The nature of carbon and oxygen transportation in the metamorphic marbles: the role of chemical reaction, dissolution and diffusion

H. Wada
M. Satish-Kumar
M. Suzuki

Department of Biology and Geosciences, Shizuoka University,
836 Ohya, Shizuoka, 422-8529 Japan

Skarn minerals in a contact metamorphic aureole often display a distinctive chemical fronts between skarns and marbles where an intensive material transport took place during their formation. A highly space resolution analyses of carbon and oxygen isotope ratio in calicte marbles developed by Wada and others (Wada, 1988; Arita and Wada, 1990; Satish, *et al.*, 1998; Wada *et al.*, 1998) make it possible to fully understand such influences on metamorphic limestones. Cathodoluminescence (CL) image can also help to offer visual information about the fluid passways in such marbles. We have examined some different types of limestone with a skarn formation collected from some contact metamorphic aureoles in Japan (Wada *et al.*, 1998), a regional metamorphic terrain in Antarctica (Satish *et al.*, 1998) and a contact followed by regional metamorphism in Adirondacks (Wada and Valley, 1998).

Diffusion controlled profiles

Carbon and oxygen isotopic profiles around a low pressure metasomatic wollastonite reaction front in a marble of the Hida metamorphic terrain, central Japan, display typical metamorphic fluid-enhanced isotopic zonations (Fig. 1). Isotopic profiles obtained from detailed microscale analyses perpendicular to the chemical reaction front in calcite marble show that diffusion-enhanced isotopic exchange may control both profiles. Carbon and oxygen isotopic behaviour within grain boundaries are remarkably different. Oxygen isotopic troughs (^{18}O depleted rims) around the calcite-grain boundaries are widely observed in this contact aureole, demonstrating that grain boundary diffusion of oxygen in calcite rims is dominates over diffusion in calcite grain cores (Fig. 1a). In contrast, no difference is observed in carbon isotopic profiles obtained from grain cores and rims (Fig. 1b). There is thus no specific role of the grain boundary for diffusion of carbonic species in the metamorphic fluid during transportation. The carbon and oxygen isotope profiles may be modelled by diffusion into a semi-infinite medium. Empirically lattice diffusion of oxygen isotopes is almost six times faster than that of carbon isotopes, and oxygen grain-boundary diffusion is ten times faster than oxygen lattice diffusion. From the stability of wollastonite and the oxygen isotopic equilibrium, we suggest that diffusion of oxygen occurred therough an aqueous fluid phase. The timescale of formation of the oxygen isotopic profile around the wollastonite vein is calculated to be about 0.76×10^6 yrs using the experimentally determined diffusion constant.

Diffusion controlled followed by chemical reaction

Carbon and oxygen isotopic profiles in the metasomatic skarn veins, showed a trend of oxygen isotopc variation along the skarn vein-marble contact (Fig. 2). We can get some isotoopic profiles perpendicular to the vein-marble contact. The oxygen isotopic zonation in the surface of the contact is best explained by the diffusion controlled isotopic profile in the first stage of metasomatic devolatilization processes and followed by later stage metasomatic reaction with metamorphic fluid and calcite. The chemical reaction cut the oxygen isotopic profiles and newly produced a profile with diffusion controled reaction. Carbon and oxygen isotopic profiles were mainly formed thus by lattice diffusion during the earlier high temperature stage of metamorphism and a mixed effect of diffusion and dissolition-precipitation mechanism during later stage (Fig. 2).

Solution-precipitation

Across a 1.2-mm wide domain, a calcite crystal from a granulite facies marble from East Antarctica

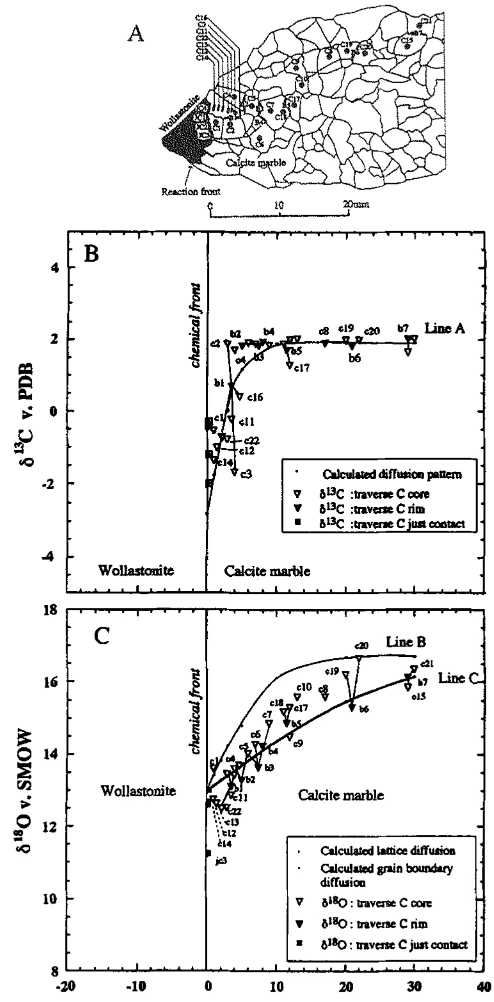

FIG. 1. Carbon and oxygen isotopic profiles along a traverses perpendicular to the reaction front of a wollastonite vein in calcite marble, Hida metamorphic terrain, central Japan. A: Sampling localities on the polished section for analyses of cores(c) and rims(b). B: carbon isotopic profile. C: oxygen isotopic profile. Data connected with tie-lines represent a group sampled from adjacent calcite cores and rims. Curves (denoted Line A, B and C) are calculated diffusion profile based on the semi-infinite one dimensional diffusion model (Wada *et al.*, 1998).

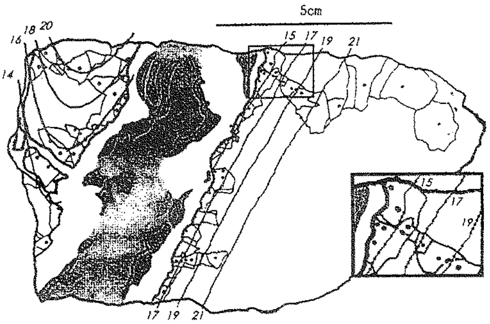

FIG. 2. Contour lines of oxygen isotopic ratios around the skarn vein, at Kushiro, Hiroshima, western Japan. Small dots represent sampling localities for isotopic analyses. Enlarged sampling localities (shown by a rectangle) are shown The reaction front cuts the contour lines.

exhibits microscale oxygen isotope heterogeneity that has been enhanced by channelized fluid flow (Satish *et al.*, 1998). The oxygen isotope compositions range over 21‰ - a gigantic zonation. Calcite along a boundary with phlogopite has an average $\delta^{18}O$ value of −5‰; along a profile that extends about 700 mm into the grain the oxygen isotope composition remains constant, indicating equilibrium with source fluids of meteoric origin. It is inferred that preferential microfracturing and hydrothermal fluid flow were the causes of ^{18}O distribution. The constant values of both $\delta^{18}O$ and $\delta^{13}C$ for the distance of 700 μm from the grain boundary suggest a solution-reprecipitation mechanism, whereas the smoothly increasing $\delta^{18}O$ and decreasing $\delta^{13}C$ values farther along the profile indicate a diffusion-controlled isotope exchange between the reprecipitated calcite and the original grain (core). Our results provide important evidence for the mechanism of isotope-exchange between fluids and minerals and have major implications for microfracture-controlled fluid-flow processes in the Earth's crust.

References

Arita, Y., Wada, H. (1990) *Geochem. J.*, **24**, 173–86.

Satish-Kumar, M., Wada, H., Santosh, M., Niitsuma, N., Yoshida, M. (1998) *Geology* (in press).

Wada, H. (1988) *Nature*, **331**, 61–3.

Wada, H., Ando, T., Suzuki, M., (1998) *Contrib. Minral. Petrol.* (submitted).