

**Sulfides from martian and lunar basalts: Comparative chemistry for Ni, Co, Cu, and Se. Range of point analyses per sample.** J.J. Papike<sup>1</sup> (jpapike@unm.edu), P.V. Burger<sup>1</sup>, C.K. Shearer<sup>1</sup>, S.R. Sutton<sup>2,3</sup>, M. Newville<sup>3</sup>, Y. Choi<sup>3</sup>, and A. Lanzirotti<sup>3</sup>. <sup>1</sup>Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, New Mexico, 87131. <sup>2</sup>Department of Geophysical Sciences, University of Chicago, Chicago, Illinois 60637. <sup>3</sup>Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637.

**SUMMARY:** As a part of our continuing campaign in the study of comparative planetary mineralogy we focus on sulfides from martian and lunar basalts. Here Mars and Moon are used as “natural laboratories” with Moon displaying lower oxygen fugacities (~IW-1) than Mars (~IW to FMQ); Moon has much lower water activity in basaltic melts than Mars, and Moon has lower concentrations of Ni and Co in basaltic melts than Mars. The major sulfides are troilite (FeS) in lunar basalts and pyrrhotite (Fe<sub>1-x</sub>S) in martian basalts.

This study focuses on the concentrations of Ni, Co, Cu, and Se. We chose these elements because of their geochemical importance and the feasibility of analyzing them with a combination of synchrotron x-ray fluorescence (SXRF) and electron microprobe (EPMA) techniques. The selenium concentrations could only be analyzed, at high precision, with SXRF techniques and are < 150 ppm, similar to concentrations seen in carbonaceous chondrites and interplanetary dust particles (IDPs). Ni and Co are in higher concentrations in martian sulfides than lunar and are higher in martian olivine-bearing lithologies than olivine-free varieties. The sulfides in individual samples show very large ranges in concentration (e.g. Ni ranges from 50,000 ppm to <5 ppm, see Fig. 1). These large ranges are mainly due to compositional heterogeneities within individual grains due to diffusion and phase separation. EPMA wavelength dispersive (WDS) mapping of Ni, Co, and Cu show the diffusion trajectories [1]. Nickel and Co have almost identical diffusion trajectories leading to the likely nucleation of pentlandite (Ni<sub>3</sub>CoFe)<sub>8</sub>S<sub>8</sub> and copper diffuses along separate pathways likely toward chalcopyrite nucleation sites (CuFeS<sub>2</sub>). The systematics of Ni and Co in lunar and martian sulfides clearly distinguish the two parent bodies, with martian sulfides displaced to higher Ni and Co values.

**SAMPLES:** For Moon we selected 6 samples: 1) 12040, an Apollo 12 olivine basalt cumulate, 2) 15555, an Apollo 15 olivine normative basalt with both olivine and pyroxene phenocrysts, 3) 15016, an Apollo 15 vesicular olivine-normative basalt with both olivine and pyroxene phenocrysts, 4) 15058, an Apollo 15 pyroxene-phyric basalt, 5) 12021, an Apollo 12 pyroxene-phyric basalt, and 6) 75038, an Apollo 17, high-Ti, ilmenite basalt. A more comprehensive overview of these rocks is provided in the Lunar Sample Compendium <http://curator.jsc.nasa.gov/lunar/compendium.cfm>,

compiled by Charles Meyer. For Mars we selected 8 samples: 1) Yamato 980459 (Y 98), an olivine-phyric basalt which erupted as a liquid and may be a primitive mantle melt, 2) Sayh al Uhaymir 005 (SAU 005), an olivine-phyric basalt cumulate, 3) Dar al Gani 476 (DAG 476), an olivine-phyric basalt cumulate, 4) LEW 88516, a lherzolite (cumulate), 5) ALHA 77005 (ALH 77005), a lherzolite (cumulate), 6) Shergotty, a pyroxene-phyric basalt, 7) Los Angeles (LA 751), a pyroxene-phyric basalt, and 8) QUE 94201, a pyroxene-phyric basalt which erupted

as an evolved liquid. Again, more detailed information about these rocks is provided in the Mars Meteorite Compendium (compiled by Charles Meyer, <http://curator.jsc.nasa.gov/antmet/mmc/>). For a concise discussion of the martian samples, including WDS maps at equivalent scales, refer to Papike et al., 2009 [2].

**SXRF TECHNIQUES:** The synchrotron x-ray microprobe (SXRF) uses synchrotron radiation as the source for XRF analyses of trace element concentrations with micrometer-scale spatial resolution [3]. Two such instruments were used during the course of this study, one at the GeoSoilEnviroCARS sector 13 at the Advanced Photon Source (APS, Argonne, IL, USA) and the X26A beamline at the National Synchrotron Light Source at Brookhaven National Lab (NSLS, Upton, NY, USA) [4]. The APS microprobe uses an undulator source, produces a 2 μm beam and has element sensitivities in the 100 ppb range. The NSLS microprobe uses a bending magnet source, produces a 7 μm beam and has sensitivities in the 1 ppm range. For the NSLS measurements, elemental maps were obtained for each grain by rastering the sample in front of the beam in a 4 μm/step grid. Full XRF spectra collected for ~10 sec. at each pixel were then integrated for those pixels with high Ni (indicative of sulfide). This integrated spectrum was then processed to extract net peak areas. For the APS measurements, line scans were obtained across each grain by slew scanning with XRF spectra saved every 500 nm. These line scans were used to select appropriate spot analysis points. Generally, this was done by evaluating two criteria, 1) the point of highest Ni intensity, and 2) a point displaced from the highest Ni intensity, still within the sulfide as determined by Fe and S profiles. Using this methodology, we hoped to get a sense for the degree of heterogeneity within any given grain (though we acknowledge that this does not necessarily yield a statistically robust average). Once spots were chosen, longer (~5 min.) dwell spectra were collected, and processed to extract net peak areas. For both data sets (NSLS and APS measurements), quantification in terms of ppm was obtained using Fe as an internal concentration reference (determined independently by EPMA) combined with relative sensitivity predictions from the XRF program NRLXRF [5]. A thickness of 30 μm was assumed (thin section thickness) except for sulfides in Y98 and 67016 for which 10 μm was used based on the cross-sectional dimensions of these grains. This procedure resulted in trace element concentrations with typical uncertainties (1σ) of ~5%. During this study, we obtained results for Se, Ni, and Cu. Co was determined by EPMA.

**DISCUSSION:** Figure 1a shows the Ni systematics. Clearly, sulfides from the olivine-rich martian lithologies, olivine-phyric or lherzolitic basalts (SAU 005, LEW 88516, DAG 476, Y 98, ALH 77005) are enriched in Ni relative to the sulfides in the pyroxene-phyric martian basalts (Shergotty, LA 751, QUE 94201). In addition, martian sulfides are enriched in Ni relative to lunar

sulfides. These systematics are also reflected in the bulk Ni values of our sample suite (see the Lunar Sample Compendium and the Mars Meteorite Compendium, previously referenced). Figure 1b shows the variation of Co abundances in martian and lunar sulfides. Although the Co does not show the high concentration and large range of Ni, it is nonetheless significant. Again, we see a correlation of olivine abundance and high Co abundance (in Y98, LEW 88516, ALH 77005, DAG 476, SAU 005) relative to the olivine-poor Shergotty, QUE 94201, and LA 751. Also, we see (on average) higher abundances of Co in martian sulfides relative to lunar. Cobalt and Ni observations suggest that the Co-Ni abundance in a given sulfide are the result of the Co and Ni concentration of the evolving melt, as well as the timing of sulfide saturation in the crystallization sequence. Later sulfides should have higher Co/Ni abundances than those that crystallized earlier. The Lunar Sample Compendium and Mars Meteorite Compendium show that the bulk S concentration of martian samples is greater than that of lunar samples; martian samples range from ~2,700-600 ppm, while lunar samples range from ~700-400 ppm in the low-Ti basalts. Thus all things being equal (which they are not), we would expect sulfur saturation earlier in the crystallization sequence in martian basalts resulting in the crystallization of sulfides with a higher Ni/Co ratio (relative to lunar). Figure 1c shows the variation of Cu abundances in martian and lunar sulfides. Most Cu abundances are <6000 ppm (as with Co) but there are a few outliers with higher values. Copper abundances do not show the strong preference for olivine bearing martian basalts that Ni and Co do. For example LA 751 contains sulfides with quite high Cu values. Again we see, generally, higher abundances of Cu in the sulfides from Mars vs. the Moon. The Cu concentrations for the bulk rocks (taken from the Martian Meteorite Compendium and Lunar Sample Compendium) show only slightly higher Cu for martian than lunar varieties with martian ranging from 26-6 ppm and lunar 11-4 ppm. Figure 1d shows the variation of Se concentration for each sample. Selenium concentrations are below the detection limit for EPMA techniques, therefore all of our data was collected by SXRF, resulting in a smaller dataset. Nevertheless, some observations can be made. All concentrations fall below 150 ppm, and in general, martian sulfides have more Se than lunar. The bulk Se contents for martian basalts, as reported in the Mars meteorite Compendium, range from ~0.30-0.47 ppm, while lunar basalts range from ~0.06-0.11 ppm (from the Lunar Sample Compendium).

**REFERENCES:** [1] Burger et al. (2011) LPSC abst. [2] Papike et al. (2009) GCA, 73, 7443. [3] Sutton et al. (2002) RiM 49, 429. [4] Sutton et al. (2004) Advances in X-ray anal. 76, 76. [5] Criss (1977) Cosmic program #DOD-00065.

**ACKNOWLEDGEMENTS:** GeoSoilEnviroCARS is supported by the National Science Foundation - Earth Sciences (EAR-0622171) and the Department of Energy - Geosciences (DE-FG02-94ER14466). Use of the APS was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract no. DE-AC02-06CH11357. X26A is supported by the Department of Energy (DOE) Geosciences (DE-FG02-92ER14244). Use of the NSLS was supported by DOE

under contract no. DE-AC02-98CH10886. A NASA Cosmochemistry grant (JJP) provided support for this research and is greatly appreciated.

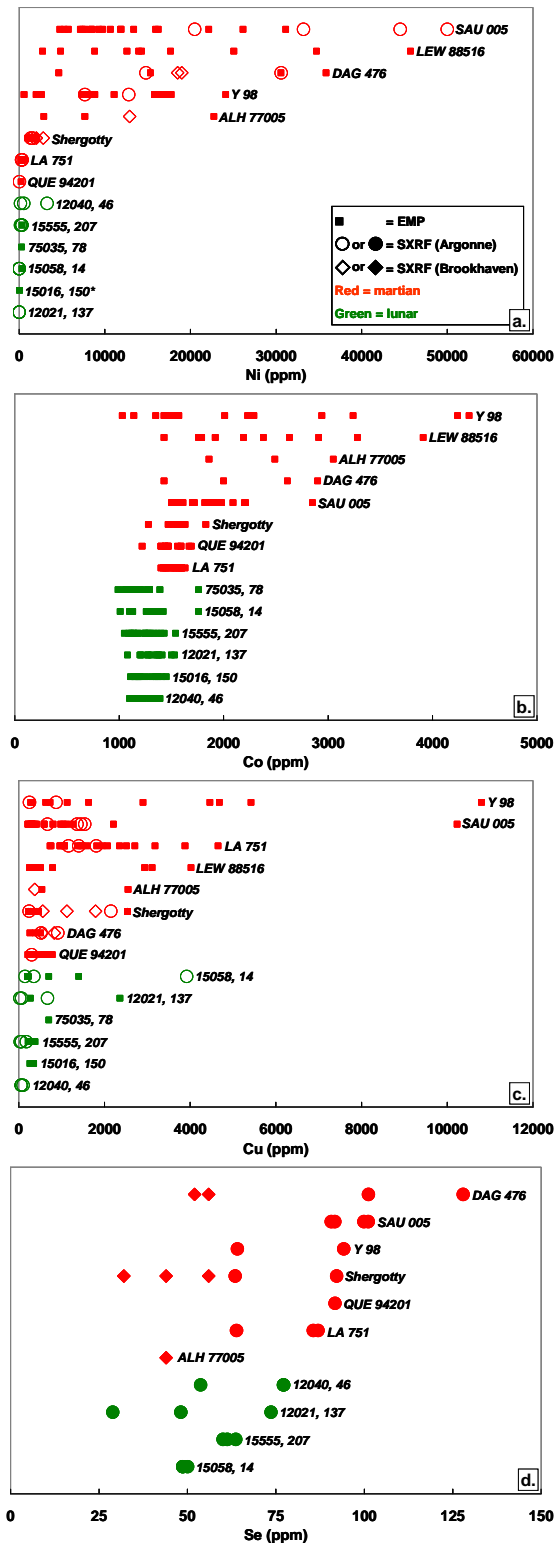


Figure 1. Histogram illustrating the trace element chemistry of martian and lunar sulfide grains. \*Value is below the limit of detection and is plotted for illustrative purposes.