# Isotopic disequilibrium during metasomatic vein formation

**R. Abart**                                      *Institute for Mineralogy und Petrography, ETH Zurich,*
*Sonneggstrasse 5, CH-8092 Zürich, Switzerland.*

## Introduction

At the southwestern border of the Adamello batholith metasomatic garnet-vesuvianite veins occur within the contact metamorphic marble sequence of the Prezzo formation. The veins are characterized by the assemblage garnet $(Ca_3Al_{1.6}Fe_{0.4}^{3+}Si_3O_{12})$ + vesuvianite $(Ca_{19}Mg_{1.2}Fe_{1.2}Al_{10.4}Ti_{0.3}Si_{18}O_{69}[(OH)_{7.5}F_{1.5}])$ + clinopyroxene $(CaMg_{0.8}Fe_{0.2}Si_2O_6)$ + wollastonite + calcite + pyrrhotite $(FeS_{1.1})$. Within the veins irregularly shaped microscopic domains with different degrees of silicification can be distinguished. Graphite is present in the contact metamorphic Prezzo Marble at 0.5 wt% concentration, but is absent in the metasomatically altered rocks.

## Carbon and oxygen isotope systematics

Calcite isotopic composition was analysed using a conventional extraction technique, sub-millimeter sized garnet grains were analysed with a laser extraction technique (Sharp, 1990). The isotopic composition of calcite in the contact metamorphic marble is $\delta^{18}O_{SMOW}$ = 21‰ and $\delta^{13}C_{PDB}$ = 0.0‰. Calcite composition is shifted towards significantly lower values in both the carbon and oxygen systems in the veins, towards minimum values of $\delta^{18}O_{SMOW}$ = 15‰ and $\delta^{13}C_{PDB}$ = 0.0‰. Within the veins the isotopic composition of calcite varies systematically with distance from the most silicified micro-domains, whereas metasomatic garnet has a constant composition of $\delta^{18}O_{SMOW}$ = 21‰ throughout the metasomatically altered zones. $\Delta^{18}O_{garnet-calcite}$ varies over two $\Delta$-units on a millimeter scale clearly indicating isotopic disequilibrium.

## Phase equilibrium constraints

Environmental conditions during metasomatism were 2800 bar and 600°C as inferred from hornblende barometry using the calibration of Schmidt (1992) and from quartz–diopside isotope thermometry based on fractionation factors given by Chiba et al. (1989). The speciation of a C–O–H–S molecular fluid in equilibrium with the metasomatic assemblage was calculated using a hybrid equation-of-state approach (Connolly and Cesare, 1993) to derive species fugacities. Calculations are based on thermodynamic data from Holland and Powell (1990) and on activity models of Hoisch (1985) and Engi and Wersin (1987) for vesuvianite and garnet solid solutions, respectively. The metasomatic mineral assemblage constrains fluid-composition along a curve in C–O–H–S composition space. The abundance of the most important carbon and oxygen bearing species may vary between $X_{H_2O}$ = 0.76, $X_{CO_2}$ = 0.17, $X_{CH_4}$ = 0.04 with C/O = 0.17 at graphite saturation (hereafter fluid A) and $X_{H_2O}$ = 0.86, $X_{CO_2}$ = 0.14, $X_{CH_4}$ = 0.00 with C/O = 0.12 at low graphite activity (hereafter fluid B).

## Fluid/rock interaction and isotopic shifts

The constant isotopic composition of garnet suggests isotopic garnet-fluid equilibrium and $\delta^{18}O_{fluid}$(SMOW) can be calculated from $\delta^{18}O_{garnet}$(SMOW) and $\Delta^{18}O_{garnet-fluid}$. Using fractionation factors from Friedman and O'Neil (1977) $\delta^{18}O$(SMOW)-values of 12.3 ‰ and 12.0 ‰ are obtained for fluid A and fluid B, respectively. The fluid is most probably of magmatic provenance and did not contain significant amounts of carbon initially. Its carbon content at the time of vein formation is ascribed to the dissolution of graphite from contact metamorphic Prezzo Marble during infiltration and $\delta^{13}C_{fluid}$(PDB) is set to −12.0 ‰, the isotopic composition of graphite. Progress in $\epsilon$-isotopic exchange in the course of fluid/rock interaction, defined as the ratio of the observed over the maximum attainable $\epsilon$-isotopic shift, may be expressed as

$$\xi_\epsilon \equiv \frac{\delta\epsilon_R^f - \delta\epsilon_R^i}{\delta\epsilon_R^{eq} - \delta\epsilon_R^i},$$

where $\delta\epsilon_R^{eq}$ is the $\epsilon$-isotopic composition of the rock in equilibrium with the infiltrating fluid. The relative rates at which carbon and oxygen isotopic

equilibrium are approached depend on the carbon and oxygen content of fluid and rock as well as on the rates of isotopic exchange reactions. Differences in calcite grain morphology and pore geometry between vein material and unaltered Prezzo Marble suggest that dissolution/reprecipitation was the relevant mechanism for isotopic exchange. In this case the rates of carbon and oxygen isotopic exchange are the same and carbon/oxygen isotopic covariation may be used to constrain the carbon/oxygen ratio of the fluid. Equation of the volumetric fluid/rock ratios obtained from the relation of Taylor (1977) for open system isotopic exchange yields:

$$ln(1 - \xi_C) = \frac{\kappa_O}{\kappa_C} \cdot ln(1 - \xi_O),$$

where $k = \frac{\kappa_O}{\kappa_C} = \dfrac{au_C^F \cdot au_O^R}{au_O^F \cdot au_C^R}$

is an expression of the atomic carbon/oxygen ratios in the rock and the fluid phase, and $au_c^F$ gives the number of moles of $c$ atoms per mole of phase F. Regression of the $ln(1 - \xi_O)$ against the $ln(1 - \xi_C)$ coordinates calculated from the isotopic compositions of vein calcite yields slopes of 0.316 and 0.363 for fluid A and fluid B. Assuming an oxygen/carbon ratio of three for the rock (calcite), atomic C/O ratios of 0.105 and 0.121 are obtained for fluid A and fluid B. For fluid B this is in good agreement with phase equilibrium constraints indicating that, provided carbon and oxygen isotopic exchange were equally fast, the metasomatic fluid was essentially a $H_2O$-$CO_2$ mixture with low graphite activity. If the infiltrating fluid was indeed graphite saturated (fluid A, C/O = 0.17) then the observed carbon/oxygen covariation would suggest that carbon isotopic exchange was slower than oxygen isotopic exchange by a factor of 1.7.

## Conclusions

Vein formation was concomitant with infiltration of a water-rich metasomatic fluid. The capacity of the fluid to lower the carbon isotopic composition of calcite is ascribed to the dissolution of isotopically light graphite. Whereas metasomatic garnet was in isotopic equilibrium with the infiltrating fluid, isotopic disequilibrium prevailed between preexisting calcite and the fluid. Carbon/oxygen isotopic covariation is compatible with equally fast carbon and oxygen isotopic exchange rates and a $H_2O$-$CO_2$ fluid of low graphite activity or with carbon isotopic exchange by a factor of 1.7 slower than oxygen exchange and a graphite saturated fluid.

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