

Metastable prograde mineral reactions in contact aureoles

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ABSTRACT

Extrapolation of reaction paths and rates of metamorphic mineral growth from experimental to natural systems is complicated by a number of factors. Many of these factors are difficult to evaluate for natural systems. A combination of textural modeling and stable isotope analysis allows for a distinction between several possible reaction paths for olivine growth in a siliceous dolomite contact aureole. It is suggested that olivine forms directly from dolomite and quartz. The formation of olivine from this metastable reaction implies metamorphic crystallization far from equilibrium. Stable and metastable reaction paths predict the textures observed (calcite haloes around bladed olivine crystals) well. It is possible to discriminate between individual reaction paths only on the basis of the oxygen isotope compositions of the minerals involved. Products were found to be in stable isotope equilibrium, but in disequilibrium with the reactants. Only the metastable overall reaction dolomite + quartz \rightarrow olivine + calcite + CO₂ produces no dolomite by local reactions, and hence agrees with the oxygen isotope data. Thus, significant mineral growth occurred far from equilibrium with respect to the thermodynamically stable reactions of the system. This amazing finding implies that metamorphism of contact aureoles has to be reinterpreted in a more complex, dynamic fashion, involving metastable reactions and metastable equilibria as well. The spatial distribution of metamorphic mineral assemblages in a contact aureole cannot be interpreted as a proxy for the temporal evolution of a single rock specimen, because each rock undergoes a different reaction path, depending on temperature, heating rate, and fluid-infiltration rate.

Keywords: nonequilibrium mineral growth, reaction path, stable isotopes, texture model, contact metamorphism.

INTRODUCTION

The occurrence of index minerals in contact aureoles is typically explained as a succession of equilibrium reactions (e.g., Dipple and Ferry, 1992; Spear, 1993). The sequence of index minerals in siliceous carbonates—talc and/or tremolite followed by diopside and/or olivine, and finally periclase—is consistent with the equilibrium phase diagram (Fig. 1). Depending on the rock's position in the aureole, the sample is interpreted to have undergone part or all of the reactions given in the phase diagram. This is a commonly used interpretation, applied to various contact aureoles (Kerrick, 1991, and references therein). It has been challenged for these rapid-heating environments by theoretical calculations using experimentally determined rate data (e.g., Lasaga and Rye, 1993). Similarly, textural studies (e.g., Holness et al., 1991) have shed doubt on the equilibrium interpretation. Until now the determination of reaction paths for the formation of silicates has been elusive, which makes the application of experimental data to contact aureoles questionable. We demonstrate that reaction paths can be determined by combining texture modeling with detailed, grain-scale isotopic studies. The data presented here have led us to conclude that olivine production in the Ubehebe Peak contact aureole (Death Valley National Park, California) was the consequence of a reaction from the metastable assemblage dolomite + quartz. This study presents an approach to distinguish between reaction paths. We propose that the stud-

ied aureole is typical, and that metastable reactions are the rule rather than the exception in contact aureoles. Hence, the often-implied interpretation that the spatial mineral distribution is a proxy for the time evolution of a sample in the aureole has to be abandoned.

GEOLOGIC SETTINGS

The petrology of the Ubehebe Peak contact aureole is well studied (Roselle, 1997). Roselle (1997) estimated pressure-temperature conditions for the contact as 1.4–1.7 kbar and 665 °C. Tremolite, forsterite, and periclase were formed in siliceous carbonates in the aureole. Calcite-dolomite solvus thermometry indicates temperatures of 410–440 °C for the tremolite zone and 475–620 °C for the forsterite zone, respectively. Temperatures of 620–665 °C are estimated for the periclase zone.

Individual lithology horizons can be traced from the contact to virtually nonmetamorphic regions. The siliceous dolomite sample studied, 02-TUB-48, was collected in the forsterite zone, ~250 m from the contact of the quartz monzonitic intrusion (Fig. 2). It was chosen because of its simple mineral assemblage of dolomite, calcite, and forsterite. Calcite is interpreted to be entirely of metamorphic origin, because of its sole occurrence as coronas around olivine, in agreement with the mostly calcite-free protolith rocks outside the aureole. Calculation of the original protolith mineral modes, by using the modal abundance of forsterite and calcite in the investigated sample, resulted in a rock containing 97% dolomite and 3% quartz. These proportions are in agreement with observed protolith compositions, albeit that the quartz content is somewhat low.

ANALYTICAL PROCEDURE

The sample 02-TUB-48 of the forsterite zone was prepared as a thick section (300 μ m). It was cut into 500 \times 500 μ m squares by using a diamond wire saw (130 μ m diameter wire), similar to the procedure described by Kohn et al. (1993). The size of a square was chosen to be smaller than the typical grain size of dolomite crystals (~600–800 μ m). Each single square contains only a small number of grains. Minerals in individual small squares were identified by X-ray transmission imaging, by using micro-X-ray tomography. Stable isotope analyses of carbonates were made according to procedures outlined by Spoetl and Vennemann (2003) with a Thermoquest-Finnigan Gas Bench linked to a DeltaPlus XL mass spectrometer. Calcite and dolomite were reacted at 90 °C (for 1 h). CO₂ was extracted in a stream

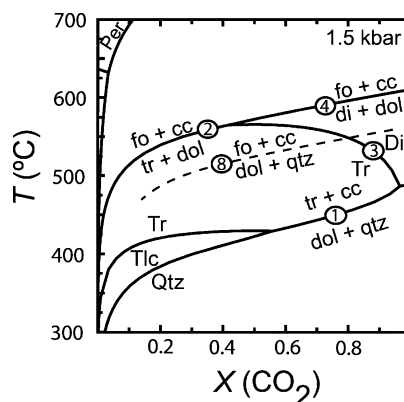


Figure 1. Phase diagram of system CaO-MgO-SiO₂-H₂O-CO₂. $X(\text{CO}_2)$ is mole fraction of CO₂ in binary H₂O-CO₂ fluid. Rocks are saturated with calcite and MgO-rich phase (dolomite, brucite, or periclase) and fluid. Note that dashed line marks metastable reaction. Numbers of reaction correspond to text. qtz—quartz; tlc—talc; tr—tremolite; cc—calcite; dol—dolomite, di—diopside; fo—forsterite.

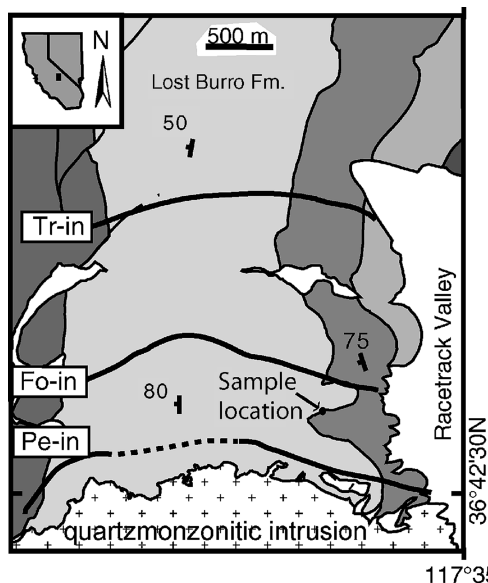


Figure 2. Simplified geologic map of Ubehebe Peak contact aureole showing sample location in forsterite zone and isograds of index minerals tremolite (Tr), forsterite (Fo), and periclase (Pe) (retrograded to brucite). Absence of diopside zone suggests fluid infiltration. Sample was collected in upper part of Hidden Valley Dolomite.

of He carrier gas. The $\delta^{13}\text{C}$ (relative to Vienna Pee Dee belemnite, VPDB) and $\delta^{18}\text{O}$ (relative to Vienna standard mean ocean water, VSMOW) values were normalized relative to those of NBS-19. Acid-fractionation factors for dolomite after Rosenbaum and Sheppard (1986) were used to calibrate a dolomite standard via conventional vacuum extraction of CO_2 . The acid-fractionation factor for dolomite using the Gas Bench was determined with the same dolomite standard. This approach resulted in a final correction of +0.5‰ relative to calcite at 90 °C.

Oxygen isotope analyses of silicates were made at the University of Lausanne by using a CO_2 laser-based extraction line and F_2 as reagent (e.g., Rumble and Hoering, 1994).

RESULTS

The $\delta^{13}\text{C}$ values of the carbonates range between -0.1‰ and -0.8‰ . Sample squares determined to be predominantly calcite have lower values, in agreement with the expected fractionation of $\sim 0.4\text{‰}$ between calcite and dolomite at 620 °C (Sheppard and Schwarcz, 1970). The calculated mean value is -0.46‰ .

Calcite is generally depleted in the heavier isotopes of carbon and oxygen compared to dolomite. However, the expected oxygen isotope fractionation between dolomite and calcite is only 0.2‰ (Sheppard and Schwarcz, 1970) at 600 °C. The range of $\delta^{18}\text{O}$ values in the studied samples is 23.6‰–25.5‰ (Fig. 3), and the values cluster into two groups. The lower values correspond to squares dominated by calcite. Hence, the larger than expected difference in the values indicates disequilibrium between calcite and dolomite (Fig. 3). Although only submillimeter-sized samples were used, some analyses may still represent mixtures of calcite + dolomite, because individual squares may contain both. The resulting analyses reflect a mechanical mixture of calcite and dolomite and can be thus discarded. This conclusion is supported by the linear mixing array between the two clusters (Fig. 3). Dolomite values define a peak at higher $\delta^{18}\text{O}$ values in the histogram (Fig. 3B). The average dolomite composition is in agreement with the bulk host rock $\delta^{18}\text{O}$ values of $25.5\text{‰} \pm 0.8\text{‰}$ (Roselle et al., 1999) for this lithology.

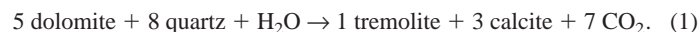
The $\delta^{18}\text{O}$ values of forsterite in the sample are between 20.2‰ and 20.5‰ ($n = 4$). The average fractionation of calcite and forsterite for the section is 4.1‰, which corresponds to an equilibrium temper-

ature of 620 °C (Chiba et al., 1989). Thermal models for the Ubehebe Peak contact aureole on the basis of calcite-dolomite solvus thermometry yield a maximum temperature of ~ 610 °C, which agrees well with this temperature.

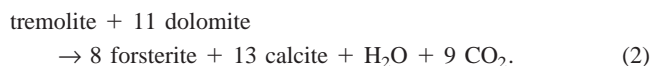
These results confirm the finding of Roselle (1997), cited in Baumgartner and Valley (2001). The products calcite and forsterite grew in isotopic equilibrium with each other and most likely with a water-rich fluid phase. In contrast, reactant dolomite did not equilibrate its oxygen isotopes with the products or the infiltrating fluid phase.

IMPLICATION FOR REACTION PATHS

The spatial distribution of the index minerals in contact aureoles (Fig. 2) reflects the mineral reactions predicted by the thermodynamic model systems (Fig. 1). This agreement has led to an equilibration interpretation of phase assemblages in the aureole. This implies that the prograde history of every rock sample can be traced in the equilibrium phase diagram. Thus, taking the spatial evolution as a proxy, the first reaction that occurred in a now forsterite-bearing rock from the forsterite zone is



With increasing temperature, reaction 1 is followed either by reaction 2, which produces forsterite, or reaction 3, which produces diopside:

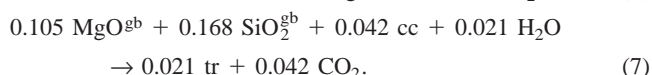


If diopside is produced, forsterite finally will be formed by



The modal abundances of forsterite, calcite, and dolomite can be used to estimate the initial modal abundances of dolomite, quartz, and calcite in the sedimentary protolith (Fig. 4). By comparison to rocks outside the aureole, we assume that quartz was evenly distributed as fine grains in the dolomite matrix. For the sample investigated, no calcite is predicted to have been in the protolith (Fig. 4A). Textures resulting from several different reaction paths were modeled using the SEG program (Foster, 1993), which assumes diffusive mass transport. The fluxes are constrained by mass balance and the local Gibbs-Duhem equations (Foster, 1990, 1999). Textural observations in natural samples reveal that olivine growth was skeletal. It is surrounded by calcite rims. Both observations suggest a diffusion-limited reaction mechanism, which is the limiting factor modeled by the SEG program.

If forsterite was produced by the breakdown of tremolite, tremolite will have grown previously by reaction 1. Tremolite forms uniformly distributed acicular, millimeter-sized porphyroblasts in a finer-grained matrix of dolomite in the rocks of the tremolite zone in the Ubehebe contact aureole. Reaction 1 will proceed by a mechanism involving three local reactions occurring in different parts of the rock:



See Figure 1 for an explanation of abbreviations used. The silica needed to grow tremolite is provided by quartz dissolution (reaction 5). Because of the low modal abundance of quartz in the protolith, a quartz-depleted zone around tremolite is formed. Silica is transported to the tremolite through the quartz-depleted zone by grain-boundary (gb) diffusion. The MgO needed for the tremolite formation is provided by the conversion of dolomite to calcite (reaction 6) in the immediate vicinity of the growing tremolite, resulting in a thin, dolomite-free calcite halo surrounding

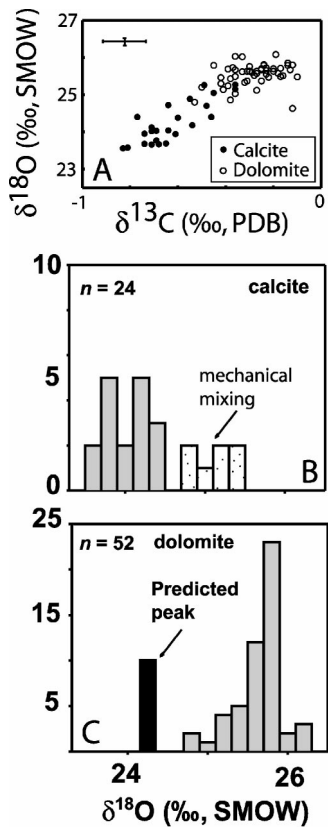


Figure 3. A: Plot of $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ values of coexisting calcite and dolomite. Note large differences in oxygen isotope composition. Two main groups are recognizable, defined by calcite and dolomite. B and C: Histograms showing $\delta^{18}\text{O}$ values for (B) calcite and (C) dolomite. Isotope standards: SMOW—standard mean ocean water; PDB—Peedee belemnite.

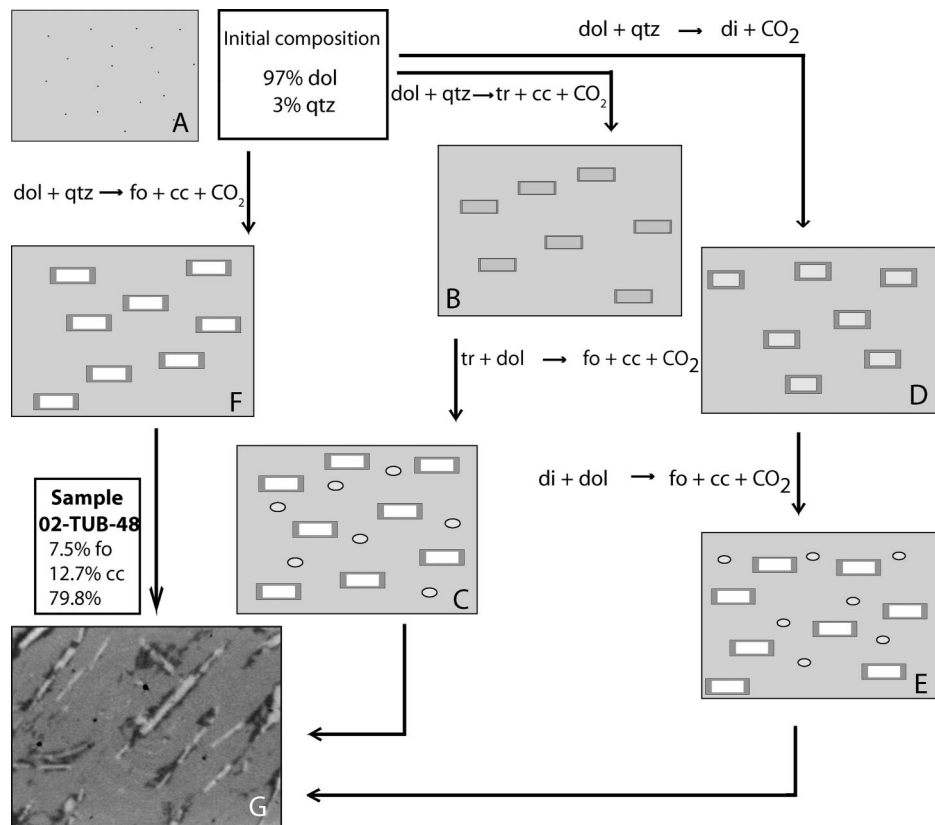
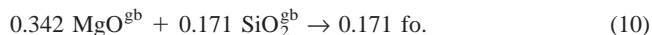
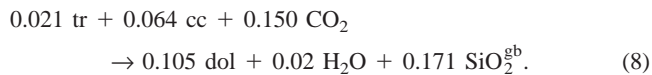


Figure 4. Results of texture models: A: Host rock consisting of dolomite and quartz. B: Newly grown tremolite (tr) with calcite (cc) halos. C: Forsterite (fo) growing from breakdown of tremolite. Ellipses mark newly grown dolomite. D: Diopside (di) growing from dolomite and quartz. E: Forsterite growing from reaction of diopside. F: Forsterite growing directly from quartz + dolomite. G: Micro-computer tomography image of sample showing actual texture of sample (bright—forsterite; dark—calcite; gray—dolomite). Note that all reaction paths explain observed texture, but only path shown in F is in agreement with stable isotope data presented in Figure 3.

the tremolite. This texture, shown in Figure 4B, compares well with those observed in the tremolite zone.

Subsequent tremolite breakdown to forsterite by overall reaction 2 is the result of three local reactions:

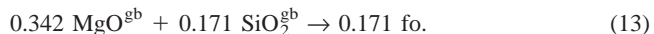


The tremolite dissolution reaction provides the silica needed to form forsterite. The MgO from the dissolution of tremolite reacts with surrounding calcite formed by the previous tremolite-forming reaction to form new dolomite (reaction 8). All that is predicted to be left of the millimeter-sized tremolite crystals is newly formed dolomite (Fig. 4C). MgO is obtained from conversion of adjacent dolomite to calcite (reaction 9) at the forsterite growth site. Reaction 9 produces a visible dolomite-free halo surrounding the growing forsterite, in agreement with the observed textures (Fig. 4G). The models predict 7 modal percent of newly formed dolomite. If this new dolomite has a grain size similar to that of the matrix dolomite, the new dolomite is impossible to identify texturally. All dolomite crystals seen in the rocks today have a similar grain size. Hence metamorphic dolomite, if formed, has a grain size of 600–800 μm .

Stable isotope analyses provide a crucial test for these models, because the isotopic composition of products differs from that of reactants as discussed here. Dolomite replacing tremolite is expected to crystallize in isotopic equilibrium with the other products, calcite and forsterite. The 7% of newly formed dolomite would represent 9% of the overall dolomite present in the section. Hence a total of about eight analyses should reflect their isotopic composition. This should result in a peak ($n \approx 8$) at $\delta^{18}\text{O}$ values of 24.3‰ in the histogram (Fig. 3C), if the median isotopic composition of pure calcite and the expected equilibrium fractionation of 0.2‰ at 620 °C (Sheppard and Schwarz, 1970) are used. While this peak might be somewhat reduced due to mixing of “old” and “new” dolomite, such mixtures are unlikely to erase this peak, since each dolomite crystal is larger than our analysis volume (see discussion). The absence of such a peak suggests that no significant amount of new dolomite was formed and hence the proposed reaction mechanism is incorrect.

An alternate reaction path produces forsterite from diopside (reaction 4). In an internally buffered system the prograde reaction of quartz with dolomite to form tremolite will increase $X(\text{CO}_2)$ until either one of the reactants is exhausted or the invariant point is reached, where diopside is formed from tremolite, quartz, and dolomite. Further increase of temperature will produce increasing modal amounts of diopside. In a rock with an initial small porosity and abundant silica, virtually all silica will react to diopside. Hence, in this case, olivine

will then form from diopside. The textural model reveals the same texture for this reaction (Figs. 4D, 4E). Diopside breakdown also produces new dolomite through the following local reactions:

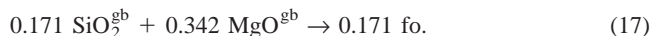


The modal amount of metamorphic dolomite (5.5%) is somewhat smaller when compared to the tremolite breakdown reaction. Nevertheless, this amount of new dolomite should result in a significant number ($n \approx 5$) of analyses in isotopic equilibrium with calcite (24.3‰ $\delta^{18}\text{O}$ [VSMOW]). The latter is not observed (Fig. 3). In addition, diopside is not present in this rock type throughout the aureole. The absence of a diopside zone for these rocks in the field indicates that the system was open to fluid infiltration (Dipple and Ferry, 1992). Roselle et al. (1999) concluded that the system was only partially internally buffered, with locally significant infiltration. This conclusion is in agreement with our isotopic results, which indicate infiltration of fluids depleted in $\delta^{18}\text{O}$ during olivine formation. Hence, growth of olivine from diopside is also unlikely.

If overstepping of the tremolite or diopside forming reactions is large, forsterite could form directly from dolomite and quartz by the metastable reaction:



Modeling of this reaction path yields the local reactions:



The quartz-dissolving reaction provides the silica needed to form forsterite (reaction 15). The MgO needed to grow forsterite comes from the conversion of dolomite to calcite by reaction 16. This conversion occurs in the vicinity of the newly growing forsterite, resulting in a dolomite-free calcite halo around the olivines (Fig. 4F). The resulting texture is identical to that of the previous reaction paths (Fig. 4G). However, this reaction does not produce metamorphic dolomite. Pre-existing dolomite did not change its isotopic composition. Hence this reaction path predicts the observed isotope compositions.

CONCLUSIONS

It is possible to distinguish between different reaction paths by combining the results of stable isotope measurements with petrologic texture models. The result of this approach indicates that forsterite was produced directly from quartz and dolomite in the Ubehebe Peak contact aureole. The stable reactions predicted by equilibrium thermodynamics apparently proceeded too slowly. The metastable reaction of quartz + dolomite \rightarrow forsterite was overstepped before much tremolite was formed. However, in the outer aureole, tremolite occurs in the same lithology. Presence of tremolite is interpreted to be the result of the fact that temperatures never significantly overstepped the tremolite stability in these samples, so that mainly tremolite was formed. The resulting mineral distribution in the aureole mimics an equilibrium phase distribution, although probably all reactions proceeded far from equilibrium. Hence, the spatial distribution of metamorphic mineral assemblages in a contact aureole cannot be interpreted as a proxy for the temporal evolution of an individual rock specimen, because each rock undergoes a different reaction path, depending on temperature, heating rate, and fluid-infiltration rate.

Analyses of isotopic compositions of minerals can give information on the reaction mechanism, but only limited information on the infiltration history. Infiltration is only recorded isotopically if the minerals recrystallize or neoform. Hence only very specific parts of the

fluid-infiltration history may be recorded, in a very diachronous way, reflecting the dynamic crystallization of products in the aureole. This study highlights the importance of understanding the coupling of metamorphic reactions with fluid flow (Baumgartner and Valley, 2001) to develop valid models of stable isotope fluid-rock interaction in contact aureoles. The observed mineral sequence in the aureole is typical for siliceous dolomite-bearing aureoles. Similar textures have been described in other aureoles (e.g., Cook and Bowman, 1994). Hence we believe this study to be representative for most contact aureoles. If this is true, we have to reinterpret a large part of the metamorphic petrology of contact aureoles.

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