

SPECTROSCOPIC CHARACTERIZATION OF HYDROTHERMAL SULFIDE CHIMNEYS AT THE JUAN DE FUCA RIDGE. M. D. Dyar¹ J. F. Holden², J. L. Bishop³, and M. D. Lane⁴. ¹Dept. of Astronomy, Mount Holyoke College, South Hadley, MA 01075, mdyar@mtholyoke.edu, ²Dept. of Microbiology, Univ. of Massachusetts, Amherst, MA 01003, jholden@microbio.umass.edu, ³SETI Institute/NASA-ARC, Mountain View, CA 94043, jbishop@seti.org, and ⁴Planetary Science Institute, Tucson, AZ 85719, lane@psi.edu.

Introduction: On Earth, deep-sea hydrothermal vents are common features along mid-ocean ridges where new seafloor is formed along plate boundaries. Seawater circulates throughout the seafloor, and at mid-ocean ridges fluid circulation is most intense due to a shallow magmatic heat source that leads to surface venting of geothermally-altered fluids. Hydrothermal sulfide chimneys form at deep-sea vents when upwelling high-temperature hydrothermal fluids mix with cold seawater resulting in precipitation of metal sulfides. Often a porous zone rich in Zn-Fe-S minerals (e.g., sphalerite, wurtzite) forms between the hot chalcocopyrite (FeCuS_2)-rich interior of these chimneys and the cool barite (BaSO_4)- and silicate-rich exterior [1]. These samples provide a provocative data set to test spectroscopic methods for characterization of mixtures of sulfide and their reaction products. We present here results of the study of a small sample suite from the Juan de Fuca Ridge using Mössbauer, mid-IR thermal emission, and visible, near-IR, and mid-IR diffuse reflectance spectroscopy.

Samples: The samples studied here were collected as part of a larger project to better understand microbe-mineral-fluid relationships in the Zn-Fe-S zone of sulfide chimneys. Four actively-venting chimneys in various stages of evolution were sampled using the deep-sea submarine *Alvin* in the summer of 2008 (Figure 1).

Three sulfide chimney samples were collected from massive sulfide deposits in the Main Endeavour vent field (2,200 m depth) while the fourth chimney was removed from a deposit named Hot Harold in the Mothra vent field 2 km to the south. The Bastille sample (Ba08) came from a chimney with a central fluid conduit venting fluids up to 282°C. The Salut sample (Sa08) was collected from the vertical side of a massive deposit that had seawater-diluted hydrothermal fluids percolating through it with temperatures up to 79°C and was covered with polychaete worms. The Dante sample (Da08) was from a chimney that had become partially sealed by a beehive mineral formation and was venting fluids up to 300°C. The Hot Harold sample (HH08) was from a chimney with a central fluid conduit venting fluids up to 321°C.

Chunks of each sample weighing ~3-5 g were removed from the main mass and dried in air; a 30 mg chip from each was removed for Mössbauer spectroscopy. Mid-IR thermal emission spectra of the chunks were analyzed at Arizona State University before the samples were lightly crushed for further emission ana-

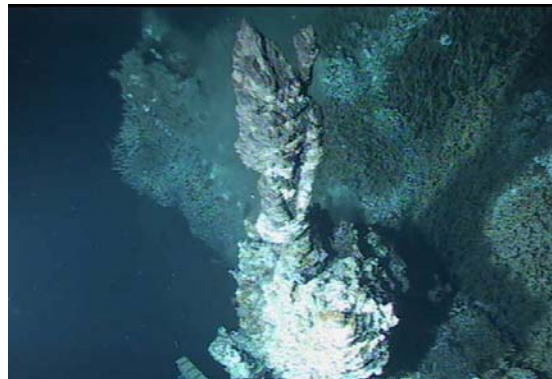


Figure 1. The Dante sulfide chimney (Da08).

lyses. Those aliquots were then sent to RELAB for reflectance studies.

Results: *Mössbauer* data are shown in Table 1 and a typical spectrum is shown in Figure 2. All the spectra are dominated by Fe^{3+} ; this doublet typically has an isomer shift (IS) of 0.31 mm/s and a quadrupole splitting (QS) of 0.57 mm/s, which is consistent with pyrite, ferrihydrite, and some sulfates such as copiapite, but not sphalerite, chalcocopyrite or wurtzite. Some samples also show a Fe^{3+} doublet with very small QS (0.2-0.1 mm/s) that is characteristic of members of the hydration series $\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, which includes quenstedtite, coquimbite, paracoquimbite, kornelite, and lausenite. Sa08 also has a small feature with IS = 0.51 mm/s and QS = 0.81 mm/s that may be a sulfate with an octahedral corner-sharing chain structure, such as butlerite. Sample HH08 is distinctive in that it has no metal and it contains three distributions: one with the ubiquitous QS = 0.62 mm/s doublet, one with a

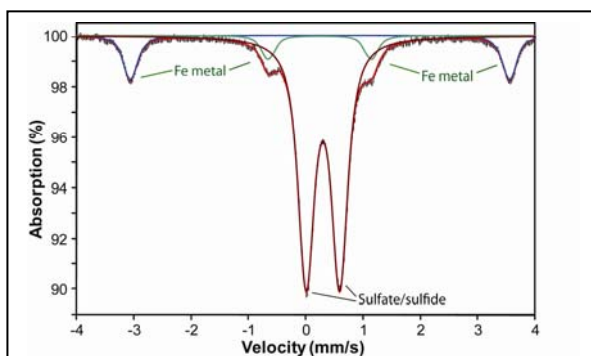


Figure 2. Mössbauer spectrum of Ba08-1, showing the inner four peaks of what is probably an Fe metal sextet, and Fe^{3+} doublet corresponding to sulfide or sulfate.

very small QS ($\text{Fe}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ or related mineral) and one with a larger QS (1.20 mm/s) that might be jarosite or fibroferrite. Sample Sa08 and two splits of Ba08 all show a magnetic sextet with parameters matching those of Fe metal; further measurements are in progress to unequivocally assign this sextet. The Mössbauer data do not show any evidence for phases such as gypsum that do not contain Fe.

Table 1. Mössbauer data

Sample	Fe Metal	Sulfate/ Sulfide	Coquim- bite?	Sulfate
Ba08-1	19	81	0	0
Ba08-2	17	83	0	0
Sa08	9	74	9	8
Da08	0	100	0	0
HH08	0	29	27	43

The visible/near-infrared (VNIR) reflectance spectra (Figure 3) of the samples are very dark, consistent with the presence of pyrite or chalcopyrite. An absorption due to an Fe^{3+} electronic transition is observed near 0.87 μm for the Ba08 samples (1,2) that is consistent with minerals such as hematite, amaranite, copiapite and fibroferrite, but is not a unique mineral identifier. A reflectance maximum is observed near 0.58 μm for samples Ba08, Da08 and Sa08 that is rather unusual. This could be caused by a mixture of coquimbite (max $\sim 0.47 \mu\text{m}$) with other minerals shown in Figure 3 (max $\sim 0.67 \mu\text{m}$). An H_2O stretch plus bend combination band is observed near 1.94 μm that is consistent with several polyhydrated sulfate minerals such as copiapite, fibroferrite and amaranite. A drop in reflectance is observed in samples Da08, Sa08, and HH08 near 2.4 μm that is characteristic of polyhydrated sulfates. The increasing spectral slope

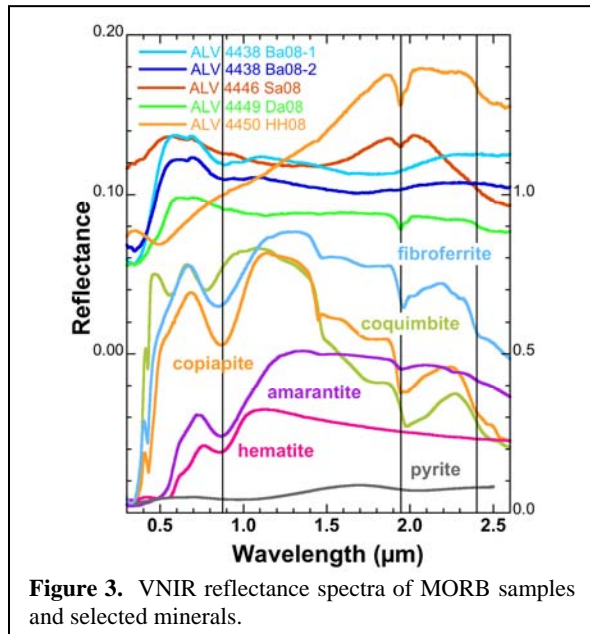


Figure 3. VNIR reflectance spectra of MORB samples and selected minerals.

observed for sample HH08 is unusual and is likely due to a mixture of phases.

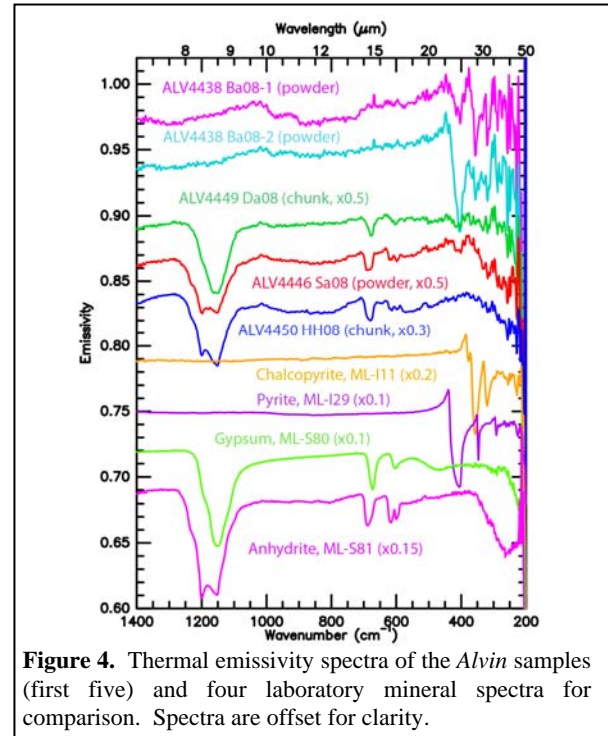


Figure 4. Thermal emissivity spectra of the Alvin samples (first five) and four laboratory mineral spectra for comparison. Spectra are offset for clarity.

The TES spectra (Figure 4) do not show any evidence of the hydrated sulfates and Fe^{3+} suggested by VNIR but are very much consistent with the Fe-rich phases identified by Mössbauer. The TES data are fairly simple spectroscopically, thus likely mineralogically. Both Ba08 spectra indicate sulfide (chalcopyrite and/or pyrite), but no sulfate. Gypsum was found in ALV4449 Da08, with a possible small amount of pyrite. Anhydrite is clearly identified in the spectrum of ALV4446 Sa08, with a very minor amount of sulfide (perhaps pyrite). Anhydrite is seen in ALV4450 (HH08). There is no evidence for carbonate in any of the sample spectra.

Conclusions: This combination of spectroscopic techniques provides multiple constraints on the mineralogy of these samples. Fe metal or oxide, pyrite, gypsum, anhydrite have been identified, along with a group of hydrated sulfates like copiapite, coquimbite, and fibroferrite. Future work will use XRD to refine these identifications.

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