

## **ELECTRONIC DEPOSIT**

### **SAMPLES AND ANALYTICAL METHODS**

#### **Electron Microprobe (EPMA)**

Electron microprobe analyses were conducted on planetary sulfide grains on the JEOL JXA 8200 electron microprobe at the UNM's Department of Earth and Planetary Sciences. Selection of analytical spots was straightforward on the EPMA: grains of sufficient size (typically >2 microns) were selected, and analytical profiles were conducted from one end of the grain to the other, thereby sampling the entire grain. In addition, wavelength dispersive maps (WDS) were collected on several samples to illustrate the elemental distribution within these grains. Analyses were conducted for S, Co, Ni, Fe and Cu. EPMA is particularly useful for Co detection where the Co K $\alpha$  peak (6.93 keV) overlaps with the Fe K $\beta$  peak (7.05 keV). In this case, the higher resolution of wavelength dispersive spectrometers (WDS) on the EPMA vs. the EDS detector on the synchrotron (~5 eV and 130 eV, respectively) make the EPMA the more suitable analytical tool.

Quantitative analyses were collected using an accelerating voltage of 15 kV, and a beam current of 50 nA. Spot size was limited to <1  $\mu\text{m}$ , and a suite of Taylor mineral standards were used to obtain calibrations. WDS maps were collected on several scales (dictated primarily by the size of the sulfide grains of interest). Operating conditions were similar to those used during quantitative analyses; dwell times were ~200 ms per pixel. Due to the low pixel resolution of these maps (sulfide grain size often approaches the spatial resolution of the electron beam), images have been interpolated for publication.

EPMA detection limits were calculated to the  $2\sigma$  level by taking the standard deviation of analysis for the first and last unknown (from any given analytical session), multiplying by 2 (to get to  $2\sigma$ ), and taking the average of the two values. This calculation is then applied to the entire dataset (for a given analytical session), as there is very little change in the standard deviation, both from one sample to another, as well as from one analytical session to another. Samples which fell below the  $2\sigma$  level were excluded from the calculation of averages, and are considered below the limit of detection. Standard deviation values ( $1\sigma$ ) for EPMA analyses are 61 ppm for S, 113 ppm for Fe, 93 ppm for Co, 105 ppm for Ni and 100 ppm for Cu.

#### **Synchrotron X-ray Microprobe Analysis (SXRF)**

The synchrotron x-ray microprobe (SXRF) uses synchrotron radiation as the source for XRF analyses of trace element concentrations with micrometer-scale spatial resolution (Sutton et al., 2002). 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 (NSLS, Upton, NY, USA) (Sutton et al., 2004). The APS microprobe uses an undulator source, produces a 2  $\mu\text{m}$  beam and has element sensitivities in the 100 ppb range. The NSLS microprobe uses a bending magnet source, produces a 7  $\mu\text{m}$  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  $\mu\text{m}$ /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 (Criss et al., 1977). This approach is somewhat imperfect, as EPMA (Fe) measurements do not always directly correlate to SXRF analytical spots (one need just consider the interaction volume of each technique to come to this conclusion), though these errors are negligible when compared to the compositional variations observed in the grains. A thickness of 30  $\mu\text{m}$  was assumed (thin section thickness) except for sulfides in Y98, for which 10  $\mu\text{m}$  was used based on the cross-sectional dimensions of these grains. This procedure resulted in trace element concentrations with typical uncertainties ( $1\sigma$ ) of ~5%. During this study, we obtained results for Se, Ni, and Cu.

Sulfide analyses suggest a large degree of heterogeneity. Because of this, we have chosen to present our dataset in two forms, one illustrating the average concentration of a given element measured in this study (Table 1), and the other as a histogram, which illustrates the compositional range measured both within samples, and in comparison to other samples in the planetary suite, as seen in Figure 1. Here, we discuss the criteria for computing the averages, the standard error of the analytical techniques, and the relative standard deviation of the sample chemistry.

### **Averages**

Averages for S and Fe and Co were calculated using EPMA analyses exclusively, as S, Fe and Co analyses were not directly measured by SXRF. Averages for Se were calculated using SXRF data exclusively. Nickel and Cu averages represent a combination of EPMA and SXRF analyses. Both EPMA and SXRF analyses were given equal weight when calculating averages, only values which fell below the detection limit for a given analytical technique (or those not meeting stoichiometric constraints, including analytical totals <95 wt.% in the case of EPMA analyses) were excluded from the calculation of the average.

### **Relative Standard Deviation**

Relative standard deviation of all analyses within a sample were calculated using available data (i.e. EPMA only for Fe, S, and Co, SXRF only for Se, and a combination of SXRF and EPMA for Ni and Cu). Again, equal weighting was given to EPMA and SXRF analyses. High values of RSD are not a reflection of the quality of analyses; rather, they are an indication of the degree of compositional heterogeneity within a sample. A table of RSDs follows.

Relative Standard Deviation (RSD, as a percent of the mean analysis) of all sulfide analyses in a given sample, for a given element.

Sample	S	Fe	Se	Co	Ni	Cu
Y 98	2.99	0.55	26.85	22.84	68.76	79.64
QUE 94201	0.61	0.34	1 analysis*	6.43	1 analysis*	56.68
Shergotty	0.23	0.36	39.58	9.31	25.10	94.61
LA 751	0.42	0.25	16.41	5.08	27.09	64.85
SAU 005	0.94	1.46	5.67	17.45	75.88	172.75
DAG 476	2.69	2.97	43.51	29.30	49.00	41.06
ALH 77005	3.70	6.87	1 analysis*	24.14	73.74	105.13
LEW 88516	1.71	2.33	N/A	31.89	74.98	99.22
12021, 137	0.36	0.35	44.71	9.66	0.00	143.85
12040, 46	0.61	0.40	19.52	7.32	129.18	35.94
15016, 150	0.49	0.23	N/A	9.13	1 analysis*	20.87
15058, 14	1.29	1.22	1.62	13.85	185.46	157.01
15555, 207	0.58	0.95	2.99	10.41	30.61	47.50
75035, 78	0.49	0.24	N/A	14.65	1 analysis*	1 analysis*

N/A = no applicable measurements

\*In cases where there is only one analysis, one cannot calculate a relative standard deviation.

## REFERENCES

Criss J. W. (1977) NRLXRF—Cosmic program #DOD-00065. U.S. Naval Research Laboratory.