

**SULFUR AND IRON GEOCHEMISTRY, AND THEIR RELATIONS TO MICROBIAL COMMUNITIES FROM THE SUBMARINE HYDROTHERMAL SITE NORTH OF PANAREA ISLAND, TYRRHENIAN SEA, ITALY.** M. Glamoclija<sup>1</sup>, J. Schieber<sup>1</sup>, A. Szykiewicz<sup>1</sup>, and B. Beard<sup>2</sup>; <sup>1</sup> Department of Geological Sciences, Indiana University, 1001 East 10<sup>th</sup> Street, Bloomington, IN 47405, mglamocl@indiana.edu; <sup>2</sup> Department of Geology and Geophysics, University of Wisconsin-Madison, 1215 W Dayton St, Madison, WI 53706.

**Introduction:** Hydrothermal systems are likely the oldest continuously inhabited ecosystems on Earth, with important influence of iron and sulfur chemistry. Microbial metabolic pathways such as iron and sulfur redox reactions are often spread across the phylogenetic tree and are considered to be important metabolic pathways in the early Earth environments [1, 2]. Cycling of sulfur and iron as related to hydrothermal systems has primarily been studied as separate subjects. Nonetheless, they are commonly interrelated in hydrothermal systems but their interactions are still incompletely understood. Comparative study of Fe and S geochemistry is a new tool in the study of ancient rocks that provides a new perspective on the origin of ecosystems, interaction among microbes and geochemistry, and the driving forces of evolution.

In this contribution we present combined  $\delta^{34}\text{S}$  and  $\delta^{56}\text{Fe}$  data obtained from geologically young, iron-rich hydrothermal crusts collected near a submarine vent site north of Panarea Island, Tyrrhenian Sea, Italy. We are integrating these data with differences in sample mineralogy, microbial morphologies, and total organic C isotope compositions.

**Materials:** Active submarine hot springs at Panarea are characterized by temperatures of  $\sim 90^\circ$  to  $200^\circ\text{C}$  [3] and are due to volcanism of 0.2 to 0.1 m.y. ago. Samples were dredged from a hydrothermal area during a 1995 exploration cruise of a CNR (Consiglio Nazionale delle Ricerche, Bologna, Italy) research team from a depth of 100-215m. Collected material consists mainly of iron oxyhydroxide deposits. The studied crusts are up to 10 cm thick and orange to dark red. Some are traversed by numerous chimneys, whereas others show  $\sim 1\text{mm}$  thick layers that have a glassy sheen and are more competent as compared to softer more massive layers that have a dull luster. Major mineral phases are poorly ordered goethite, iron hydroxides, iron oxyhydroxide, and amorphous iron hydroxidesulfates. Barite, quartz, halite, sulfur, plagioclase and nontronite minerals occur as minor constituents.

**Methodology:** We followed a dual approach for the identification of biosignatures in our hot spring crusts. Morphological signatures were studied with petrographic microscope, Scanning Electron Microscopy (SEM) [4], whereas potential chemical biosignatures

were examined with C, S and high-resolution (micro-drilling) Fe isotope studies.

**Sulfur Isotopes:** Good correlation of  $\delta^{34}\text{S}$  values of water- and acid-soluble sulfates ( $R^2=0.93$ ) indicates the same origin of both phases. The general increase of sulfate content with increasing Fe content suggests that water- and acid-soluble sulfates are mainly represented by the amorphous phases of water soluble and insoluble iron sulfates, respectively (Fig. 1a).

SEM analysis has shown that chromium reduced sulfur and Parr Bomb fractions are mainly represented by small grains of pyrite and barite as the secondary phases. The range of  $\delta^{34}\text{S}$  values for pyrite and barite from  $-5.43$  to  $0.48\%$ , values that are consistent with sulfur derivation from igneous sources such as hydrothermal fluids

The observed large variation in  $\delta^{34}\text{S}$  values of water- and acid-soluble iron sulfates, from  $-2.98$  to  $18.78\%$ , coupled with a negative correlation between  $\delta^{34}\text{S}$  and sulfate content is consistent with mixing of sulfur from two isotopically distinct sources. Marine sulfate is enriched in  $\delta^{34}\text{S}$  (average  $\delta^{34}\text{S}=20\%$ ) in comparison to magmatic sulfur which is enriched in  $^{32}\text{S}$  (average  $\delta^{34}\text{S}=0\%$ ). M2A and E1 samples may be considered as end members, with M2A having  $\delta^{34}\text{S}$  values of sulfates close to magmatic origin and E1 characteristic of marine origin, other samples have intermediate values and sulfates of mixed S sources (fig.1b).

Based on average values of  $\delta^{34}\text{S}$  for pyrite and the average value of  $\delta^{34}\text{S}$  for recent marine sulfate, isotope mass balance equations indicate that contribution of marine sulfate during precipitation of iron sulfates varied widely from 1 to 95 %.

Sulfates are the most abundant S-bearing phases in all samples, it may be proposed that oxidation of magmatic fluids proceeded near and/or directly on the surface of the sea floor in a highly oxidative environment. Additionally, there is no clear evidence that microorganisms observed by SEM might have importantly controlled the sulfur isotope fractionation.

**Iron Isotopes:** Different layers from each sample were sampled, taking into account textural variations and differences in relations with observed microbial morphologies. The  $\delta^{56}\text{Fe}$  values of the soft samples range from  $-0.06$  to  $1.01\%$  (Fig. 1d) where as glassy layers within five of the seven analyzed soft deposits define a narrow range in  $\delta^{56}\text{Fe}$  values ( $0.41\%$  to  $0.44$

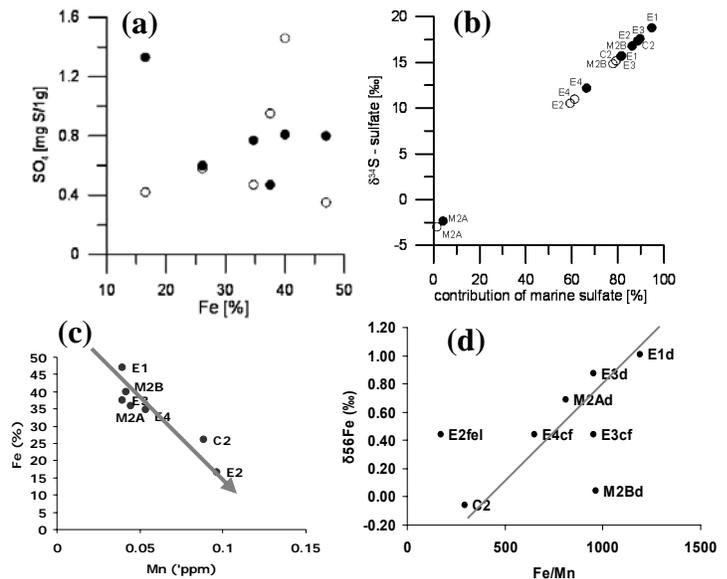
‰). The soft deposits define a positive correlation between Fe/Mn ratio and  $\delta^{56}\text{Fe}$  values (Fig. 1d). Previous studies [e.g. 5] have shown that high Fe/Mn ratios are associated with sites proximal to the hydrothermal vent. We interpret the positive correlation in Fe/Mn and  $\delta^{56}\text{Fe}$  values to be a result of partial oxidation of the hydrothermal fluids as a function of proximity to the vent (Fig. 1c, d). Assuming a 1.5‰ fractionation between aqueous Fe(II) and iron hydroxide and a hydrothermal fluid with a  $\delta^{56}\text{Fe}$  value of -0.5 (e.g., [6, 7]) sample E1 would represent the most proximal vent sample and represent about 1% removal of Fe from the fluid by oxidation and precipitation whereas sample C2 would represent the most distal sample and the iron oxide would have formed from a fluid from which approximately 50% of the Fe would have been removed by oxidation and precipitation. There are three samples that do not plot along this trend (Fig. 1d); samples M2B, E3, and E2. M2B and E3 had significant quantities of biofilms and perimineralized cell membranes that were coated by Fe oxy/hydroxides capable of trapping only small quantities of Mn. The E2 sample showed different biomineralization with a very low content of Fe oxy/hydroxides. High Mn content of E2 sample was rather influenced by oxidized hydrothermal fluid, than by Fe oxy/hydroxides produced by bacteria. We suggest that biologically induced Fe oxy/hydroxides changed the Fe/Mn ratio of the sample relative to the Fe/Mn ratio that would be predicted based on the inferred distance from the hydrothermal vent using Fe isotope composition.

The origin of the constant  $\delta^{56}\text{Fe}$  values of the glassy layers is uncertain but it might represent a pervasive input of hydrothermally derived Fe with a constant Fe isotope composition from either local or distal sources.

**Conclusions:** Iron crusts from submarine hot springs near Panarea Island contain a wide range of morphological features that resemble fossilized microbial forms [8]. The microbial forms are entirely permineralized by iron-oxides and most of them were found in association with sulfur- and iron-bearing minerals. Sulfur isotope compositions are consistent with mixing of S derived from marine and magmatic sources and do not require S isotope fractionation by bacteria. The  $\delta^{56}\text{Fe}$  values of the soft deposits can be explained by partial oxidation (1-50%) of hydrothermally derived Fe which appears to be a function of distance from the vent. The proximity to the vent as inferred by Fe/Mn ratio, however, is presumed to be affected by biofilms that absorbed Mn-Fe hydroxides.

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**Figure 1:** (a) graph shows correlation of  $\text{SO}_4$  and Fe contents, filled and unfilled circles correspond to water- and acid-soluble  $\text{SO}_4$  respectively; (b) plot shows contribution of marine S in  $\delta^{34}\text{S}$  fractionation of  $\text{SO}_4$  (c) correlation of Fe and Mn contents from the crusts illustrate samples' distance from the venting site, the arrow points toward the inferred increase in distance from vent (d) the  $\delta^{56}\text{Fe}$  of porous deposits "d", chimney fill "cf" and red Fe layer "fel". Correlated to Fe/Mn it shows changes in fractionation that follows the trend of the fluid oxidation (full line) for samples C2, E4cf, M2Ad, E3d, and E1d; whereas samples E3cf, M2Bd and E2fel do not plot along this trend, because of an inferred fractionation of Mn relative to Fe caused by the presence of biofilms and mineralized cells.