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## Fluid-rock interactions during thrusting of the Glarus nappe – evidence from geochemical and stable isotope data\*

by M. Burkhard<sup>1</sup> and R. Kerrich<sup>2</sup>

### Abstract

Limestone mylonites from the Glarus thrust are <sup>18</sup>O-depleted by up to 15‰ with respect to the supposedly marine carbonate protoliths (δ<sup>18</sup>O = 26‰). A pronounced trend of increasing depletion is observed from N to S. At the Lochseite type locality, limestone mylonites have δ<sup>18</sup>O values around 20‰, at Grau Berg in the south they are 8 to 14‰. If the mylonite is derived from marine carbonates as generally assumed, then its stable isotope composition requires exchange with isotopically depleted fluids at relatively high water/rock ratios. Possible sources for these are dewatering of the underlying Flysch and/or metamorphic fluids or formation brines expelled along the thrust from greater depth. Calculated water/rock ratios (minima) vary as a function of the postulated fluid source and temperature and range from > 2 to > 30, which is easily accounted for by compaction and dewatering of the Flysch in the northern part of the thrust. In the south however, where Verrucano is thrust over parautochthonous Mesozoic carbonates, the extreme <sup>18</sup>O-depletion of the calc-mylonite has to be explained by fluid advection within the Verrucano hangingwall and thrust zone or alternatively by exchange with metamorphic fluids expelled along the thrust.

As an alternative to the classical interpretation, where the limestone mylonite represents an extremely deformed Mesozoic limestone of Helvetic provenance, this horizon could also be interpreted as an entirely or partly secondary calcite mineralization. From solubility considerations, this interpretation requires much higher (> 10<sup>4</sup>) water/rock ratios than those calculated from the stable isotope data.

*Keywords:* Glarus thrust, mylonite, stable isotopes, fluid, Helvetic nappes.

### Introduction

The Glarus overthrust is one of the major thrust structures within the Swiss Alps. An estimated 35 km of translation is accommodated by deformation within an extremely narrow calc-mylonite zone, the so-called Lochseiten mylonite (HEIM, 1921; SCHMID, 1975). Based on crustal scale balancing, PFIFFNER (1985) argues that this thrust reaches at least mid crustal levels some 10 to 20 km south of the southernmost exposures. From this general setting, and given  $p_{\text{fluid}} \approx p_{\text{lithostatic}}$  the Glarus thrust may have acted as a "collector" of fluids produced within the foot-wall, undergoing prograde metamorphism (FYFE et al., 1978; CONNOLLY and THOMPSON, 1989) following the Oligocene continent-continent collision. Are such fluids expelled along thrust

planes as predicted by various authors (e.g. FYFE and KERRICH, 1985; OLIVER, 1986), and is it possible to identify fluid sources and estimate fluid fluxes from the observable fluid/rock interactions in shallow level thrust rocks? Here we try to characterize and quantify fluid/rock interaction within the calc-mylonite and mylonitized Verrucano above the thrust using geochemical whole rock and trace element data combined with stable isotope analyses of calcites from the mylonite. This abstract adds some new results to an old discussion concerning the origin and significance of the Lochseiten mylonite interpreted either as an extremely deformed Mesozoic carbonate sequence (HEIM, 1921, p. 387 ff.) or a secondary ("mineralized") fault gouge (ROTHPLETZ, 1883, p. 168).

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### Structural observations

At Grau Berg (coord. 736.25/192.87) Permian Verrucano siltstones are thrust over lower Cretaceous limestones with an intermediate metric layer of extremely deformed calc-mylonite of undetermined provenance. For a description of the structural context in this area see FUNK et al. (1983; p. 97–104). However, I interpret the strong mylonitic deformation in the Verrucano above the contact as contemporaneous and not prior to thrusting of the Glarus nappe (for a different opinion see SCHMID, 1975). Microstructurally, even at 50 m above the thrust, Verrucano siltstones have a pronounced mylonitic foliation developed where white mica forms continuous layers with micro-shearbands and "mica fish" all indicating N-directed shear. Chlorite is found as a secondary mineral precipitated in pressure shadows. Quartz is recrystallized to finegrained (5 to 30  $\mu\text{m}$ ) ribbons. Close to the thrust, grain size of mica and quartz decrease and secondary calcite and quartz in both schistosity parallel and oblique veinlets is frequently observed. With increasing deformation, these veinlets are reoriented into the foliation and veins are difficult to distinguish from the matrix. Both are equally recrystallized to an ultra-fine grained (3–15  $\mu\text{m}$ ) aggregate of mainly quartz, muscovite (illite) and calcite. These veins formed during the thrusting event and could be interpreted as indicators for high fluid pressures and hydrofracturing (HUBBERT and RUBEY, 1959; ETHERIDGE et al., 1983; SECOR, 1965). The same observation can also be made within the calc-mylonite itself; differently coloured millimetric bands of calcite alternating with dark stylolitic bands are due to concomitant crystal-plastic and brittle (veining, pressure solution) deformation.

### Mineralogical and Geochemical observations

A striking feature within the Verrucano above the thrust contact is variable additions of carbonate, mainly calcite, to the normally carbonate-free green siltstones. Up to 15 wt %  $\text{CO}_2$  was added to the strongly mylonitic Verrucano within the first metre above the thrust. The  $\text{CO}_2$  content diminishes rapidly to less than 2% at 50 m (Fig. 1A). This "dilution" masks more subtle geochemical trends and therefore, the  $\text{CaCO}_3$  content, as based on volumetric (HCl dissolution)  $\text{CO}_2$  determinations, has been removed from all samples. Clear trends in ( $\text{CO}_2$ -free) element abundances vs. increasing deformation toward the thrust are seen for Si, K, Mg (increase)

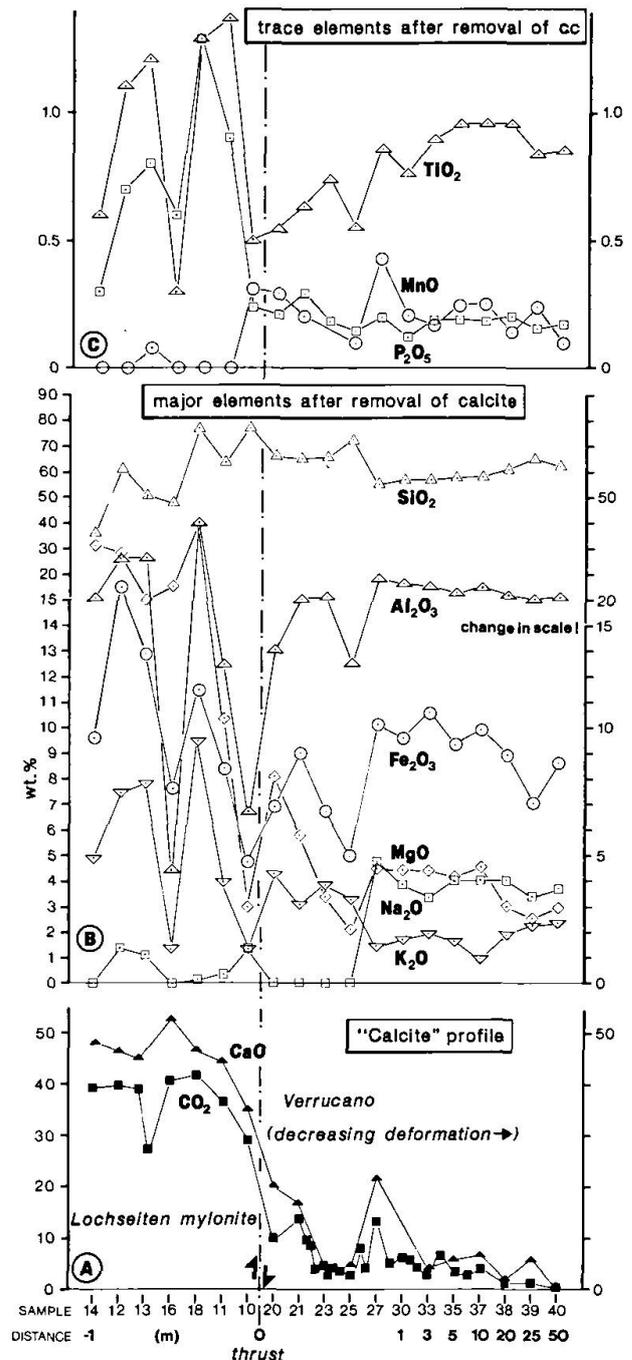


Fig. 1 Relative abundance of elements is plotted in a profile across the Lochseiten calc-mylonite and superjacent Verrucano (Grau Berg locality). Sample numbers and corresponding distance from the thrust contact are indicated on the x-axis.

A)  $\text{CO}_2$  (volumetric determination) and CaO (XRF) contents illustrate the "calcite" dominated Lochseiten mylonite and variable addition of cc to the first metres of Verrucano above the thrust. Note that there are more  $\text{CO}_2$  than w.r. analyses.

B, C) Whole rock geochemical (XRF) analyses, after removal of the calcite content ( $2.27 \cdot \text{CO}_2$ ; Fig. 1A) are plotted in order to show eventual trends with increasing deformation toward the thrust.

and Na, Fe, Al (decrease) (Fig. 1B) and correspond mineralogically (XRD determinations) to an increase of quartz and muscovite at the expense of albite and chlorite. These trends were confirmed when plotted as ratio element/Ti, assuming that Ti represents an immobile phase. In the absence of a better knowledge of the protolith composition and sedimentary compositional trends, these results are difficult to interpret in terms of gains or losses due to fluid transport accompanying deformation. Thin section observations are consistent with the Na-loss reflecting an increasing saussuritization and finally disappearance of albite adjacent to the thrust. Chlorite also diminishes toward the thrust, whereas  $\text{SiO}_2$  seems to be augmented in the form of secondary ultra fine grained quartz.

Most trace elements seem to behave isochemically reflecting a "dilution effect" by calcite addition and therefore decrease slightly in absolute abundance toward the thrust (V, Zr, Rb, Cs, Ga, Zn, Co) or remain approximately constant (Cr, B, Ba, Nb, Y, U, Th, Cu, Ni); some elements of the former group may represent absolute losses (Sb, Zn), whereas some of the latter may be added (Cu, Y). Absolute gains or losses are difficult to identify without a more precise knowledge of the sedimentary protolith and of the volume change. Other elements (Sr, S, As; corresponding to carbonate and pyrite respectively) are clearly enriched, and interestingly, these are the only traces that are also abnormally high within the calc-mylonite itself (abnormal with respect to Mesozoic marine carbonates according to WEDEPOHL [1978]).

In summary, apart from a clear carbonate (and minor quartz) addition to the Verrucano, and some minor mineralogic changes (chlorite and albite "dissolution"), there are no marked geochemical anomalies associated with the Glarus thrust at the Grau Berg locality.

### Stable isotope results

Calcites from four sites of the calc-mylonite along a N-S profile have been analyzed for their  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  composition.  $\delta^{18}\text{O}$  results are plotted in Fig. 2 together with a schematic geologic profile. All values are depleted with respect to the supposedly marine carbonate protolith ( $26 \pm 2\text{‰}$ , BURKHARD and KERRICH, 1988) and there is a clear tendency to lower values toward the south, reaching a maximum depletion of around  $-16\text{‰}$  at Grau Berg. The various other tectonic units i.e. Flysch, Verrucano and crystalline basement involved in this cross section have also

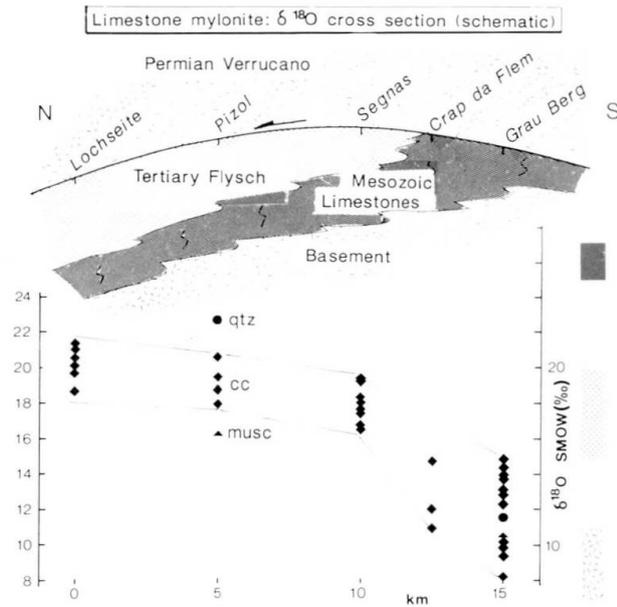


Fig. 2 Individual  $\delta^{18}\text{O}$  calcite values from the Lochseiten calc-mylonite (microsamples) are plotted vs. horizontal distance in a schematic N-S cross section of the Glarus thrust. Ranges of whole rock isotopic compositions of the different major tectonic units (potential fluid reservoirs) around the Glarus thrust are indicated to the right of the  $\delta^{18}\text{O}$  scale using the corresponding shadings (according to data from: BURKHARD and KERRICH (1988); marine carbonates; HUNZIKER et al., 1986; Flysch; HOEFS and STALDER (1977); HOERNES and FRIEDRICHSEN, 1980; FOURCADE et al., 1989; crystalline basement; and unpublished data from this study: Verrucano, Flysch).

been shaded (Fig. 2) according to their stable isotope w.r. composition. Possible interactions of these units with the calc-mylonite will be discussed below.

$^{87}\text{Sr}/^{86}\text{Sr}$  ratios have been measured in a series of limestone mylonites in order to test whether these ratios reflect "marine" signatures or to identify some contamination with radiogenic  $^{87}\text{Sr}$  derived from an external source (Fig. 4).

### Discussion

The stable isotope results from the Grau Berg locality are critical to the discussion of possible sources of light  $^{18}\text{O}$  fluids responsible for the observed  $^{18}\text{O}$ -depletion within the mylonite. At Grau Berg, the footwall carbonates display normal, high marine  $\delta^{18}\text{O}$  values and interaction with these cannot account for the  $^{18}\text{O}$ -depletion. Water in equilibrium with the Grau Berg mylonites at  $300\text{ °C}$  had a calculated isotopic composition of around  $5\text{‰}$ . Possible sources for such  $^{18}\text{O}$

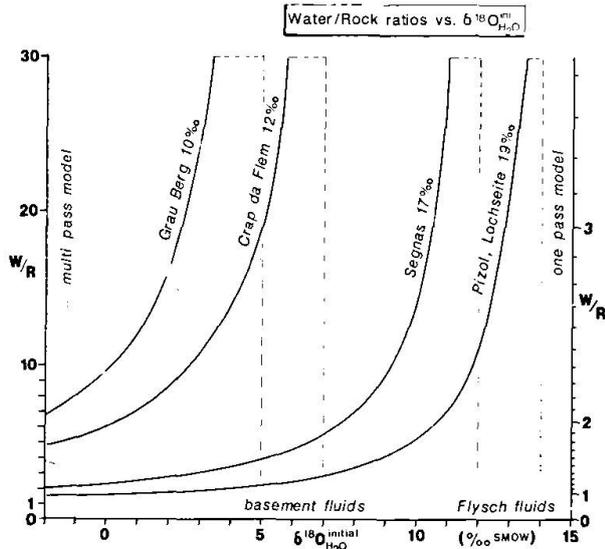


Fig. 3 For the different sites along the Glarus thrust and their respective isotopic calcite composition ( $\delta^{18}\text{O}_{\text{cc}}^{\text{final}}$ ) calculated molar water/rock ratios are plotted vs. the unknown initial isotopic composition of water ( $\delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ini}}$ ) at  $T = 300^\circ\text{C}$  ( $\Rightarrow \delta^{18}\text{O}_{\text{cc-H}_2\text{O}} = 5\text{‰}$ ) for TAYLOR's closed (multipass model:

$$W/R = 3 \times \frac{\delta^{18}\text{O}_{\text{cc}}^{\text{final}} - \delta^{18}\text{O}_{\text{cc}}^{\text{ini}}}{\Delta\delta^{18}\text{O}_{\text{cc-H}_2\text{O}} - \delta^{18}\text{O}_{\text{cc}}^{\text{final}} + \delta^{18}\text{O}_{\text{H}_2\text{O}}^{\text{ini}}}$$

scale to the left) and open system (one pass model:  $W/R = \ln(W/R_{\text{multi}} + 1)$  scale to the right) respectively (e.g. VALLEY et al., 1986, p. 504). Possible initial water compositions are indicated for different fluid sources: metamorphic fluids from the crystalline basement or Verrucano and Tertiary Flysch. Isotopic water compositions in equilibrium with the respective mylonites are indicated with the vertical dashed lines (corresponding to  $W/R = \text{infinity}$ ).

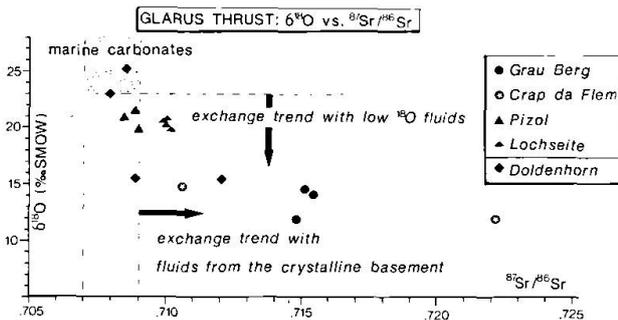


Fig. 4 Measured individual  $\delta^{18}\text{O}$  values of calcites are plotted vs.  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (determined from cold 1N HCl leachates). The stippled "marine carbonate box" is outlined according to HOEFS (1973) and CLAUER (1976) for  $\delta^{18}\text{O}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  respectively.

depleted waters are 1) Verrucano derived waters, 2) metamorphic fluids, or 3) low  $^{18}\text{O}$  (evolved) formation brines. Water/rock ratio calculations show that large integrated W/R ratios are required to explain the observed depletion with

fluids from either source (Fig. 3). The first hypothesis requires advection of large amounts of fluids from the hangingwall, whereas the second and third imply relatively lesser amounts of fluids being transported over kilometric distances from the underlying crystalline basement. Vertical fluid fluxes on the order of  $0.5 \cdot 10^{-12} \text{g/cm}^2\text{s}$  were calculated for the latter (single pass model) and an assumed 10 Ma time span of thrusting. This is comparable to the fluid flux predicted above regional metamorphic terranes by CONNOLLY and THOMPSON (1989). Assuming that all the fluid is expelled along the thrust, this number has to be multiplied by the length of the thrust in cm and adds up to  $10^{-8} \text{g/cm}^2\text{s}$  for 20 km of thrust.

For the remaining localities, overlying a thick layer of Flysch, fluids derived from these through compaction/dewatering and e.g. smectite-illite transformation could easily account for the observed  $^{18}\text{O}$ -depletion within the calc-mylonite. Even large calculated W/R ratios of 3 (one pass model) in a 1 m thick mylonite layer need for instance no more than a 0.15% compaction (water loss) within a 1 km column of Flysch below to account for the needed amount of water. From this estimation, it is clear, that sections overlying Flysch cannot provide any additional information about the possible participation of "metamorphic" fluids from greater depth in the deformation of the Glarus mylonite.

Some high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (Fig. 4) are an additional argument that calcite from the Lochseiten mylonite may have exchanged with fluids that were in equilibrium with an external rock reservoir: crystalline basement, Verrucano or Flysch which provided the radiogenic  $^{87}\text{Sr}$  to shift the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from marine to "intermediate" signatures.

### Lochseiten calc-mylonite – a secondary calcite precipitation?

Specific conditions are required to produce and preserve this thin calcite layer over areas as large as 15 by 20 km, coating the bottom of the Verrucano thrust sheet. Stylolites and veinlets within the mylonite testify to ongoing dissolution and crystallization processes during deformation and these had to balance each other out in order to preserve the calcite layer. Even a minor volume loss could have removed the calcite altogether (compare: O'HARA and BLACKBURN, 1989). On the other hand, the mylonite calcite could also be interpreted as a secondary mineralization of the thrust surface (an idea formulated already by ROTHPLETZ, 1883; p. 168). Due to the inverse

temperature dependence of calcite solubility (HOLLAND and MALINN, 1979), and assuming that the calcite source was located in the footwall (Flysch, crystalline basement), this hypothesis requires an inverse temperature gradient and/or drop in CO<sub>2</sub> pressure at the contact. A discontinuous metamorphic zonation is in fact observed at the Glarus thrust today (GROSHONG et al., 1984; FREY, 1988) – but did such a gradient exist during thrusting deformation? If this was the case, rising fluids saturated with respect to calcite could have precipitated part of their dissolved calcite at the bottom of the slightly hotter over-riding Verrucano. In this model, assuming an extreme temperature difference (250–300 °C) and high CO<sub>2</sub> pressure (HOLLAND and MALINN, 1979, Fig. 9.14), 0.37·10<sup>5</sup>g of solution would be needed to account for the deposition of 1 g of calcite. This translates to a minimum necessary vertical fluid flux of ~0.3·10<sup>-7</sup> g/cm<sup>2</sup>s, five orders of magnitudes higher than fluxes calculated from the stable isotopes, and even from a thick section of Flysch it may seem intractable to produce such large amounts of fluid.

### Conclusions

With the present data, it is not yet possible to decide whether the Lochseiten mylonite is derived from Mesozoic carbonates, from secondary calcite precipitation or some combined process. Geochemical and isotope results, however, indicate that large quantities of fluids of metamorphic origin have interacted with this mylonite. These fluids may also have played an important role during deformation.

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