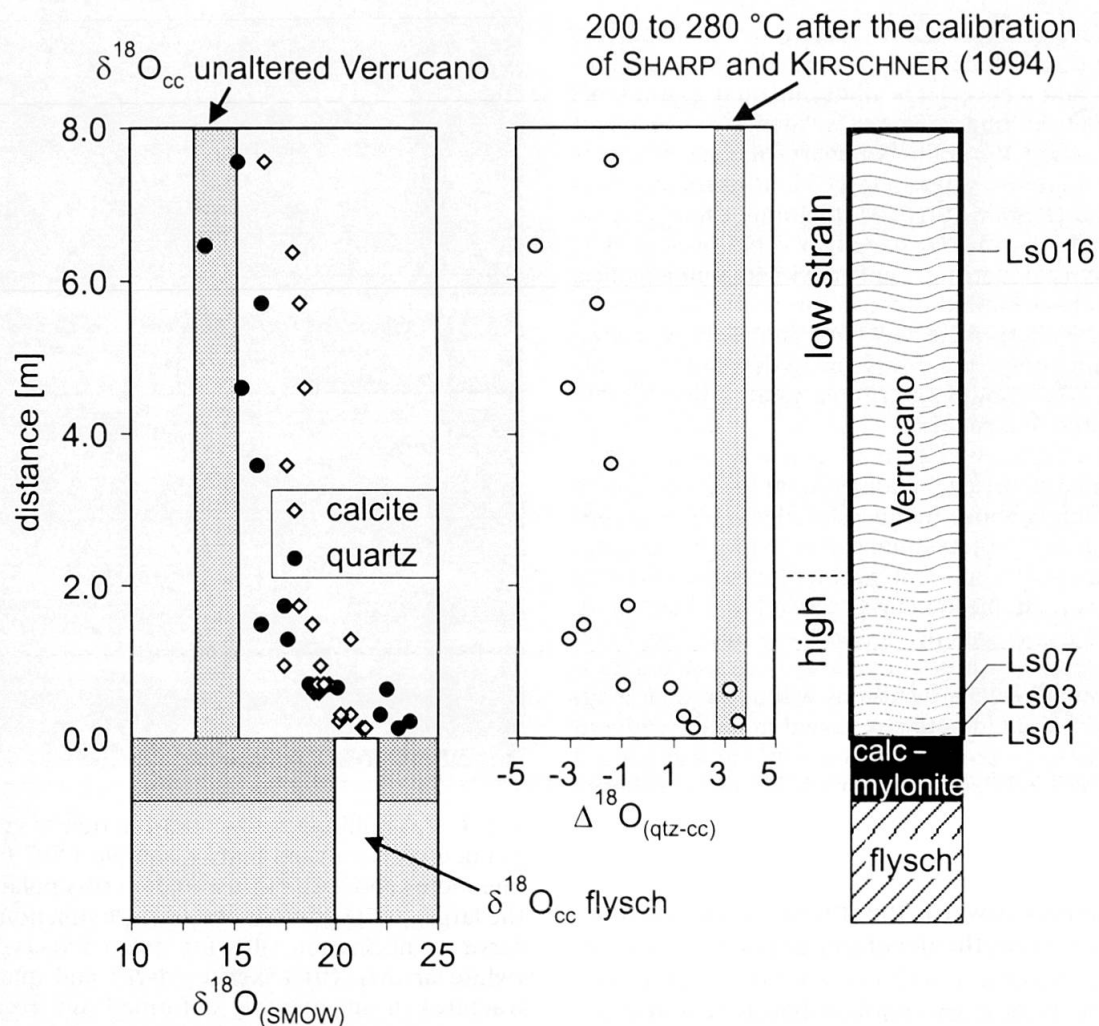

Fig. 4 Oxygen isotope compositions of calcite and coexisting quartz and corresponding inter-mineral oxygen isotope fractionations from the hangingwall Verrucano at the Lochseiten locality, data points represent bulk quartz and calcite from individual hand specimen, for comparison the range of oxygen isotope compositions of calcites from the footwall (and from the calc-mylonite) as well as from unaltered Verrucano are also indicated; equilibrium quartz-calcite fractionations as predicted for temperatures in the range of 200 to 280 °C from the calibration of SHARP and KIRSCHNER (1994) are indicated by the vertical gray bar; also indicated are samples for which microtextures are presented, the lowermost two meters of the Verrucano are intensely deformed.

note, that the domains of fracture related recrystallization correspond to domains of brown luminescence within otherwise blue to violet luminescent detrital quartz grains (Figs. 2c–d). The brown luminescence most likely indicates low temperature recrystallization (MATTER and RAMSEYER, 1985; STEVENS KALCEFF et al., 2000) during thrust related deformation.

The most advanced stage of quartz recrystallization is represented by sample LS03 taken from 0.3 meters above the thrust. In this sample detrital quartz grains have almost entirely recrystallized to form fine-grained polycrystalline aggregates (Figs. 2e and f). Detrital quartz grains are rare and are most easily identified in cathodoluminescence, where the extent of "ghost clasts" is revealed by a slight brightness contrast as compared to the similarly brown luminescent, recrystallized quartz matrix. All detrital luminescence signatures of quartz have been obliterated by deformation induced grain size reduction and recrystallization during low-grade metamorphism. The quartz aggregates show abundant inclusions of small calcite grains (spots with bright luminescence in Fig. 2f). This feature is not observed in the original detrital quartz grains further away from the thrust. This calcite "impregnation" of the
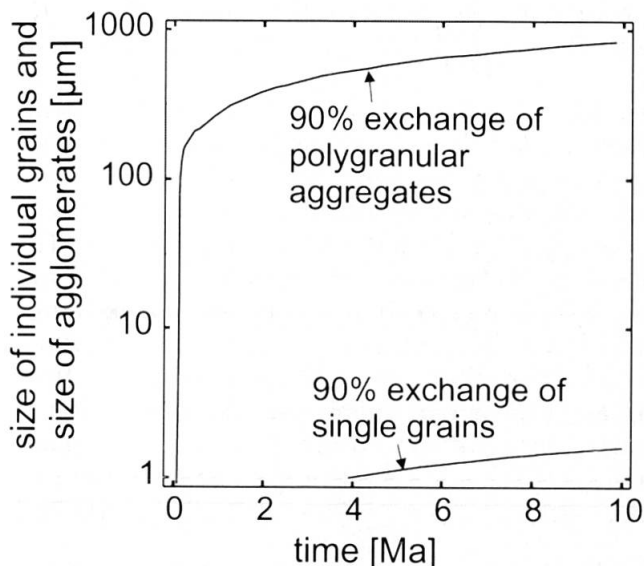

Fig. 5 Contours showing 90% oxygen isotope exchange between an aqueous fluid and quartz single crystals and polycrystalline aggregates as a function of time and grain size and aggregate size, respectively; the exchange progress was calculated according to CRANK (1975) (eq. 6.20) based on diffusivities calculated for 300 °C from the data of FARVER and YUND (1991a) for oxygen volume diffusion in quartz and from the measurements by FARVER and YUND (1991b) of oxygen grain boundary diffusion in polycrystalline quartz aggregates, see also Table 1.

lowermost Verrucano increased the whole-rock CO_2 content (ABART et al., 2002) and is probably due to introduction of carbonate bearing species during fluid infiltration from the footwall flysch.

Another thrust related feature occurring only in the lowermost one to two meters of the Verrucano are abundant fractures in detrital quartz and albite grains sealed with quartz and ankerite (Fig. 3b) and quartz pressure fringes around rigid objects such as pyrite (Fig. 3c). The fractures are preferentially oriented in the plane normal to the N–S stretching lineation associated with deformation along the Glarus thrust. Typically, they are sealed with syntaxial fibrous quartz, ankerite, and calcite. Quartz fibers in the pressure fringes around pyrite are parallel to the maximum N–S stretching direction associated with thrust related deformation. The quartz fibers are often affected by bulging recrystallization indicating that fractures were continuously deformed.

Oxygen isotope systematics of the Verrucano

Oxygen isotope compositions of calcite and quartz from the lowermost eight meters of the Verrucano at the Lochseiten Locality are shown in Fig. 4. For a detailled discussion of these data, the reader is referred to ABART et al. (2002). Here, only those aspects that are relevant for the discussion of the relations between deformation and quartz-fluid oxygen isotope exchange are briefly reviewed.

Both calcite and quartz show a trend of increased ^{18}O enrichment from higher positions within the Verrucano towards the thrust. This trend was interpreted by ABART et al. (2002) and by BADERTSCHER et al. (2002) as an isotope front that developed as a consequence of fluid infiltration from the footwall flysch. Whereas the oxygen isotope composition of calcite from the footwall flysch is 20 to 22‰, the $\delta^{18}O$ of calcite from unaltered Verrucano is 13 to 15‰ (BADERTSCHER et al., 2002). A pore fluid in oxygen isotope equilibrium with the footwall flysch is isotopically too heavy to be in equilibrium with the Verrucano. Oxygen isotope exchange between a flysch derived fluid and the Verrucano will hence cause ^{18}O enrichment of the minerals in the Verrucano.

An oxygen isotope alteration front is defined by a 5 per mil increase of the $\delta^{18}O_{cc}$ values from approximately 16‰ at eight meters above the thrust to approximately 21‰ at the base of the Verrucano. The $\delta^{18}O_{cc}$ value of 16‰ at eight meters above the thrust is still somewhat higher than the expected "background" composition of 13 to 15‰, i.e. at eight meters above the thrust, the

introduction of relatively ^{18}O enriched fluid from the footwall is still recorded by the oxygen isotope signature of calcite. The concomitant shift in $\delta^{18}O_{qtz}$ is over about 9 per mil from 14‰ to about 23‰. The gradient in $\delta^{18}O_{cc}$ is relatively smooth, whereas the ^{18}O enrichment trend of quartz is weak at distances of more than two meters above the thrust and increases dramatically within the lowermost two meters of the Verrucano (Fig. 4). Consequently the quartz-calcite oxygen isotope fractionations increase systematically towards the thrust. In equilibrium oxygen isotope fractionation between quartz and calcite is such that quartz is enriched in ^{18}O with respect to calcite, i.e. $\Delta^{18}O_{qtz-cc}$ is positive for geologically relevant temperatures (O'NEIL, 1986). At Lochseiten the $\Delta^{18}O_{qtz-cc}$ values are negative at distances of more than one meter above the thrust indicating that quartz-calcite oxygen isotope equilibrium was not attained during fluid-rock interaction. From experiment (for a review see COLE and OHMOTO, 1986) and from field studies (e.g. EPPEL and ABART, 1997) it is known that mineral-fluid oxygen isotope exchange is more rapid for calcite than for quartz. During alteration of the lowermost Verrucano calcite was probably able to maintain local oxygen isotope equilibrium with the infiltrating fluid, and the ^{18}O enrichment trend observed in calcite probably reflects the spatial variation of the oxygen isotope compositions of the pore fluid. Calcite-fluid oxygen isotope equilibrium is also corroborated by calcite textures, which indicate that most of the calcite was precipitated or at least re-mobilized during thrust-related deformation. In contrast, quartz-fluid oxygen isotope exchange was relatively sluggish and quartz generally did not attain local oxygen isotope equilibrium with the infiltrating fluid. Only in the lowermost meter above the thrust exchange was sufficiently efficient to allow significant ^{18}O enrichment of quartz. In this domain quartz was shifted towards oxygen isotope equilibrium with the externally derived, isotopically relatively heavy fluid. Locally, quartz-fluid oxygen isotope equilibrium may have been attained as indicated

by quartz-calcite fractionations, which are in the range of equilibrium fractionations predicted for temperatures of 200 to 280 °C (Fig. 4). The zone of enhanced quartz-fluid oxygen isotope exchange coincides with the domain of intense thrust related deformation.

Discussion

From the oxygen isotope composition of calcite it is inferred that a relatively ^{18}O enriched fluid originating from the footwall flysch infiltrated the Verrucano in the hangingwall of the Glarus thrust. Whereas quartz in the lowermost one to two meters of the Verrucano retained an oxygen isotope memory of this infiltration event, quartz from samples further away from the thrust appears to have been inert to oxygen isotope exchange during the infiltration event. The correlation of the extent of oxygen isotope alteration with strain intensity suggests that quartz-fluid oxygen isotope exchange was enhanced by thrust related deformation.

DISSOLUTION-REPRECIPITATION

Pressure solution is an important deformation process at low metamorphic grade (PASSCHIER and TROUW, 1998). Despite the considerable solubility of quartz in aqueous fluids, the oxygen introduced into the fluid by SiO_2 from the dissolution of quartz is a vanishingly small fraction of the bulk oxygen in the pore fluid. The oxygen isotope signature of any quartz precipitate will thus be controlled by a fluid-buffered equilibrium. This renders dissolution-reprecipitation a viable mechanism of quartz-fluid oxygen isotope exchange, which may be operative also at low temperatures (CLAYTON et al., 1972; MATHEWS et al., 1983). Even if, in a particular case, the dissolution of quartz may not go to completion, and relic quartz may retain its original isotope signature, the oxygen isotope composition of bulk quartz will

Table 1 Coefficients of oxygen volume diffusion in quartz and of oxygen grain boundary diffusion as well as oxygen bulk diffusion in a polycrystalline quartz aggregate with grain size of 1.2 μm for 300°C. D^0—pre-exponential factor, Q—activation energy, δ—grain boundary width, d—grain size.

Volume diffusion FARVER and YUND (1991a)	$D_v^0 = 2.9\times10^{-5}\,m^2/s$	$Q = 243\,kJ/mol$	$D_v = 2\times10^{-27}\,m^2/s$
Grain boundary diffusion FARVER and YUND (1991b)	$D_{gb}^0\times\delta = 2.6\times10^{-17}\,m^3/s$	$Q = 113\,kJ/mol$	$D_{gb}\times\delta = 1.3\times10^{-27}\,m^3/s$
Bulk diffusion in polycrystalline aggregate	$D^{bulk} \cong D_{gb}\,\delta/d\pi$		$D^{bulk} \cong 3\times10^{-22}\,m^2/s$

change in the course of successive dissolution re-precipitation. Stylolitic bands rich in sheet sili-cates that define the foliation in the highly strained siliciclastic rocks at the base of the Verru-cano formation suggest pressure solution as a dominant process during thrust related deforma-tion. At least part of the silica that was introduced into the pore fluid via pressure solution was re-precipitated locally to form syntaxial quartz seals in fractures and quartz fibers in pressure fringes (Figs. 3b–c) . The contribution of this mechanism to bulk quartz-fluid oxygen isotope exchange is hard to quantify, because features such as fractur-ing and subsequent sealing by newly precipitated quartz were partially obliterated in the course of ongoing deformation and recrystallization. Even in the most intensely deformed samples only about 10 to 20 vol% of the total quartz present can be unambiguously identified as newly precip-itated quartz. Dissolution-reprecipitation proba-bly was an important mechanism of quartz-fluid oxygen isotope exchange during thrusting at the Glarus thrust, but alternative mechanisms must also be explored.

VOLUME DIFFUSION

Oxygen isotope alteration of pre-existing quartz grains requires transport of oxygen from the pore fluid into the grain interiors. In the absence of re-crystallization such transport can only occur by diffusion through the crystal lattice, i.e. by volume diffusion. It has been shown by FARVER and YUND (1991a) that oxygen volume diffusion in quartz is controlled by the diffusion of molecular water in the quartz structure and thus depends on water fugacity. It has been argued by ABART et al. (2002) that the pore fluid in the Verrucano was essentially pure water corroborating oxygen vol-ume diffusion. POST and TULLIS (1998) showed that during experimental deformation of quartz aggregates the penetration of oxygen into individ-ual quartz grains is controlled by oxygen volume diffusion and that the oxygen volume diffusion in quartz is not influenced by variations in disloca-tion densities produced by deformation. This jus-tifies estimation of the extent of quartz-fluid oxy-gen isotope exchange by diffusion based on the experimental data of FARVER and YUND (1991a) (Table 1, Fig. 5). At the low temperatures at which deformation occurred at the Glarus thrust, re-gardless of the water fugacity, oxygen volume dif-fusion is much too slow to account for the isotopic alteration of millimeter sized detrital grains with-in geologically reasonable duration for deforma-tion and fluid-rock interaction (Table 1, Fig. 5).

However, in the zone of intense thrust related de-formation, detrital grains were fragmented and recrystallized to fine grained quartz aggregates with a grain size of the individual quartz crystal-lites on the order of 1 to 10 µm. Given such a small grain size volume diffusion may have contributed significantly to quartz-fluid oxygen isotope ex-change despite of the low oxygen diffusivity in quartz. At 300 °C one micron sized quartz grains may attain 90% equilibration with the pore fluid within about four million years, which is a reason-able estimate for the duration of movement and fluid rock interaction at the Glarus thrust. For grain sizes in excess of about 10 µm oxygen vol-ume diffusion is, however, too slow to allow for significant exchange within time scales reasona-ble for movement and deformation along the Gla-rus thrust (Fig. 5).

GRAIN BOUNDARY DIFFUSION

Another effect of grain size reduction during frag-mentation and recrystallization is the generation of grain boundaries. Grain boundaries probably provide fast pathways for oxygen diffusion (JOESTEN, 1991). The rate of oxygen grain bounda-ry diffusion in natural, fine grained quartz aggre-gates was measured by FARVER and YUND (1991b). Provided a grain size on the order of 1 to 10 µm grain boundary diffusion may significantly contribute to bulk oxygen diffusion in polycrys-talline aggregates and it provides a viable mecha-nism to introduce oxygen from the pore fluid into the interior of quartz aggregates (Table 1, Fig. 5). It has been shown by FARVER and YUND (1992) that oxygen bulk diffusion in quartz aggregates strongly depends on the wetting characteristics of the pore fluid. Provided a wetting fluid such as water is present, oxygen bulk diffusivities are 4 to 5 orders of magnitude greater than in samples with a non wetting pore fluid at the same P-T con-ditions. We think that at the base of the Verrucano grain boundary diffusion was quick and facilitat-ed quartz-fluid interaction also in the internal portions of millimeter sized quartz aggregates that were derived from detrital grains. Small cal-cite inclusions dispersed in these quartz aggre-gates (Fig. 2f) show that the fine-grained quartz matrix was also permeable for carbonate species.

LIMITED GRAIN BOUNDARY MIGRATION – BULGING RECRYSTALLIZATION

From Fig. 5 it is seen that at the presumed condi-tions of thrust related deformation quartz-fluid

oxygen isotope exchange by volume diffusion may be significant for a grain size on the order of a few micrometers, but complete equilibration between quartz and a pore fluid is still difficult to attain for geologically reasonable duration of fluid rock interaction and deformation, in particular when the average grain size is on the oerder of 10 μm or larger. We suggest that slow grain boundary migration in the course of bulging recrystallization (STIPP et al. 2002) may have been an important control on quartz-fluid oxygen isotope exchange. Limited grain boundary migration associated with bulging as is evident from the locally irregular grain boundaries may be an important process during syndeformational recrystallization (STÜNITZ, 1998; STIPP et al., 2002). Grain boundary migration requires material to be transferred from one grain to the next across their common grain boundary. It has been shown (HAY and EVANS, 1987; STÜNITZ, 1998) that grain boundary migration is an efficient mechanism for chemical mineral-fluid exchange. We argue, that oxygen isotope exchange between water molecules at wetted grain boundaries and quartz was greatly enhanced during mass transfer associated with grain boundary bulging.

INTRACRYSTALLINE STRAIN

Uptake of oxygen from the fluid into the quartz structure may also have been enhanced by intracrystalline strain. Crystal plastic deformation produced a heterogeneous strain distribution within individual grains. Particularly strongly deformed domains are characterized, at least transiently, by high dislocation densities. These domains are the first portions of a detrital grain that lose their original cathodoluminescence signature (Fig. 2c, d). From a qualitative correlation between changes in the luminescence signature and oxygen isotope alteration we suggest, that the most intensely deformed portions within a detrital quartz grain are the first to exchange their oxygen with the pore fluid. Partial oxygen isotope exchange between quartz and albite grains with heterogeneous internal strain distribution were also reported by O'HARA et al. (1997). Stretched Si–O bonds in strained silica have been shown to be the sites of stress corrosion (MICHALSKE and FREIMAN, 1982). They are probably very reactive and are thus prone to oxygen isotope exchange with the pore fluid.

Deformation at low metamorphic grade typically leads to heterogeneous strain distribution. Domains with high and low finite strain can alternate on all scales. Heterogeneous strain distribution in the lowermost Verrucano probably brought about locally highly variable rates of quartz-fluid oxygen isotope exchange. As a result, the oxygen isotope compositions of quartz and, hence, also the quartz-calcite inter-mineral fractionations are highly variable (Fig. 4).

IMPLICATIONS FOR QUARTZ-CALCITE OXYGEN ISOTOPE THERMOMETRY

The dependence of quartz-fluid oxygen isotope exchange on deformation and the different behavior of calcite during water rock interaction may have important implications for oxygen isotope thermometry. In those portions of the Verrucano that were not or only weakly affected by thrust related deformation, quartz did not exchange with the pore fluid that infiltrated from the footwall flysch during and after thrusting. In contrast, calcite-fluid oxygen isotope exchange is relatively fast and calcite was most probably in oxygen isotope equilibrium with the infiltrating fluid even in the absence of deformation. As a consequence observed quartz-calcite oxygen isotope fractionations do not reflect equilibrium isotope distributions and, if applied as geothermometers, will yield erroneous temperature estimates (e.g. BURKHARD et al., 1992; VAN DAALEN, 1998).

Conclusions

Quartz and calcite from the Permian Verrucano formation in the hangingwall of the Glarus thrust show different records of fluid infiltration from the footwall flysch associated with thrusting during low-grade metamorphism. Whereas calcite probably attained oxygen isotope equilibrium with the infiltrating fluid, quartz retained a memory of fluid-rock interaction only in the lowermost one to two meters above the thrust, where the Verrucano shows intense thrust related deformation. We propose that thrust related deformation was an indispensable pre-requisite for quartz-fluid oxygen isotope exchange. Processes that allowed for quartz-fluid oxygen isotope exchange are mass transfer in the course of dissolution reprecipitation as evident from vein fillings and pressure fringes, on the one hand, and grain size reduction by fracturing and limited bulging recrystallization, on the other. Transport of oxygen from the pore fluid into the interior of millimeter sized fine-grained quartz aggregates, which were derived from former detrital grains was probably facilitated by grain boundary diffusion. Oxygen isotope exchange between the fluid species and the quartz crystals was enhanced by ma-

terial transfer associated with deformation induced grain boundary bulging as well as by the chemical reactivity of stretched Si–O bonds produced by deformation.

References

ABART, R., BADERTSCHER, N., BURKHARD, M. and PO-VODEN, E. (2002): Oxygen, carbon and strontium isotope systematics in two profiles across the Glarus thrust: implications for fluid flow. Contrib. Mineral. Petrol. 143, 192–208.

ABART, R., and SPERB, R. (1997): Grain-scale stable isotope disequilibrium during fluid-rock interaction I: analytical solutions for advective-dispersive transport and coupled first-order kinetic mineral-fluid exchange. Am. J. Sci. 297, 679–706.

BADERTSCHER, N. and BURKHARD, M. (2000): Brittle-ductile deformation in the Glarus thrust Lochseiten (LK) calc-mylonite. Terra Nova 12 281–288.

BADERTSCHER, N., ABART, R., BURKHARD, M. and Mc-CAIG, A. (2002): Fluid flow pathways along the Glarus overthrust derived from stable and Sr-isotope patterns. Am. J. Sci. 302 (in press)

BAKER, J. and SPIEGELMAN, M. (1995): Modeling an infiltration-driven geochemical front. Earth Planet. Sci. Lett. 136, 87–96.

BURKHARD, M., KERRICH, R. and FYFE, W.S. (1992): Stable and Sr-isotope evidence for fluid advection during thrusting of the Glarus nappe (Swiss Alps). Contrib. Mineral. Petrol. 112, 293–311.

CLAYTON R.N., O'NEIL J.R, and MAYEDA, T.K. (1972): Oxygen isotope exchange between quartz and water. J. Geophys. Res. 77, 3057–3067.

COLE, D.R. and OHMOTO, H. (1986): Kinetics of isotope exchange at elevated temperatures and pressures. In: VALLEY, J.W., TAYLOR, H.P.Jr., O'NEIL, J.R. (eds): Stable isotopes in high temperature geological processes. Rev. Mineral. 16, 41–90.

COLE, D.R., OHMOTO, H. and LASAGA, A.C. (1983): Isotopic exchange in mineral-fluid systems. I. Theoretical evaluation of oxygen isotopic exchange accompanying surface reactions and diffusion. Geochim. Cosmochim. Acta 47, 1681–1693.

CRANK, J. (1975): The Mathematics of Diffusion. Oxford, Clarendon press, 347 pp.

CRISS, R.E., GREGORY, R.T. and TAYLOR, H.P.Jr (1987): Kinetic theory of oxygen isotopic exchange between minerals and water. Geochim. Cosmochim. Acta 51, 1099–1108.

EPPEL, H. and ABART, R. (1997): Grain-scale stable isotope disequilibrium during fluid-rock interaction II: an example from a Penninic-Lower Austroalpine tectonic contact in eastern Switzerland. Am. J. Sci. 297, 707–728.

FARVER, J.R. and YUND, R.A. (1991a): Oxygen diffusion in quartz – dependence on temperature and water fugacity. Chem. Geol. 90, 55–70.

FARVER, J.R. and YUND, R.A. (1991b): Measurement of oxygen grain boundary diffusion in natural, fine-grained quartz aggregates. Geochim. Cosmochim Acta, 55 1597–1607.

FARVER, J.R. and YUND, R.A. (1992): Oxygen diffusion in a fine-grained quartz aggregate with wetted and nonwetted microstructures. J. Geophys. Res. 97, 14017–14029.

FREY, M. (1988): Discontinuous inverse metamorphic zonation, Glarus Alps, Switzerland: evidence from illite crystallinity data. Schweiz. Mineral. Petrogr. Mitt. 68, 171–184.

GREGORY, R.T., CRISS, R.E. and TAYLOR, H.P.Jr. (1989): Oxygen isotope exchange kinetics of mineral pairs in closed and open systems: applications to problems of hydrothermal alteration of igneous rocks and precambrian iron formations. Chem. Geol. 75, 1–42.

HAY, R.S. and EVANS, B. (1987): Chemically induced grain boundary migration in calcite: temperature dependence, phenomenology, and possible applications to geologic systems. Contrib. Mineral. Petrol. 97, 127–141.

HEIM, A. (1921): Geologie der Schweiz, Bd. II. Tauchniz, Leipzig.

HUNZIKER, J.C. (1987): Radiogenic isotopes in very low grade metamorphism. In: FREY, M. (ed.): Low grade metamorphism, Blackie, Glasgow, 200–226.

HUNZIKER, J.C., FREY, M., CLAUER, N., DALLMEYER, R.D., FRIEDRICHSEN, H., FLEHMIG, W., HOCHSTRASSER, K., ROGGWILER, P. and SCHWANDER, H. (1986): The evolution of illite to muscovite: mineralogical and isotopic data from the Glarus Alps, Switzerland. Contrib. Mineral. Petrol. 92, 157–180.

JOESTEN, R. (1991): Grain-boundary diffusion kinetics in silicate and oxide minerals. In: GANGULY, J. (ed.): Diffusion, atomic ordering and mass transport: selected problems in geochemistry (Advances in physical geochemistry 9) Springer-Verlag, Berlin, Heidelberg, New York, 345–395.

KIRSCHNER, D., TEYSSIER, C., GREGORY, R.T. and SHARP, Z. (1995a): Effect of deformation on oxygen isotope exchange in the Heavitree Quartzite, Ruby Gap duplex, central Australia. J. Struct. Geol. 17, 1407–1423.

KIRSCHNER, D.L., SHARP, Z.D. and MASSON, H. (1995b): Oxygen isotope thermometry of quartz-calcite veins; unraveling the thermal-tectonic history of the subgreenschist facies Morcles Nappe (Swiss Alps). Geol. Soc. Am. Bull. 107, 1145–1157.

MATTHEWS, A., GOLDSMITH, J.R. and CLAYTON, R.N. (1983): On the mechanisms and kinetics of oxygen exchange in quartz and feldspars at elevated temperatures and pressures. Geol. Soc. Am. Bull. 94, 396–412.

MATTER, A. and RAMSEYER, K. (1985): Cathodoluminescence microscopy as a tool for provenance studies of sandstones. In: ZUFFA, G.G. (ed.): Provenance of arenites. NATO ASI Series C: Mathematical and Physical Sciences. Reidel Publishing Company, 191–211.

MICHALSKE, T.A. and FREIMAN, S.W. (1982): A molecular interpretation of stress corosion in silica. Nature 295, 511–512.

MILNES, A.G. and PFIFFNER, O.A. (1980): Tectonic evolution of the central Alps in the cross section St. Gallen-Como. Eclogae geol. Helv. 73, 619–633.

NABELEK, P.L. (1991): Stable isotope monitors. In: KER-
RICK, D.M. (ed.): Contact metamorphism, Rev. Min-
eral. 26, 395–435.
O'HARA, K.D., SHARP, Z.D., MOECHER, D.P. and JENKIN,
G.R.T. (1997): The effect of deformation on oxygen
isotope exchange in quartz and feldspar and the sig-
nificance of isotopic temperatures in mylonites. J.
Geol. 105, 193–204.
O'NEIL, J.R. (1986): Theoretical and experimental
aspects of isotopic fractionation. In: VALLEY, J.W.,
TAYLOR, H.P.Jr., O'NEIL, J.R. (eds): Stable isotopes
in high temperature geological processes. Rev. Min-
eral. 16, 1–37.
PASSCHIER, C.W. and TROUW, R.A.J. (1998): Microtec-
tonics, Springer, Berlin, 289 pp.
PFIFFNER, O.A. (1977): Tektonische Untersuchungen im
Infrahelvetikum der Ostschweiz. Mitt. geol. Inst.
ETH u.\ Univ. Zürich [N.F.], 217.
POST, A. and TULLIS, J. (1998): The rate of water penetra-
tion in experimentally deformed quartzite, implica-
tions for hydrolytic weakening. Tectonophysics 295,
117–137.
RAHN, M., MULLIS, J., ERDELBROCK, K. and FREY. M.
(1995): Alpine metamorphism in the North Helvetic
Flysch of the Glarus Alps, Switzerland. Eclogae geol.
Helv. 88, 157–178.
RAMSEYER, K., FISCHER, J., MATTER, A., EBERHARDT, P.
and GEISS, J. (1989): A cathodoluminescence micro-
scope for low intensity luminescence. J. Sedim. Pet-
rol. 59, 619–622.
SCHMID, S.M. (1975): The Glarus overthrust: field evi-
dence and mechanical model. Eclogae geol. Helv. 68,
247–283.
SCHMID, S.M., PFIFFNER, O.A., FROITZHEIM, N., SCHÖN-
BORN, G. and KISSLING, E. (1996): Geophysical-geo-
logical transsect and tectonic evolution of the Swiss-
Italian Alps. Tectonics 15, 1036–1064.

SHARP Z.D. and KIRSCHNER D.L. (1994): Quartz-calcite
oxygen-isotope thermometry – a calibration based
on natural isotopic variations. Geochim. Cosmo-
chim. Acta 58, 4491–4501.
SHEPPARD, S.M.F. (1986): Characterization and isotopic
variations in natural waters. In: VALLEY, J.W., TAY-
LOR, H.P.Jr., O'NEIL, J.R. (eds): Stable isotopes in
high temperature geological processes. Rev. Miner-
al. 16, 165–183.
SIDDANS, A.W. (1979): Deformation, metamorphism and
texture development in Permian mudstones of the
Glarus Alps. Eclogae geol. Helv. 72, 601–621.
STEVENS KALCEFF, M.A., PHILLIPS, M.R., MOON, A.R.
and KALCEFF, W. (2000): Cathodoluminescence
microcharacterization of silicon dioxide poly-
morphs. In: PAGEL, M., BURBIN, V., BLANC, P. and
OHNENSTETTER, D. (eds): Cathodolominescence in
geosciences, Springer, Berlin. 514 pp.
STIPP, M., STÜNITZ, H., HEILBRONNER, R. and SCHMID,
S.M. (2002): The eastern Tonale fault zone: a "natu-
ral laboratory" for crystal plastic deformation of
quartz over a temperature range from 250 to 700 °C.
J. Struct. Geol. (in press).
STÜNITZ, H. (1998): Syndeformational recrystallization
– dynamic or compositionally induced? Contrib.
Mineral. Petrol. 131, 219–236.
VAN DAALEN, M. (1998): Microfabric analysis of natural-
ly deformed quartz veins deformed near the brittle-
ductile transition (examples from the Glarus Alps
and Schlinig fault). PhD thesis Basel University, 170
pp.