IRONSTONE CONCRETIONS – ANALOGS TO MARTIAN HEMATITE SPHERULES. A. D. Aubrey[1], E. Parker, J. H. Chalmers, D. Lal and J. L. Bada, Geoscience Research Division, Scripps Institution of Oceanography (aaubrey@ucsd.edu).

Introduction: The discovery of ubiquitous hematite-rich spherules upon the surface on Mars by the MERs Spirit and Opportunity remain one of the most perplexing mission discoveries [1]. We report herein ironstone concretions found throughout San Diego county that are new terrestrial analogs to the Martian spherules. Physical similarities between the concretions are profiled, and the presence of organic components and visual bacterial remnants make a strong case for microbial mediation of these ironstones during their formation. The possibility of microfossil and biomolecule preservation within these ironstones is emphasized because the Martian concretions may be good geological targets for the 2009 MSL and 2011 ESA ExoMars missions to search for life on Mars.

Background: Terrestrial spherules, formed via the flow of groundwater through porous rock and along cracks and fissures, have recently been suggested as analogs to Martian 'blueberries' [2]. Precipitated iron oxides, primarily in the form of hematite, constitute a significant portion of these concretions. The discovery of hematite concretions on Mars may therefore be strong evidence of aqueous processes, as water is thought to be necessary for their formation [1].

San Diego county hosts a diversity of marine terraces formed in the late Quaternary due to marine transgressions related to cyclic changes in climate and sea level [3]. Ubiquitous features within these terraces are small centimeter-scale concretions within the host paleosol [4]. Examination of these concretions provides compelling visual similarities to the hematite spherules imaged on Mars (Figure 1).

These concretions are localized within the B_{ir} horizon of acidic iron-rich soils, cemented by iron oxides, and are products of formation from a previous era [5]. One site at Sunset Cliffs is an exposed coastal marine terrace that offers an ideal location for the study of these Martian analogs. Similar coastal marine terraces have been dated between 80ka and 120ka by amino acid racemization studies on fossil mollusks [3], and radiometric dating has confirmed an age of 120$\pm$10ka [6].

Results and Discussion: The San Diego ironstones have been physically and chemically characterized. Scanning Electron Microscopy (SEM) was used to look for evidence of microbial microfossils. Chemical characterization included determination of elemental abundances, total organic carbon (TOC), total organic nitrogen (TON), stable carbon and nitrogen isotopes ($\delta^{13}C$, $\delta^{15}N$), amino acids, and nucleobases.

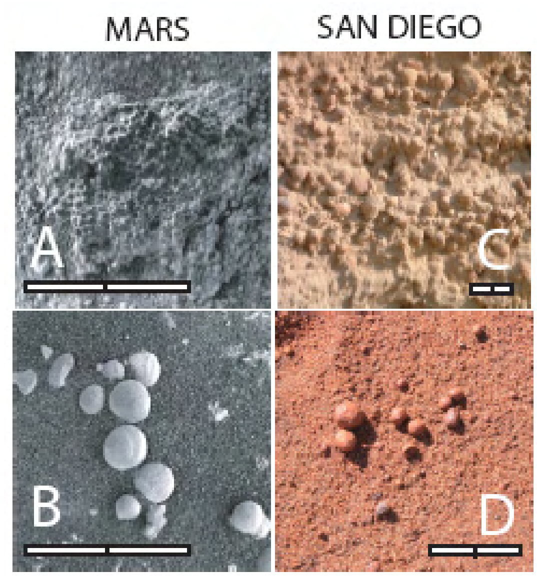

Figure 1. Comparison between Mars 'blueberries' and San Diego ironstones. Scale Bars represent 2cm. (A=Spirit image ID 2M218252997; B=Opportunity image ID 1M132266828, C=Sunset Cliffs; D=UCSD Canyon).

Physical Characterization. The diameters of the Sunset Cliff concretions vary from small (0.5cm) to large (3cm) and are present within a host rock of Pleistocene sandstone. The ironstones show evidence of moderate interior layering. Analysis by SEM on ironstone thin sections reveals the presence of colonial coccoidal microfossils.

Chemical Characterization. The samples are enriched compared to the host matrix in several elements, especially biologically mobile iron and manganese. This enrichment may be due to concentration or secretion by microbial life.

The average TOC and TON concentrations in these samples are 1.9 and 0.12 mg/g, respectively. The amino acids constitute approximately 1.3% of the TOC, and correspond to total concentrations in the low-ppm range (Figure 2). The amino acid compositions are similar to bacterial distributions [7]. No nucleobases were detected in formic acid hydrolyzed crushed ironstones or water-extract hydrolyzed fractions. This may be due to the low stabilities of nucleobases compared to those of amino acids.

The enantiomeric ratios of the amino acids provide a method of determining the ages of the San Diego ironstones. The amino acids show significant racemization with average D/L ratios between 0.21 and 0.29. Heating experiments on the ironstone samples yield a first-order racemization rate constant of ~$3x10^{-4}$ yr^{-1}, assuming an average exposure temperature of 10°C. This gives bulk ironstone ages on the timescale of thousands of years. Because of the time that ironstones take to form, it is highly probable that the ironstone cores are much older than the bulk samples.

Formation Model: The marine terraces formed as wave-cut platforms during times of higher sea level, and the beach ridges accumulated during pauses in the retreat of the sea from the land. Upon withdrawal of the sea, the exposed wave-cut platforms and beach ridges were exposed to Pleistocene climates that were wetter than today. These paleoclimates produced iron and manganese-rich leachates that led to the formation of a subsurface horizon within which ironstone concretions formed in situ. If we accept that the age of Sunset Cliffs sedimentary soils are approximately 100ka, this places an upper age for the formation of the ironstones. Further studies on the Sunset Cliffs ironstone cores and surrounding layers will better define the formation model on a geological timescale.

Conclusions: The San Diego county ironstones appear to be a unique analog to the concretions found upon Mars. Our ironstone formation model requires vertical aqueous activity within sedimentary deposits, which supports the hypothesis that the Mars 'blueberries' require liquid water to form. The visual and chemical evidence of microbial life within these ironstones provides evidence that bacteria may have mediated the formation of concretions in this environment. A more detailed profile of the San Diego ironstones will be presented with the calculated ages of the ironstone concretions and a more detailed explanation of the formation model.

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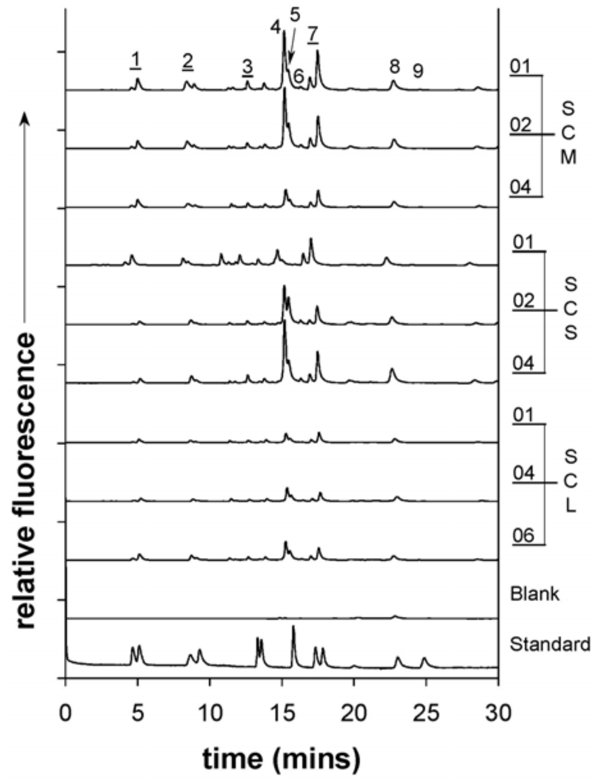

Figure 2. HPLC chromatograms of total hydrolyzable amino acids (THAA) detected in small (SCS), medium (SCM), and large (SCL) Sunset Cliffs ironstone concretions. 1=D/L-aspartic acid, 2=L/D-glutamic acid, 3=D/L-serine, 4=glycine, 5=β-alanine, 6=γ-aminobutyric acid, 7=D/L-alanine, 8=L-valine, 9=D-valine.