OXYGEN ISOTOPE VARIATION IN Ca-Mg CARBONATE CEMENTS IN THE CALIFORNIA COAST RANGE OPHIOLITE: GEOCHEMISTRY OF MARTIAN ANALOG ENVIRONMENTS.

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Introduction: We studied the oxygen isotope geochemistry of fine-scale laminar banding in carbonate cements precipitating in stream beds in highly-serpentinized, ophiolite terrain. From a planetary science perspective, these cements are interesting because they are hosted in mafic and ultramafic rocks, which are abundant on Mars. In addition, the cements of our study are in contact with seasonal, freshwater microbial mats. Of particular interest is whether we can distinguish a biological signature in the cements, which would be preserved in the rock record. This work is part of a larger project to characterize microbial ecosystems associated with ophiolites as possible analogs for Mars.

Field Area: Our field area is located within the Del Puerto Ophiolite, approximately 100 km SE of San Francisco. The ophiolite is part of the California Coast Range and is Cretaceous in age [1]. High-pH waters from this setting were interpreted previously to represent active serpentinization [2]. We collected rock, water, and microbial samples from the drainage area within a few hundred meters of Adobe Springs, located near the confluence of Del Puerto and Adobe Creeks. Water emanating from Adobe Springs has interacted with serpentinized ultramafic rocks to yield alkaline fluids (pH > 8.3) high in Mg (~120 mg/L) and bicarbonate (> 400 mg/L) [3]. During the dry summer months, the only flows in this region are those fed by the springs, and surface flow is intermittent. Carbonate cements line the creek beds, producing a conglomerate with clasts that range from submillimeter-sized grains to pebbles several cm in diameter. The site supports unusual microbial communities, including seasonal microbial mats that form in direct contact with the carbonates; these microbial communities are the focus of a companion investigation.

Petrography and EMP analysis: Several dozen thin sections were made from representative carbonate samples collected from within a few meters of the active stream beds. Sections were impregnated in epoxy in order to retain their integrity, polished, then examined petrographically. The sections revealed complex mineralogy. Clasts consisted of highly-altered mafic and ultramafic as well as metasedimentary rock fragments, all of which exhibited multiple, cross-cutting fractures and in-filling. At least three kinds of carbonate cements were present: (1) fine-scale (few to tens of micron-wide bands) laminae, (2) massive zones continuous for up to several mm with variable textures; and (3) equigranular teeth-like grains present in sub-mm-sized pore spaces, a texture typical of phreatic calcite. Electron microprobe (EMP) analyses of the cements were conducted using methods described in [4]. XRD and STEM analyses of carbonates from this and similar locations [5] indicate that the samples are calcian dolomites (protodolomites) and magnesian calcites. Analytical measurements were conducted on a 10x10 micron square raster. Probe analyses were made on each of the three different cements and revealed compositions ranging from the dolomite to calcite endmembers. Additional measurements were made immediately adjacent to each ion probe transect point.

Carbonate Oxygen Isotope Analysis using SIMS: Here we focus on results obtained from a single section of carbonate laminae, found adjacent to a conglomerate clast (Fig.1).

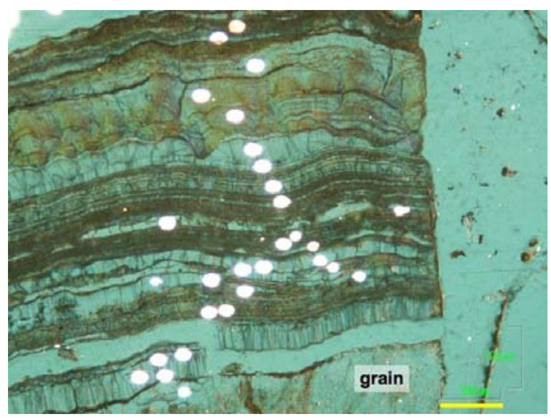

Fig. 1. Photomicrograph of sample in transmitted light, illustrating fine-scale Mg-Ca carbonate laminae deposited outward from a serpentinized clast. Transect points (in white) were created by the SIMS beam. The polished sample surface was coated with a thin layer of gold prior to analysis; gold in and adjacent to the analysis was sputtered during analysis, leaving gold-free regions wider than their corresponding pits (here, the pits are ~8 or ~15 microns) in the sample. Yellow scale bar represents 100 microns; width of cement section is ~ 550 microns.

In-situ oxygen isotopic measurements were made using the CAMECA1280 SIMS at the University of Wisconsin. The Cs^+ ion beam was focused to two different diameters: ~15 microns and ~8 microns. Secondary ^{16}O and ^{18}O ions were analyzed simultaneously by multiple Faraday cup detectors (see, Kita et al., this meeting). Analyses of laboratory calcite and dolomite standards were used to calibrate instrument matrix effects. All sample analyses were bracketed by calcite standards, which indicate measurement precision of ~0.2‰ (1σ) for the 15 micron spot sizes and ~0.3‰ for the 8 micron spots. An instrumental isotopic correction factor corresponding to the Ca mole fraction of the carbonate (determined by EMP) was applied to the measured values to determine the actual oxygen isotopic composition vs. VSMOW [6].

Results: The most dolomitic samples have $\delta^{18}O$ values similar to those reported for a bulk cement analysis [2] from the same location (Fig. 2). The dolomitic material (Ca# <0.6) records the entire range of observed variation in $\delta^{18}O$, 3.7‰, whereas the variation observed among samples with 0.6 < Ca# < 0.8 is significantly less (1.7‰). In general, the more Ca-rich samples have lower $\delta^{18}O$ values.

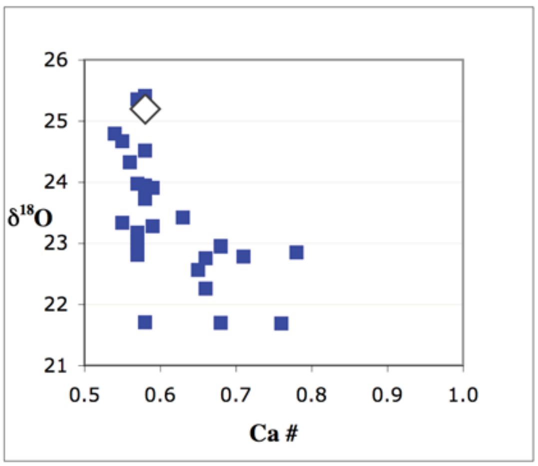

Fig. 2. Correlation between $\delta^{18}O_{VSMOW}$ and Ca#, the mole fraction of Ca in the Ca-Mg carbonate. Data for bulk carbonate cement sample from the same location [2] are included for comparison (diamond).

The $\delta^{18}O$ values of the carbonates decrease with increased distance from the clast boundary, though the trend defines a band rather than a simple line (Fig. 3a). Moving away from the clast, laminae within the first 350 microns are dolomitic; there is a larger variation in Ca# after this point. Multiple measurements within the single carbonate lamina (directly adjacent to the grain) reveal a systematic $\delta^{18}O$ variation of 1.2‰ over a ~30 micron transect, while the corresponding Ca# is approximately constant (Fig. 3b).

Using the end-member water temperatures measured in the creek water during the past year (13.3° and 29.2°C) and the composition-dependent O-isotope fractionation factor determined by [2], we calculated $\delta^{18}O$ values for the creek water that bracket an average value reported for the area (-7.3‰) [2].

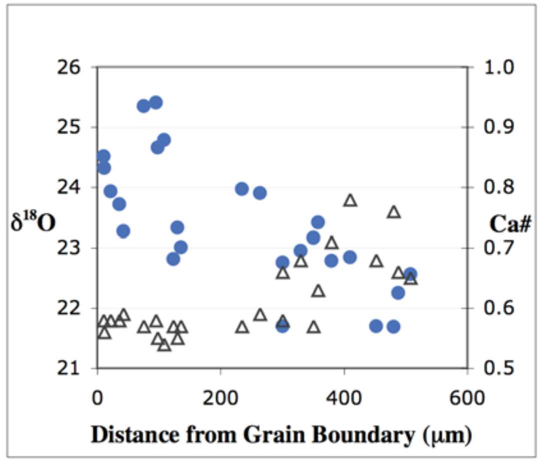

Fig. 3a. Variation in $\delta^{18}O_{VSMOW}$ values (circles) and Ca# (triangles) as a function of distance from the clast boundary.

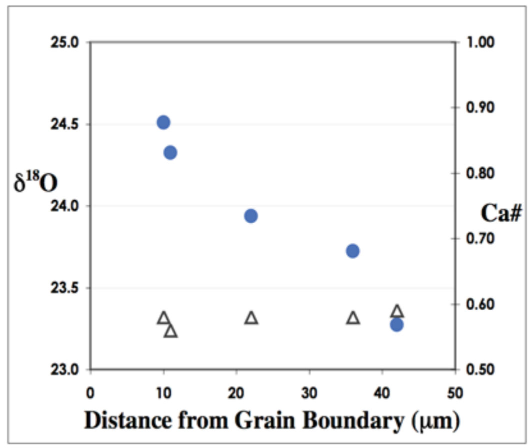

Fig. 3b. Variation in $\delta^{18}O_{VSMOW}$ values and Ca# within a single carbonate lamina, symbols denoted in 3a caption.

Conclusions: Several processes can influence the observed variations in $\delta^{18}O$ values and Ca# of the carbonate cements examined in this study. Seasonal variations (temperature, rainfall, and evaporation) will influence the carbonate chemistry as well as the precipitation rate of the cement and can be modeled. The effect of microbial activity on the cement formation is less well understood but should produce deviations from the isotopic correlations predicted for inorganic processes. The relative influence of these factors will be discussed within the context of our data.

References: [1] Shervais et al. (2005) *GSA Bull.* 117, 633-653; [2] Barnes I. and O'Neil J.R. (1971) *Geochim. Cosmochim. Acta* 35, 699-718; [3] Mason, P., *www.mgwaters.com*; [4] Lane S.J. and Dalton J.A (1994) *Amer. Mineral.* 79, 745-749; [5] Blake, D.F. and Peacor, D.R. (1985) *Amer. Mineral.* 70, 388-394; [6] Valley, J.W. et al. (1997) *Science* 275, 1633-68.