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16. Sr AND O ISOTOPIC RATIOS OF ARAGONITE VEINS FROM SITE 895[1]

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ABSTRACT

The aragonite veins from Site 895 have been analyzed for Sr contents and Sr, carbon and oxygen isotopic compositions. The $\delta^{18}O$ values are uniform and quite high (+33.9 to 36.1‰), which suggests low formation temperature (<7°C). The $^{87}Sr/^{86}Sr$ ratios range from 0.709136 to 0.709195 indicating that the aragonites crystallized from present-day seawater. The aragonite veins at Site 895 formed from ambient seawater after tectonic exposure of the peridotites.

INTRODUCTION

The interaction of seawater with oceanic crust plays an important role in changing the chemistry of seawater and in modifying the composition of pristine oceanic crust and mantle. Low temperature alteration is manifested by crystallization of carbonates. Calcite and aragonite, which represent the latest and lowest temperature products of seawater-rock interactions, are useful materials in assessing the timing and extent of alteration. There are numerous studies about such processes in the upper oceanic crust, but only a few investigations have been carried out on lower crustal rocks (e.g., Hart et al., 1994) and peridotitic mantle (e.g., Bonatti et al., 1980; Agrinier et al., 1988; Silantyev et al., in press; Snow and France-Lanord, 1994). Abyssal peridotites are generally highly altered, with a variety of alteration products such as serpentine, hornblende, chlorite, smectite, and carbonates (Dick, 1989). Aragonite is the major carbonate precipitated in abyssal peridotite.

During ODP Leg 147, young (about 1 Ma) sections of the lower crust and shallow mantle located at the western tip of the Cocos-Nazca Ridge (Hess Deep) were recovered. Site 895 cored peridotites that were processed at the East Pacific Rise and tectonically exposed by the propagating Cocos-Nazca Ridge. The peridotites are extensively serpentinized (Gillis, Mével, Allan, et al., 1993). Petrological studies suggest successive stages of seawater/rock interaction, as evidenced by numerous veins exhibiting cross-cutting relationships (Fruh-Green et al., this volume; Mével and Stamoudi, this volume). Aragonite veins (up to 5 mm thick) that fill discrete, straight to wavy fractures occur sporadically in harzburgites and dunites and form the last generation of alteration products. This paper reports Sr contents and Sr, carbon and oxygen isotopic data of aragonite veins from serpentinized harzburgites and dunites (Table 1).

METHODS

Carbonate veins were spalled from host rock, crushed gently, and a few fragments were hand picked to be of maximum purity and clarity. All samples (1 to 3 mg) were dissolved in ^{84}Sr spike plus 2.5N HCl for 10–15 min at about 50°C, without leaving any residue. $^{87}Sr/^{86}Sr$ is reported relative to 0.710240 for NBS987. The oxygen temperatures were calculated after O'Neil et al. (1969), using correction for aragonite of Tarutani et al. (1969), assuming interglacial and glacial vein fluid $\delta^{18}O$ (SMOW) equal to 0‰ and 1.2‰, respectively.

RESULTS AND DISCUSSION

The $\delta^{13}C$ values of Site 895 aragonites vary from –0.64 to 2.59‰, which are within the range of inorganically formed marine carbonates. The oxygen isotope values range from +33.9 to +36.1‰. They are higher than the values reported for carbonates from upper oceanic crust (e.g., Lawrence 1980, 1991; Staudigel et al., 1981) and lower crust (Hart et al., 1994), but similar to those reported in aragonite from abyssal peridotites (Bonatti et al., 1980) (Fig. 1). The oxygen isotope temperatures of aragonite formation cover a small range, from 0°C to 7°C, and overlap with bottom-water temperatures. It seems that crystallization of aragonites generally occurs at lower temperatures than that of calcites. The very low crystallization temperature of aragonite inferred from the oxygen isotope data suggests that oceanic mantle at Site 895 was at ambient water temperature during the time of aragonite precipitation. It is not clear why aragonite and not calcite occurs in abyssal peridotites. Bonatti et al. (1980) suggested that seawater circulating through ultramafic rocks is enriched in Mg, and this inhibits the precipitation of calcite. Hart et al. (1994) noticed that aragonite in lower oceanic crustal gabbros was formed close to a high Mg troctolite unit. The fact that aragonite is not common within the basaltic section of the upper oceanic crust (note however the aragonite occurrence in the upper part of Hole 504B [Hart et al., 1994]) supports the idea that the crystallization of aragonite is related to the primary composition of the crust and mantle host rocks.

The Sr content in aragonites varies over a relatively large range, from 8900 ppm to 14,200 ppm. These concentrations are higher than those reported by Hart et. al., (1994) for aragonite from basaltic upper crust (Hole 504B) and lower crust gabbros (Hole 735B), but they are similar to those reported for abyssal peridotites (Bonatti et al., 1980; Silantyev et al., in press). The amount of Sr precipitated in aragonite is controlled by the Sr/Ca ratio of the solution and the Sr/Ca distribution coefficient between aragonite and seawater. This latter factor is inversely correlated with temperature, seems to increase with precipitation rate, and also depends on solution and rock composition. We observed a negative correlation between Sr content and oxygen isotope composition (Fig. 2), which suggests that the colder seawater vein solutions precipitate aragonite that has a lower Sr concentration. These data are opposite to those reported for aragonite from higher temperature corals (Beck et al., 1992). It seems that the composition of peridotite is an important factor that determines the Sr content in

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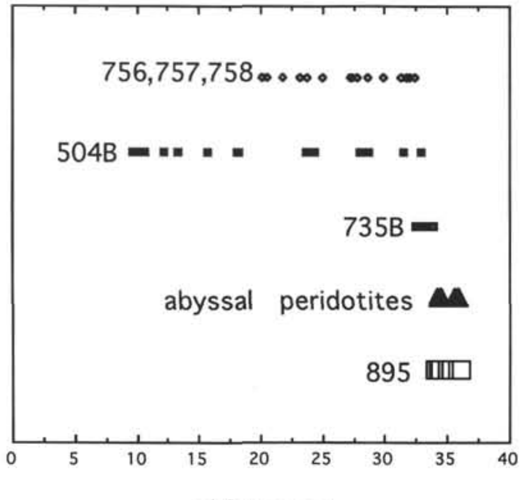

Figure 1. Range of oxygen isotope ratios in aragonite veins from Site 895 and aragonite from abyssal peridotites (after Bonatti et al., 1980). The oxygen isotopic composition of carbonate from lower gabbroic oceanic crust (Hole 735B; Hart et al., 1994), middle oceanic crust (Hole 504B; Alt et al., 1986) and upper oceanic crust (Sites 756, 757, and 758; Lawrence, 1991) are shown for comparison.

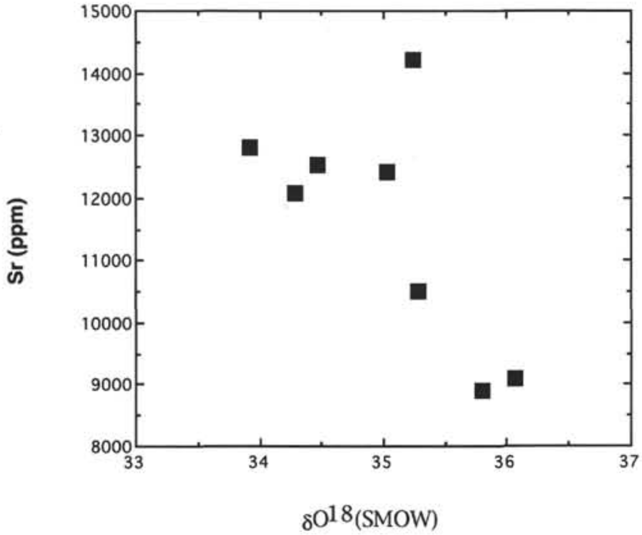

Figure 2. Strontium content vs. oxygen isotope ratio for Site 895 aragonites.

the aragonite; however, there is no correlation between rock type (dunite or harzburgite) and Sr content. All peridotites from Site 895 are variably serpentinized, a process that occurs at high temperatures (>350°C) (Fruh-Green et al., this volume), preceding the deposition of aragonite. This suggests that the extent of serpentinization might influence the Sr content of the aragonite.

The aragonite samples show a very small variation in $^{87}Sr/^{86}Sr$, with an average of 0.709174 (Table 1, Fig. 3). Except for Sample 147-895E-9W-1, which has the lowest ratio (0.709136), all of the other samples are uniform within 2-sigma error. The Sr isotopic compositions of the vein aragonites are identical to those of present-day seawater (0.709177, Hodell et al., 1990), indicating that the aragonites crystallized from virtually pure seawater. Carbon isotope data also support this conclusion. There are two possible explanations for the lower isotopic composition in Sample 147-895E-9W-01 (which also has the lowest Sr content). This sample might have crystallized from present-day seawater with a minor peridotite component (fresh abyssal peridotite has $^{87}Sr/^{86}Sr$ of about 0.7027), which caused a decrease of $^{87}Sr/^{86}Sr$. However, calculation of the Ca/Sr ratio in the solution from which this sample crystallized gives a seawater Ca/Sr ratio and this argues against a significant rock component in the vein fluid. It seems more probable that Sample 147-895E-9W-01 precipitated from slightly older seawater; according to Hodell et al., (1990) the $^{87}Sr/^{86}Sr$ in seawater 0.3 Ma was equal to 0.709144.

Our results indicate that aragonite veins at Site 895 formed from ambient, cold seawater relatively soon after tectonic exposure of the peridotites. These results confirm that aragonite veins correspond to the last episode of alteration and show that they crystallized from seawater penetration in already serpentinized peridotites at the seafloor or at quite a shallow level.

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REFERENCES

Agrinier, P., Mével, C., and Girardeau, J., 1988. Hydrothermal alteration of the peridotites cored at the ocean/continent boundary of the Iberian Margin: petrologic and stable isotope evidence. *In* Boillot, G., Winterer, E.L., et al., *Proc. ODP, Sci. Results,* 103: College Station, TX (Ocean Drilling Program), 225–234.

Alt, J.C., Muehlenbachs, K., and Honnorez, J., 1986. An oxygen isotopic profile through the upper kilometer of the oceanic crust, DSDP Hole 504B. *Earth Planet. Sci. Lett.,* 80:217–229.

Beck, J.W., Edwards, R.L., Ito, E., Taylor, F.W., Recy, J., Rougerie, F., Joannot, P., and Henin, C., 1992. Sea-surface temperature from coral skeleton strontium/calcium ratio. *Science,* 257:644–647.

Bonatti, E., Lawrence, J.R., Hamlyn, P.R., and Breger, D., 1980. Aragonite from deep sea ultramafic rocks. *Geochim. Cosmochim. Acta,* 44:1207–1214.

Dick, H.J.B., 1989. Abyssal peridotites, very slow spreading ridges and ocean ridge magmatism. *In* Saunders, A.D., and Norry, M.J. (Eds.), *Magmatism in the Ocean Basins.* Geol. Soc. Spec. Publ. London, 42:71–105.

Gillis, K., Mével, C., Allan, J., et al., 1993. *Proc. ODP, Init. Repts.,* 147: College Station, TX (Ocean Drilling Program).

Hart, S.R., Blusztajn, J., Dick, H.J.B., and Lawrence, J.R., 1994. Fluid circulation in the oceanic crust: contrast between volcanic and plutonic regimes. *J. Geophys. Res.,* 99:3163–3174.

Hodell, D.A., Mead, G.A., and Mueller, P.A., 1990. Variation in the strontium isotopic composition of seawater (8 Ma to present): implications for chemical weathering rates and dissolved fluxes to the oceans. *Chem. Geol.,* 80:291–307.

Lawrence, J.R., 1980. Temperatures of formation of calcite veins in the basalts from Deep Sea Drilling Project Holes 417A and 417D. *In* Donnelly, T., Francheteau, J., Bryan, W., Robinson, P., Flower, M., Salisbury, M., et al., *Init. Repts. DSDP,* 51, 52, 53 (Pt. 2): Washington (U.S. Govt. Printing Office), 1183–1184.

Lawrence, J.R., 1991. Stable isotopic composition of pore waters and calcite veins. *In* Weissel, J., Peirce, J., Taylor, E., Alt, J., et al., *Proc. ODP, Sci. Results,* 121: College Station, TX (Ocean Drilling Program), 447–455.

O'Neil, J.R., Clayton, R.N., and Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. *J. Chem. Phys.,* 51:5547–5558.

Silantyev, S., Dick, H.J.B., Bazylev, B., Dmitriev, L.V., Xia, C., Bougalt, H., Rona, P.A., and Blusztajn, J.S., in press. Mantle peridotites, tectonics and hydrothermal activity at 15°20′ fracture zone. *Mar. Geophys. Res.*

Snow, J.E., and France-Lanord, C., 1994. The use of Sr isotopic stratigraphy to date abyssal peridotite alteration. *In* Lanphere, M.A., Dalrymple, G.B., and Turrin, B.D. (Eds.), *Abstracts of ICOG8.* Geol. Surv. Circ. (U.S.), 1107:298.

Staudigel, H., Muehlenbachs, K., Richardson, S.H., and Hart, S.R., 1981. Agents of low temperature ocean crust alteration. *Contrib. Mineral. Petrol.*, 77:150–157.

Tarutani, T., Clayton, R.N., and Mayeda, T.K., 1969. The effect of polymorphism and magnesium substitution on oxygen isotope fractionation between calcium carbonate and water. *Geochim. Cosmochim. Acta*, 33:987–996.

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Table 1. Sr content and Sr, carbon, and oxygen isotopic data of aragonite veins, Site 895.

Hole	Core, section, interval (cm)	Piece	Rock type	Sr content (ppm)	$^{87}Sr/^{86}Sr$ (± 2σ)	$\delta^{13}C$ PDB	$\delta^{18}O$ SMOW	Temp.1 (°C)	Temp.2 (°C)
895A	2R-1, 85–87	14	Harzburgite	8899	0.709164 ± 22	−0.64	35.8	−4.7	0.6
895C	3R-2, 16–19	2	Harzburgite	10496	0.709171 ± 24	1.53	35.28	−2.9	2.4
895D	5R-2, 97–102	14	Harzburgite	14214	0.709181 ± 20	1.67	35.24	−2.8	2.6
895D	7R-2, 90–94	12A	Harzburgite	12801	0.709186 ± 22	1.50	33.92	2.0	7.4
895D	8R-1, 122–126	19	Harzburgite	12532	0.709178 ± 22	2.22	34.47	0.0	5.4
895D	9R-1, 126–129	19	Dunite	12080	0.709185 ± 22	0.60	34.28	0.7	6.1
895E	6R-1, 61–63	11	Dunite	12413	0.709195 ± 22	1.18	35.03	−2.0	3.3
895E	9W-1, 15–17	3	Dunite	9096	0.709136 ± 24	2.60	36.06	−5.6	−0.4

Note: Temp. 1 and Temp. 2 were calculated assuming a vein fluid $\delta^{18}O$ equal to 0‰ and 1.2‰, respectively.

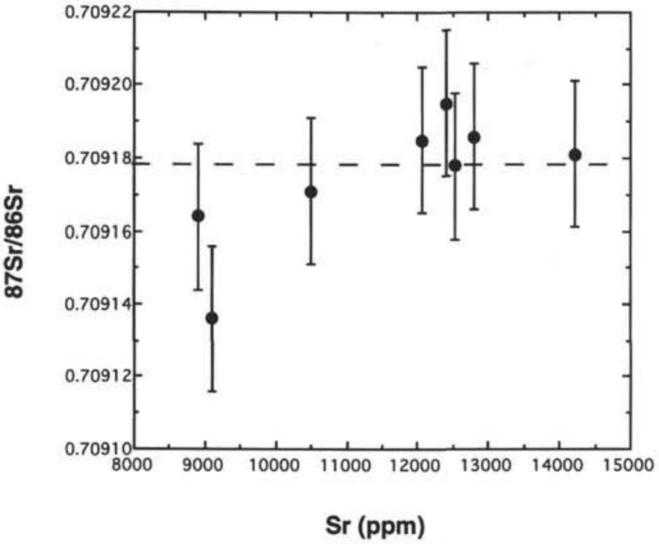

Figure 3. $^{87}Sr/^{86}Sr$ vs. Sr content for aragonite veins, Site 895. The dashed line represents the $^{87}Sr/^{86}Sr$ of present-day seawater (after Hodell et al., 1990). Error bars represent 2σ uncertainties.