# An Alkaline Spring System within the Del Puerto Ophiolite (California USA): A Mars Analog Site

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Key words: Mars analog, dolomite, alkaline springs, biosignature

## Abstract

Mars appears to have experienced little compositional differentiation of primitive lithosphere, and thus much of the surface of Mars is covered by mafic lavas. On Earth, mafic and ultramafic rocks present in ophiolites, oceanic crust and upper mantle that have been obducted onto land, are therefore good analogs for Mars. The characteristic mineralogy, aqueous geochemistry, and microbial communities of cold-water alkaline springs associated with these mafic and ultramafic rocks represent a particularly

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compelling analog for potential life-bearing systems. Serpentinization, the reaction of water with mafic minerals such as olivine and pyroxene, yields fluids with unusual chemistry (Mg-OH and Ca-OH waters with pH values up to ~12), as well as heat and hydrogen gas that can sustain subsurface, chemosynthetic ecosystems. The recent observation of seeps from pole-facing crater and canyon walls in the higher Martian latitudes supports the hypothesis that even present conditions might allow for a rock-hosted chemosynthetic biosphere in near-surface regions of the Martian crust. The generation of methane within a zone of active serpentinization, through either abiogenic or biogenic processes, could account for the presence of methane detected in the Martian atmosphere. For all of these reasons, studies of terrestrial alkaline springs associated with mafic and ultramafic rocks are particularly timely. This study focuses on the alkaline Adobe Springs, emanating from mafic and ultramafic rocks of the California Coast Range, where a community of novel bacteria is associated with the precipitation of Mg-Ca carbonate cements. The carbonates may serve as a biosignature that could be used in the search for evidence of life on Mars.

## 1. Introduction

A critical challenge facing the search for life in the solar system is the identification of unambiguous evidence of life (cf., Beaty et al., 2005). The presence of microbial life on Earth or an extraterrestrial planet does not ensure our ability to detect it. Evidence of life must be distinctive from a landscape created by abiotic processes (cf., Dietrich and Perron, 2006). The presence of water is deemed to be one of the key requirements for identifying an environment capable of hosting life on Mars (e.g., Knoll and Grotzinger, 2006). The goal of this study is to identify possible biosignatures from a Martian analog environment, namely, alkaline springs associated with ophiolites, sections of ocean crust and upper mantle that have been obducted onto continental crust, experiencing varying degrees of hydrothermal alteration in the process.

Serpentinization, the reaction of water with olivine- and pyroxene-rich rocks common in mafic and ultramafic rocks to form serpentine, also produces heat and hydrogen gas that can sustain subsurface, chemosynthetic ecosystems, and also results in the formation of Mg-rich alkaline fluids. These fluids, when mixed with seawater (as seen at Lost City; Kelley et al., 2005) or emanating as surface waters (e.g., as described comprehensively by Pentecost, 2005) can produce substantial volumes of secondary carbonate deposits (e.g., Surour and Arafa, 1997). Alkaline springs associated with mafic and ultramafic rocks are model settings in which to identify possible mechanisms of biosignature formation because these compositions of rocks have persisted throughout all of the Earth's history. More importantly, low-temperature aqueous alteration processes (such as serpentinization) associated with mafic and ultramafic rocks on Earth are thought to be geologically similar to those occurring on Mars (e.g., Boston et al., 1992; Ming et al., 2006; Wyatt and McSween, 2006).

### *1.1 Mafic and ultramafic rocks as analog settings for early Earth, early Mars, and other rocky planets*

Interaction between reducing rocks (e.g., unweathered basalts and ultramafic rocks) and water results in an exothermic reaction that also produces hydrogen and methane, both potential energy sources for chemosynthetic microorganisms (Kelley et al., 2005; Sleep et al., 2004). Unfortunately, more detailed characterization of these systems is often limited by their relative inaccessibility - whether in the deep-sea hydrothermal environments or deep within the continental crust. More accessible systems are offered by ophiolite terranes, sections of oceanic crust and upper mantle that have been obducted onto land and which include both basaltic and ultramafic rocks. Similar rock types are (and were) abundant on planetary bodies - the crusts of differentiated bodies (such as Earth, Mars, Venus, and 4 Vesta) contain basaltic and ultramafic rock, and most undifferentiated bodies (chondritic asteroids) are composed entirely of ultramafic rocks.

The serpentinization of mafic and ultramafic rocks can provide reduced substrates suitable for microbial growth, and can yield secondary phases that may act as a preservation medium for microbial organisms and their biosignatures (Fisk and Giovannoni, 1999). The liberation of $H_2$ in these systems by mineral-water interaction may be partially self-sustaining, given that a volume increase of as much as 60% during serpentinization (Shervais et al., 2005a) creates the potential for mechanical fracturing, which continually exposes new, unreacted mineral surfaces to water and, potentially, organisms. Such an environment can persist for long periods, as the heat generated by serpentinization has been shown to be sufficient to drive hydrothermal circulation of highly reducing fluids over tens of thousands of years (Früh-Green et al., 2003).

On the early Earth, mafic and ultramafic rocks occurring in oceanic-type crust were abundant, but little of this ancient crust remains today in a form that has not been highly altered. Where present, obducted mafic and ultramafic rocks associated with ophiolite terranes may represent an excellent terrestrial analog to Martian geology, since identified Martian meteorites are either basalts or ultramafic rocks (e.g., Singer and McSween, 1993), and recent mapping of the Mars surface has revealed the dominance of mafic rocks (Christensen et al., 2005). Any aqueous alteration of the Martian surface would thus involve interaction with mafic and ultramafic rocks. This hypothesis is supported by evidence from Martian meteorites, in which the predominant style of aqueous alteration is that of olivine to phyllosilicates (Newsom et al., 2001; Treiman and Goodrich, 2002; Leshin and Vicenzi, 2006), and to carbonates (Treiman and Romanek, 1998; Leshin et al., 1998; Eiler et al., 2002), analogous to serpentinization of ophiolites. Additionally, the recent discovery of hematite at the Meridiani Planum on Mars (Squyres et al., 2004a, b) and quartz veinlets in eucrite meteorites (Treiman et al., 2004) and in a Mars meteorite (Valley et al., 1997) are indicative of a history of aqueous alteration and activity on the surface of Mars and other planetary bodies (e.g., asteroids). The generation of methane within a zone of active serpentinization on Mars (through either abiogenic or biogenic processes) could account for the presence of methane detected in the Martian atmosphere (Formisano et al., 2004). Although currently Earth is the only planet we know of where liquid water is stable at the surface, models based on recent satellite and Mars rover observations of aeolian and fluvial sediments (e.g., Baker, 2006; Andrews-Hanna et al., 2007) conclude that water was once present at the Martian surface, implying that both surface and subsurface environments could have undergone serpentinization reactions, and potentially supported life. While carbonates have not been identified on the surface of Mars to date (although their presence is suggested by early returns from the Phoenix Mars Lander), and recent detection of jarosite and other sulfate minerals hints that portions of the surface of Mars are acidic today (Squyres and Knoll, 2005; Squyres et al., 2006), carbonates may have been present at the surface of Mars early in this planet's history (e.g., Treiman, 1998: Treiman and Romanek, 1998; Eiler et al., 2002), when more widespread fluvial activity occurred (e.g., McEwan et al., 2007).

The continental borderland of California contains numerous ophiolite blocks of similar age, ranging from ~172–164 Ma (Shervais et al., 2005b). Groundwaters circulating within a number of ophiolite bodies found in the California Coast Range have reacted, and continue to react, with the ultramafic rocks to yield cold springs with unusual chemistry (Mg-OH and Ca-OH waters with pH values up to ~12; e.g., Barnes and O'Neil, 1971). Schulte et al. (2006) describe the petrology and mineral chemistry of the ophiolite-hosted Complexion Spring (pH ~ 12), and have proposed criteria for identifying serpentinized mafic rocks on Mars that may sustain chemosynthetic life. While such waters can support a significant microbial load (Sleep et al., 2004), the springs and their associated carbonate cements have not been studied in the context of biosignature formation. The characteristic mineralogy and aqueous geochemistry of ophiolite-hosted alkaline springs suggest that they may represent a particularly compelling analog for potential life-bearing systems on early or modern Mars, and on the early Earth. For all of these reasons, studies of terrestrial ophiolite-hosted alkaline springs and their associated biota and secondary minerals are particularly timely.

### *1.2 Del Puerto Ophiolite, California Coast Range*

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 Jurassic in age (Evarts et al., 1992; Shervais et al., 2005b). The area is marked by rugged, sparsely vegetated terrain, and outcrops exhibit extensive hydrothermal alteration (Evarts and Schiffman, 1983). The ophiolite has been mapped as three distinct rock units: a basal alpine peridotite member, a middle plutonic member, and an upper volcanic member (Evarts, 1977). The study area and surrounding drainage system is hosted within the peridotite body. Del Puerto Creek, the principal drainage for this region, flows eastward toward the San Joaquin Valley. Adobe Springs are low-flow-rate features that discharge into Adobe Creek, a tributary of Del Puerto Creek. The water in the creeks is a mixture of seasonal surface run-off and local spring water.

Previously, two distinct alkaline water compositions were identified at the Adobe Spring site: a high-pH (~12) Ca-OH water interpreted by Barnes et al. (1967) as evidence of active serpentinization, and an alkaline (pH ~9) Mg-OH water interpreted to be a mixture of ultramafic-derived and meteoric waters (Barnes and O'Neil, 1971). Barnes and O'Neil (1971), O'Neil and Barnes (1971), and Blake and Peacor (1985) noted the presence of calcite and dolomite cements in the drainages where these alkaline waters occur.

The high pH Ca-OH springs reported by Barnes et al. (1967) are no longer active at the Adobe Springs site. However, the Mg-OH waters, which emanate from Adobe Springs and are also present in the Del Puerto Creek and Adobe Creek drainages, appear to be the source of the carbonate cements that line the drainages. A well drilled into the hillside adjacent to Adobe Springs also produces moderately alkaline Mg-OH water, which is bottled and sold for its reputed medicinal benefits (www.mgwater.com).

Initial research at this site has focused on characterizing and understanding the micron-scale mineral, morphological and/or stable isotopic biosignatures in carbonate cements associated with ophiolite-hosted alkaline springs. Detection of diagnostic biosignatures would serve to suggest technologies or methodologies most useful for identifying past or presently habitable zones on Mars during flight or sample-return missions. In addition, characterization of the link between precipitating carbonate cements and microbial activity within an ophiolitic terrain increases our understanding of the phylogeny and physiology of microorganisms, including extremophiles, whose characteristics may reflect the nature of primitive environments.

## 2. Methods

Water, rock, and microbial samples were collected in 2006 and 2007 from the drainage area within a few hundred meters of Adobe Springs, near the confluence of Del Puerto and Adobe Creeks (Figure 1). Water samples were periodically collected at three sample sites near the confluence of the Del Puerto and Adobe Creeks: (1) Del Puerto Creek (the main drainage within the Del Puerto Ophiolite), (2) Adobe Creek (a tributary of Del Puerto Creek), which has intermittent flow, and (3) Adobe Springs well water (Figure 1). Field measurements of pH and water temperature were recorded. Water samples were filtered using a 0.45 micron filter and were kept cold prior to analysis. Water chemistry analyses were performed by BC Laboratories (Bakersfield CA). Oxygen and hydrogen isotopic analyses were conducted by the UC Berkeley Laboratory for Environmental and Sedimentary Geochemistry. SOLVEQ (Reed, 1982), a computer program developed to compute aqueous-mineral-gas equilibria, was used to determine mineral saturation indices using measured Mg-OH water compositions.

Carbonate samples were collected at the two creek sites (Figures 1 and 2) for petrographic and chemical analysis. Petrographic characterization of the cements was conducted at Lawrence Berkeley National Laboratory. Selected carbonate samples were analyzed for major and trace elements using an electron microprobe (EMP) at NASA/Johnston Space Center. SEM images were collected at NASA/Ames and NASA/JSC. Analysis of O-isotope variations in the cements on a microscopic scale was conducted using a Secondary Ion Mass Spectrometry (SIMS) CAMECA ims-1280 instrument at the University of Wisconsin (Kita et al., 2007; Page et al., 2007; Blank et al., 2007; Bowman et al., 2008). Instrumental bias of SIMS analysis is corrected by the measurements of calcite and dolomite isotope standards and the spot to spot precision of these in situ analyses is typically 0.3‰. (2σ).

A variety of water samples (well water, Adobe and Del Puerto Creek waters) and microbial mat and sediment samples were collected for biologic characterization.

Genomic DNA was extracted from water samples using a commercial DNA extraction procedure (Mo Bio Laboratories, Carlsbad, CA) after an initial filtration of the water through a 0.2 micron filter. DNA was extracted from microbial mat and sediment samples using a modified bead-beating method developed and tested in our laboratory (Green et al., 2008). Samples were PCR-amplified with a variety of primer sets targeted to ribosomal RNA (rRNA) genes of bacteria and Archaea, as well as functional genes for sulfate-reducing prokaryotes (dissimilatory sulfite reductase, *dsrAB*) (Muyzer et al., 1993; Muzyer and Smalla, 1998; Casamayor et al., 2002; Geets et al., 2006) and methanogens (Methyl Coenzyme M Reductase A, *mcrA*) (Luton et al. 2002). Bacterial and cyanobacterial primer sets (Muzyer et al., 1993; Muzyer and Smalla, 1998; Nubel et al., 1997) were utilized for rapid community structure analysis using denaturing gradient gel electrophoresis (DGGE).

## 3. Results

### *Water chemistry*

As noted earlier, the highly alkaline (pH ~12) Ca-OH springs described by Barnes et al. (1967) are no longer active, so sampling was confined to the Mg-OH alkaline waters found in the well, springs, and creeks near Adobe Springs. During the dry summer months, the only flows in this region are those fed by springs, and surface flow is intermittent. Geochemical results of analyses of water samples collected from the Adobe Creek well and Del Puerto Creek are presented in Table 1. Calculated log (Q/K) values for disordered dolomite (1.76 and 2.30) and calcite (0.27 and 0.61) for the Adobe Creek well water and Del Puerto Creek water, respectively, are positive, indicating that the Mg-OH waters are supersaturated with respect to these carbonate phases. However, previous studies have noted that precipitation of dolomite under ambient conditions is inhibited by kinetic factors (e.g., Land, 1998).

### *Carbonate Cements*

Carbonate cements line the creek beds, producing a conglomerate with clasts of carbonate and fragments of eroded peridotite that range from sub-millimeter to tens-of-cm in size. Initial investigations of the carbonate cements (Blank et al., 2006) have revealed at least three distinct cement textures: laminated cements, massive or hummocky cements, and dentate calcite crystals lining open pore space. Electron microprobe analysis (Figure 3) indicates that the carbonates range in composition from dolomite to calcite.

We detected $\delta^{18}O$ compositions for laminated carbonate ranging from 19.8–25.4 ‰$_{VSMOW}$ over a ~500 μm transect perpendicular to a serpentinite fragment grain boundary (Figure 4). For these samples, $\delta^{18}O$ values generally increase with increasing Mg content in the carbonates, consistent with the observation by Tarutani et al (1969) that magnesian calcites have a larger isotope fractionation relative to water than pure calcite. The range in isotopic composition is consistent with compositions ($\delta^{18}O$ = 23.9–25.2 ‰) for 3 bulk Ca-Mg carbonate samples from Del Puerto Creek reported by Barnes and O’Neil (1971). These bulk samples also exhibited a similar positive correlation between Mg content and oxygen isotopic composition. We also observed variations in $\delta^{18}O$ values along-strike within individual bands, with a variation of 1.2 ‰ encountered within a single ~50 µm-thick dolomite band. This within band variability is significantly larger than analytical uncertainty and attests to the heterogeneous environment of carbonate deposition. Using the measured oxygen isotopic compositions and temperatures of the sampled waters and dolomite-water and calcite-water oxygen isotope fractionation curves for both abiotic and biotic systems (Tarutani et al., 1969; Schmidt et al., 2005; Vasconcelos et al., 2005; O'Neil et al., 1969; Horita and Clayton, 2007), dolomite $\delta^{18}O$ values ranging from 24.3 to 26.6‰ and calcite $\delta^{18}O$ values ranging from 21.3 to 22.3‰ were calculated (Table 2). The dolomite $\delta^{18}O$ values determined using the microbially mediated fractionation factor of Vasconcelos et al. (2005) are 0.4 to 1.8‰ lower than those calculated using the abiogenic fractionation factors of Tarutani et al. (1969) and Schmidt et al. (2005). There is close agreement between the calcite isotopic compositions calculated using O'Neil et al. (1969) (as modified in Friedman and O'Neil, 1977) and Horita and Clayton (2007). In general, the dolomite $\delta^{18}O$ values calculated using the Vasconcelos fractionation equation more closely match the measured $\delta^{18}O$ values obtained for the dolomitic portions of the laminated carbonates, suggesting that dolomite precipitation at Adobe Springs was microbially mediated.

### *Microbial Communities*

A small-scale analysis of the microbiology of ophiolite-hosted waters was conducted during the summers of 2006 and 2007. All water samples had a pH of approximately 9, as did the water overlying the microbial mats. At the Adobe Springs field site, there are a variety of different photosynthetically driven microbial communities, ranging from laminated microbial mats to amorphous algal conglomerates, or periphyton (Figure 2). Because of the ephemeral, and presumably seasonal, presence of these photosynthetic communities, we have not yet ascertained their relationship to the deposition of the Ca-Mg carbonate cements. However, the presence of laminated microbial mats in this alkaline environment is a peculiar phenomenon that merits further investigation.

A clone library of approximately 150 16S rRNA gene sequences was generated from three distinct microbial mat layers as well as water overlying the mat, from nearby water wells, and from Del Puerto Creek water. The microbial mat clone library, composed of 75 sequences, reveals a diverse microbial community dominated by Cyanobacteria (40%), Proteobacteria (27%), Bacteroidetes (13%) and Firmicutes (11%). Most of the cyanobacterial sequences belong to two novel lineages of cyanobacteria, a finding confirmed by the recovery of near full length rRNA gene sequences (Genbank accession numbers EU255702-EU255722; www.ncbi.nih.gov**)**. These cyanobacterial sequences belong to the order Oscillatoriales (filamentous, nonheterocystous cyanobacteria) and are most similar to cyanobacterial sequences detected other in freshwater or brackish microbial mats.

The most abundant bacterial phylum detected in the clone library generated from the water samples is the phylum Bacteroidetes. In the Del Puerto Creek water, the microbial community is dominated by a single species of Bacteroidetes (13 sequences of 29 total) most closely related to the organism *Chimaereicella alkaliphila*, a species isolated from a highly alkaline (pH 11.4) groundwater environment (Tiago et al., 2006). We have also detected the presence of Archaea (including methanogens) and sulfate-reducing prokaryotes in the mats and from well water from Adobe Springs by PCR with rRNA gene and *dsrAB* gene primer sets, though these organisms have not yet been identified via sequence analysis. Many of the methanogens, detected with archaeal 16S rRNA gene primers and with *mcrA* gene primers, are closely related to the *Methanobacterium alcaliphilum* strain DSM3387, an alkaliphilic hydrogen-consuming ($H_2/CO_2$) methanogen from a deep coal seam groundwater sample with a pH of ~8.4 (**DQ649335**). The putative identification of alkaliphilic organisms in the Del Puerto Creek and cultivation analyses of cyanobacteria from the microbial mats suggest that the elevated pH in this environment most likely exerts a selective influence on the composition of the microbial communities.

## 4. Discussion

There is an extensive literature demonstrating that the presence and activity of microbial populations are critical to the precipitation of carbonates, particularly magnesium-rich carbonates, such as dolomite (e.g., Vasconcelos et al., 1995; Wright, 1999; Warthmann et al., 2000; Barton et al., 2001; van Lith et al., 2003; Roberts et al., 2004; Altermann et al., 2006). Microbial involvement in carbonate precipitation has been demonstrated for stratified, laminated structures such as stromatolites (Dupraz and Visscher, 2005), and these structures, generally composed of limestone or dolomite, have been found in the sedimentary record dating back almost 3.5 billion years (Awramik, 1984; Altermann et al. 2006). The best-studied environments for production of stromatolites are marine or hypersaline environments. Although such systems have relatively high concentrations of sulfate, which generally inhibits the precipitation of dolomite (Baker and Kastner, 1981), dolomite or Mg-rich carbonates can be precipitated under appropriate environmental conditions. Microorganisms can provide the conditions required for precipitation of carbonates: elevated pH (photosynthesis and anaerobic respiration), elevated dissolved inorganic carbon (respiration), and nucleation sites from extracellular polymeric substances (EPS), or degradation of EPS resulting in the release of cations (Dupraz and Visscher, 2005). However, microbial activities may also inhibit the precipitation of carbonates, by cation capture by EPS, consumption of DIC, and acidification (sulfide oxidation) (Barron et al., 2006; Dupraz et al., 2004; Dupraz and Visscher, 2005; Hartley et al., 1996). In marine environments, the key microbial functions involved in the precipitation of carbonates appear to be photosynthesis and anaerobic heterotrophic oxidation of organic matter, generally coupled to sulfate reduction (cf., Visscher et al., 1998; Wright and Altermann, 2000; Visscher et al., 2000; Visscher and Stolz, 2005; Altermann et al., 2006).

In alkaline, hypersaline lakes in South Australia, the heightened activity of sulfate-reducing bacteria (SRB) during seasonal evaporation events was correlated with the precipitation of dolomite (Wright, 1999). Carbonate deposits can also occur under freshwater conditions, and have been observed in association with alkaline springs emanating from altered ophiolites (Barnes and O'Neil, 1971). While cyanobacterial activity has been implicated for some freshwater carbonate deposits (e.g. Freytet and Verrecchia, 1998; Merz-Preiss and Riding, 1999), the association of microbial activity with carbonates precipitating in ophiolite environments has not been studied in detail. However, in our initial characterization of the Adobe Creek locality, identified populations of alkaliphilic organisms in the Del Puerto Creek and cyanobacteria from the microbial mats are similar in nature to the types of organisms encountered in stromatolite ecosystems, which are closely linked to biological precipitation of carbonates. The good match between $\delta^{18}O$ values calculated using the microbially mediated isotopic fractionation equation of Vasconcelos (2005) and measured $\delta^{18}O$ values from the laminated carbonates supports the idea that precipitation of dolomites at Adobe Springs under ambient temperature conditions (18–24°C) is facilitated by the presence of the alkaliphilic microbial community.

## 5. Conclusions

The process of serpentinization of mafic and ultramafic rocks produces Mg-rich alkaline waters, which are associated with Mg-Ca carbonate cements and unusual microbial communities. The process of serpentinization can generate methane and hydrogen, two potential sources of energy for chemosynthetic organisms. Such a setting (where water is in contact with mafic and ultramafic rocks) may serve as a good analog for similar environments on Mars that may be capable of supporting life.

We have focused our initial investigation on three critical components of the Adobe Springs system:  1) the chemistry of the alkaline waters emanating from mafic and ultramafic rocks; 2) the types and compositions of actively precipitating carbonate cements found lining the adjacent creek drainages, and; 3) the novel microbial communities associated with the alkaline waters and carbonate cements.  The deposition of dolomite cements from these low temperature cements may require microbial mediation, which would thus represent a biosignature of this particular biogeochemical environment.

Additional work is needed to confirm the hypothesis that serpentinite-associated carbonate cements can be a biosignature.  One possible approach would be to examine the stable isotope composition of carbon in the cements to ascertain whether they contain a biogenic signature (e.g., García del Cura et al., 2001; Peckman et al., 1999; Cavagna et al., 1999).  Laboratory precipitation experiments conducted using sterilized stream fluids with and without microbial cultures selected from those identified in the alkaline waters may also provide information on the possible role that biomineralization may play in the generation of the carbonate cements, in particular, the dolomite. If such a link can be demonstrated, then dolomite precipitation in hydrothermally altered mafic and ultramafic rocks could be used as a biomarker on Mars and other planets.

## Acknowledgments

Financial support for our work at Adobe Springs came from the NASA Astrobiology Institute Grant ("Linking Our Origins to Our Future", P.I. David Des Marais, NASA/Ames Research Center) and a sub-contract to the SETI Institute (Cooperative Agreement NNA06CB35A). Additional financial support came from the NASA Postdoctoral Program, managed by Oak Ridge Associated Universities. Support to P. Dobson at Lawrence Berkeley National Laboratory was provided under Contract No. DE-AC02-05CH11231 with the U.S. Department of Energy. Wisc-SIMS, the Wisconsin SIMS Laboratory, is partially funded by NSF-EAR (0319230, 0509639, 0744079), DOE (93ER14389), and the NASA Astrobiology Institute.

This work was a natural outgrowth of a related project conducted by Professor Mitch Schulte (U. Missouri) and Dr. Dave Blake (NASA/Ames) and funded by NASA's Exobiology Program. We thank Dr. Robert Coleman for his suggestion to explore the site at Adobe Springs and for sharing his knowledge of the Del Puerto Ophiolite. We thank Bill Evans and Bob Mariner and other members of the Hydrology Branch of the U.S. Geological Survey, Menlo Park, CA, for discussions concerning California spring chemistry. Bob Mariner shared the field notebook of the late Ivan Barnes, who studied the waters at Adobe Springs extensively in the 1960's. We thank our colleagues Kendra Turk and Mike Kubo (SETI Institute) and Alaina Brinley (National Science Foundation Research Experience for Undergraduates Grant to the SETI Institute, P.I. Cynthia Phillips) for laboratory and field assistance. We appreciate the assistance of Linda L. Jahnke in visual characterization of cyanobacterial isolates from the microbial mats. We also wish to thank Paul Mason (Mgwaters.com) for granting permission to conduct this work on his property and for his enthusiastic support of this project. We thank Gian

Gabriele Ori, Goro Komatsu, and an anonymous reviewer for their constructive reviews of this paper.

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## Figure Captions

**Figure 1.** Field site showing locations of the three sampling sites (indicated by the push pin icons) associated with alkaline waters in the Del Puerto Ophiolite, CA: **DP6**, at the Del Puerto Creek, **Adobe Springs Well**, and **AC6**, at Adobe Creek, a tributary of Del Puerto Creek. Figure made using GoogleEarth.

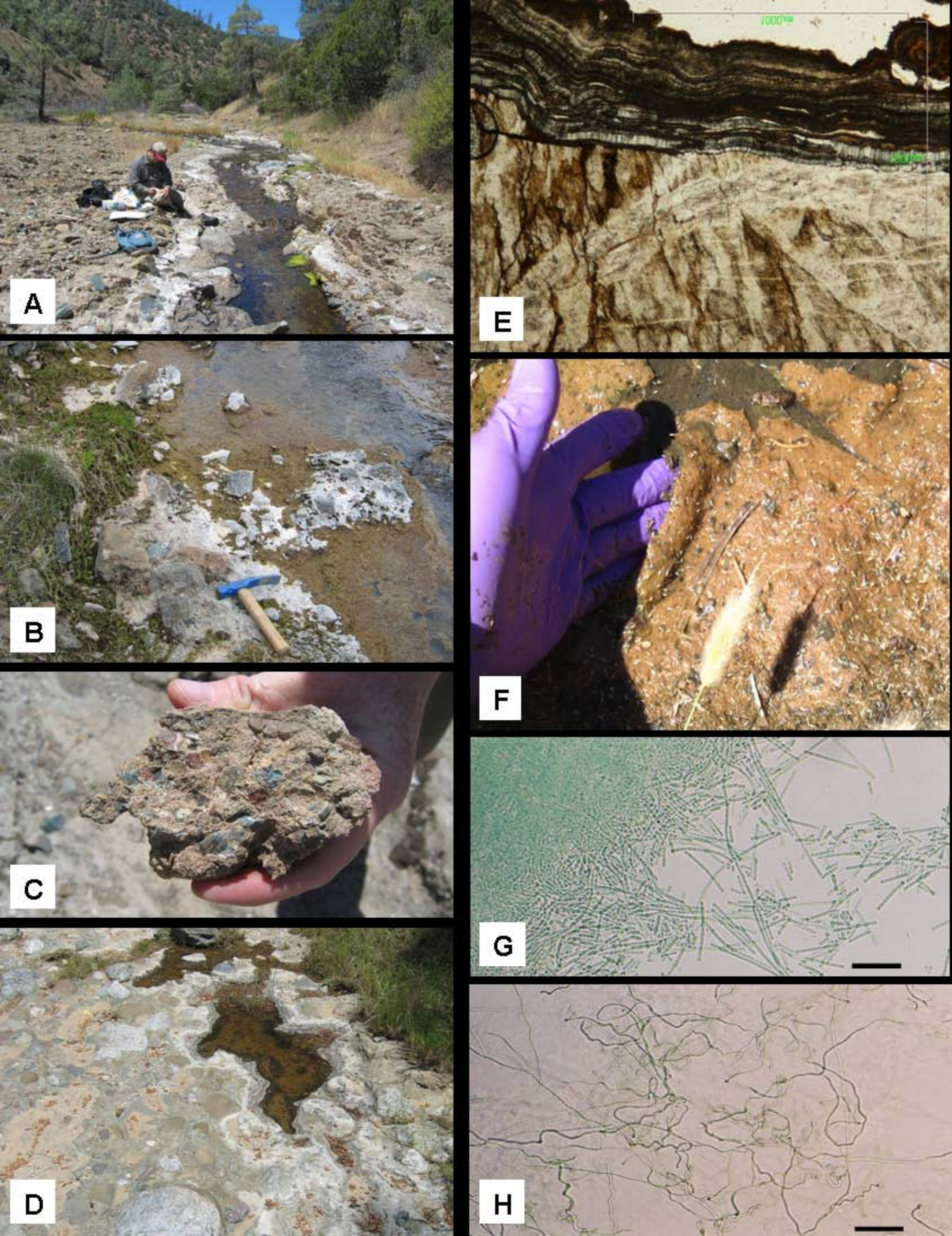
**Figure 2. (A-H)** Photographs of carbonate cements and microbial communities from the Adobe Springs sampling sites, April-June 2006. **(A)** Del Puerto Creek (DPC) and **(B)** Adobe Creek, June 2006, showing carbonate cements and microbial biomass (periphyton). **(C)** Hand sample of DPC carbonate cement. **(D)** DPC, 10 miles downstream of sampling site, parallel to the year-round main creek flow. **(E)** Thin section of serpentine grain bordered by banded carbonate from DPC. White scale bar indicates 1 mm (horizontal and vertical). **(F)** Thin, laminated microbial mat underlain by anaerobic mud (AC6). **(G)** *Leptolyngbya*-like and **(H)** *Arthrospira*-like cyanobacteria recovered from microbial mat samples. Scale bars indicate 30 μm.

**Figure 3.** Mole fraction of major cations of carbonate cement from Del Puerto Creek, as determined from electron microprobe analysis.

**Figure 4.** Results of EMP and SIMS analysis of a banded cement from the Del Puerto Creek. (A) Photomicrograph of sample in transmitted light, illustrating fine-scale Mg-Ca carbonate laminae deposited outward from a serpentinized clast. In-situ oxygen

isotopic measurements were made using a CAMECA ims-1280 SIMS at the University of Wisconsin; 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 pits was sputtered during analysis, leaving gold-free regions wider than their corresponding pits (here, the pits are ~8 or ~15 microns diameter) in the sample. Yellow scale bar represents 100 µm; width of cement section is ~ 550 µm. (B) Variation in $\delta^{18}O$ and Ca# (the mole fraction of Ca/(Ca + Mg) as a function of distance from the serpentine grain boundary.


DP 6
N
Del Puerto Creek
Adobe Creek
Adobe Springs Well
AC 6
500 m
Image © 2008 DigitalGlobe
©2008
Google
37°24'24.96" N 121°24'34.12" W
Nov 23, 2004
Eye alt 1.61 km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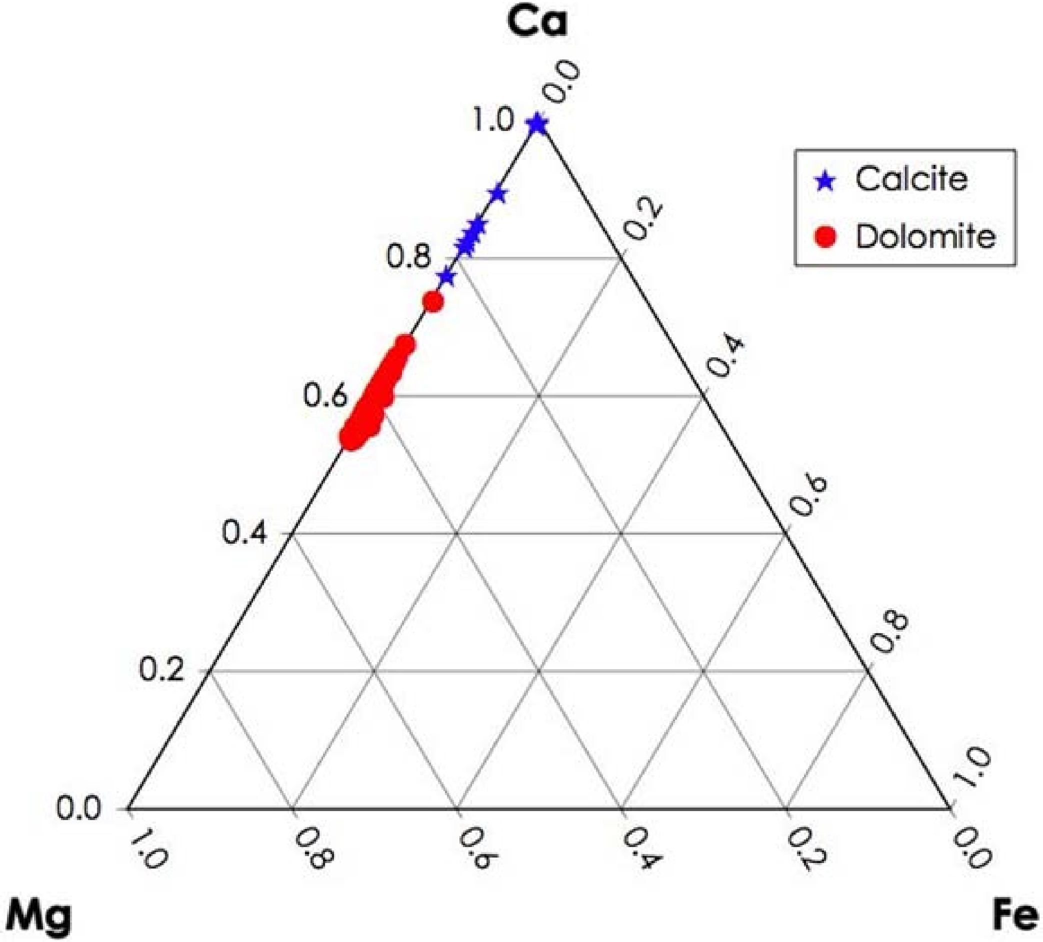
Ca
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★ Calcite
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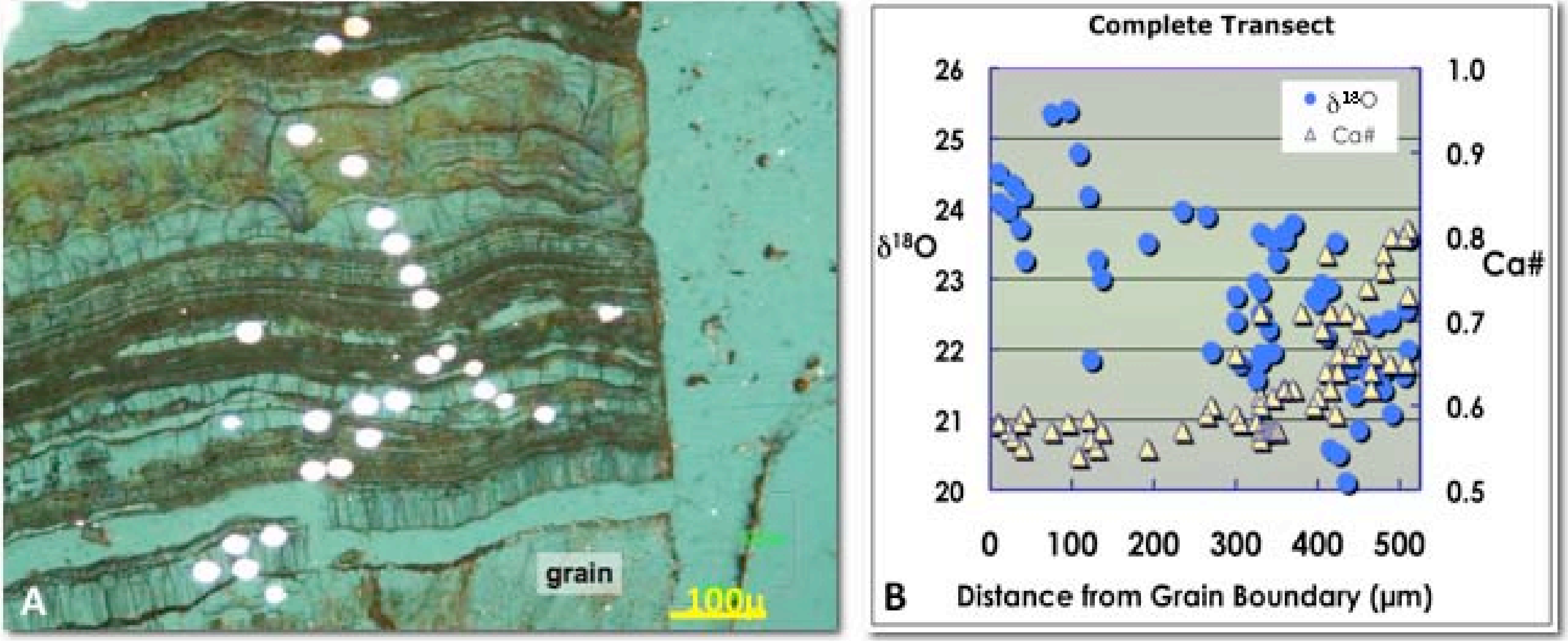
A
grain
100µ
Complete Transect
26
25
24
23
22
21
20
δ18O
1.0
0.9
0.8
0.7
0.6
0.5
Ca#
δ18O
Ca#
0
100
200
300
400
500
B
Distance from Grain Boundary (µm)

Table 1: Fluid chemistry of representative water samples

| | Adobe Springs Well | Del Puerto Creek |
|---|---|---|
| Collection date | June 9, 2007 | June 9, 2007 |
| $Ca^{2+}$ | 3.5 | 8.1 |
| $Mg^{2+}$ | 110 | 150 |
| $K^+$ | 0.31 | 0.6 |
| $Na^+$ | 5.4 | 9.6 |
| $HCO_3^-$ | 400 | 550 |
| $CO_3^{2-}$ | 66 | 89 |
| $Cl^-$ | 4.8 | 9.5 |
| $NH_3$ (total as N) | 0.01 | 0.018 |
| $SO_4^{2-}$ | 16 | 10 |
| $SiO_2$ | 5.6 | 13 |
| $OH^-$ | <1.6 | <1.6 |
| Alkalinity as $CaCO_3$ | 440 | 600 |
| Field pH | 8.73 | 8.52 |
| Lab pH | 8.69 | 8.61 |
| Collection T°C | 17.8 | 24.2 |
| $\delta^{18}O$ | -7.9 | -7.1 |
| $\delta D$ | -57 | -52 |

Concentrations of dissolved species given in mg/L; isotopic values reported in permil relative to VSMOW.

Table 2: Calculated Equilibrium Carbonate Oxygen Isotope Compositions

| | Adobe Springs Well | Del Puerto Creek |
|---|---|---|
| Collection date | June 9, 2007 | June 9, 2007 |
| Collection T°C | 17.8 | 24.2 |
| $\delta^{18}O_{VSMOW}$ (per mil) | -7.9 | -7.1 |
| **Predicted dolomite compositions (‰)** | | |
| Tarutani et al. (1969) | 25.3 | 24.7 |
| Schmidt et al. (2005) | 26.6 | 26.1 |
| Vasconcelos et al. (2005) | 24.9 | 24.3 |
| **Predicted calcite compositions (‰)** | | |
| O'Neil et al. (1969) | 22.3 | 21.7 |
| Horita and Clayton (2007) | 21.8 | 21.3 |

Fractionation equations used:
$1000 \ln \alpha = 2.78 \times 10^6 T^{-2} + 0.11$ (Tarutani et al., 1969; corrected in Friedman and O'Neil, 1977, for the case of Mg mole fraction = 0.5)
$1000 \ln \alpha = 2.63 \times 10^6 T^{-2} + 3.12$ (Schmidt et al., 2005)
$1000 \ln \alpha = 2.73 \times 10^6 T^{-2} + 0.26$ (Vasconcelos et al., 2005)
$1000 \ln \alpha = 2.78 \times 10^6 T^{-2} - 2.89$ (O'Neil et al., 1969; corrected in Friedman and O'Neil, 1977)
$1000 \ln \alpha = 0.9521 \times 10^6 T^{-2} + 11.59 \times 10^6 T^{-1} - 21.56$ (Horita and Clayton, 2007)