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**In situ measurements of lead and other trace elements in abyssal peridotite sulfides**

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Electronic Supplementary Text, Figures, and Tables

**Supplemental Methods**

**Figure S1:** Calibration curves for SHRIMP-RG measurements using  $O_2^-$  source (Fe, Ni)

**Figure S2:** Calibration curves for SHRIMP-RG measurements using  $Cs^+$  source (As, Se, Sb, Te, Ag, and Au)

**Table S1:** Average major element compositions of sulfide grains in wt%

**Table S2:** Accepted values of the sulfide reference materials

**Table S3:** Trace element concentrations and ratios in unaltered sulfides, averaged by grain

**Table S4:** Trace element concentrations and ratios in altered sulfides, averaged by grain

**Table S5:** Individual analyses of Pb in sulfides

**Table S6:** Individual analyses of other trace elements in sulfides

## Supplemental Methods

### 1. Sulfide major element analyses by electron microprobe

Analyses were performed with 1  $\mu\text{m}$  beam diameter at a 15 kV accelerating potential and 40 nA current. Peak counting intervals were 20 s for all elements and the ZAF matrix correction method was used. Sulfur was measured using a PETJ crystal and calibrated on troilite. Iron was calibrated on hematite, while Ni, Cu and Co were calibrated using pure metal alloys. These four metals were measured using a LiF crystal. Zn and Si were calibrated on willemite and collected using a TAP crystal. Oxygen was calibrated on hematite and measured using LDE1. Off-peak backgrounds were fit with a linear model for all elements except for O, for which an exponential fit was used. Using the LDE1 light element detector on the hematite standard, we set the location of the O K $\alpha$  peak and background positions, then manually set off-peak backgrounds to avoid interferences. Oxygen ranged from below the detection limit ( $<0.1$ - $0.2$  wt%) up to 19 wt% (Table 2).

### 2. Pb analyses in sulfide by SHRIMP-RG with the $\text{O}_2^-$ source

On the SHRIMP-RG,  $^{206}\text{Pb}$ ,  $^{208}\text{Pb}$ ,  $^{64}\text{S}_2$ ,  $^{80}\text{Se}$ ,  $^{110}\text{Fe}_2$ ,  $^{118}\text{Ni}_2$ ,  $^{168}\text{Fe}_3$ ,  $^{200}\text{Fe}_3\text{O}_2$  were measured during three separate analytical sessions (denoted D1 to D3): session D1 on 7/24/2014 included PS59-235-01; session D2 on 2/04/2015 included re-analyzing PS59-235-01 and analyzing PS59-235-18, HLY0102-70-75, PS59-201-39 and PS59-238-75; session D3 on 5/29/2015 included HLY0102-70-62, PS59-235-17, Van7-85-47, Van7-85-49, Van7-96-28 and Van7-96-21. Individual trace element analyses using the  $\text{O}_2^-$  source are reported in Table S3.

For the first and third sessions, only one cycle of data was collected (peak-hopping through the run table). Four cycles of data were collected in the second session to try to obtain Pb isotopic ratios. In addition,  $^{207}\text{Pb}$  was added to the run table for this session (with a count time of 75 s), but  $^{207}\text{Pb}$  count rates were too low to measure accurate Pb isotope ratios. For calculation of Pb concentrations,  $^{208}\text{Pb}$  was used because it has the highest count rates. Data from all sessions were reduced using only the first cycle of data, as count rates changed on average by 15% and up to 113% between cycles, suggesting changes in the secondary ionization efficiency with time.

The SHRIMP-RG has nominally high mass resolving power and the instrument was tuned to a mass resolving power of 9000 – 9500. With these conditions, as well as the high abundance sensitivity of the instrument, the peak width of  $^{208}\text{Pb}$  is 0.025 AMU. The background was measured at  $\sim 0.1$  AMU above the  $^{208}\text{Pb}$  peak position, which is four peak-widths away from the  $^{208}\text{Pb}$  mass position and in a quiet area of the mass spectra.

As part of the data analysis, primary and secondary beam intensities were monitored during each analysis. By session, sulfide data were excluded if the primary beam current decreased by  $>70\%$ , which was likely due to sputtering into non-sulfide material. Data were also excluded if the secondary beam monitor changed by  $>20\%$  over the duration of an analysis, which was assumed to indicate a change in stability (e.g., sample charging), secondary ionization efficiency, or some other factor. In addition, we excluded analyses if the total counts of  $\text{S}_2$  deviated by more than two-sigma from the average for a given session. This criterion was

relaxed for sulfides with Cu-bearing phases, under the assumption that ionizing efficiency varies with sulfide mineralogy. As a result, two of the 12 analyses on Cu-bearing phases in the dataset have high  $S_2$  counts that deviate by more than two-sigma from the average, while the other 10 analyses fall with the criterion. Finally, individual elements with counting statistic error  $>80\%$  were excluded as these were considered below the detection limit.

### *3. Trace element analyses by SHRIMP-RG with $Cs^+$ source*

Two separate analytical sessions using the  $Cs^+$  source were used to analyze elements that ionize better in negative ionization mode. Session C1 (4/16/2013) was developmental work to determine which elements could be measured successfully and sulfides were only analyzed in sample PS59-235-01. Session C2 included samples PS59-201-39, PS59-235-17, PS59-238-75, HLY0102-70-75, Van7-96-21V, Van7-96-21M and Van7-96-28. Details of the calibration, error estimate, and data reduction are presented below for each trace element measured using the  $Cs^+$  source. Accepted values (published or reported by personal communications) for the sulfide reference materials are given in Supplemental Table S1, individual trace element analyses in Supplemental Table S4, and calibration curves for each session in Supplemental Fig. S2.

#### *3.1. Arsenic*

The lowest concentration reference sulfide, UQAC-MSS1, has 2 ppm As, while the other four standards have 70-132 ppm As (Table S1). In the first session, measurements on UQAC-MSS1 yielded 0-1 counts, suggesting that the As detection limit was  $>2$  ppm. As a result, the calibration curve did not include UQAC-MSS1 and was forced through the origin. We do not report concentrations  $<5$  ppm for this session, as exclusion of UQAC-MSS1 results in the working curve only being constrained by concentrations  $>70$  ppm. In session C2, improved tuning resulted in greater As sensitivity, with count rates corresponding to 2 ppm As in UQAC-MSS1 resolvable above the background. Hence, this standard was included in the calibration curve, which again was fixed through the origin. As UQAC-MSS1 was not detectable in the first session, we used the reproducibility of UQAC-MSS1 from session C2 (89%) as the uncertainty for the first session. This approximation – due to the lack of low concentration standards – likely underestimates the error. For session C2, we do not have confidence in the accuracy of sulfides with  $<3$  ppm As due to  $>75\%$  error. However, detection of some counts indicates that these grains contain some As and these analyses are reported as containing  $<3$  ppm (Table S4).

#### *3.2. Selenium*

The Se concentration for sulfide reference materials ranges from 6.4-650 ppm (Table S1). In order to fit the calibration curve through all standards, we did not force the curve through the origin (Fig. S2). In the first session, reproducibility was similar for all standard reference materials, therefore we took an average of the 1 sigma reproducibility (%) to calculate the % error for each measurement. In session C2, we observed that reproducibility of the standard reference materials increased linearly with increasing concentration and therefore error for all analyses was calculated accordingly.

*D'Errico, Coble, and Warren: Trace Elements in Abyssal Peridotite Sulfides*

### 3.3. Silver

The reference materials have reported Ag concentrations from 0.16-250 ppm (Table S1), which brackets the range of calculated unknown concentrations in our samples. In session C1, we attempted to measure  $^{107}\text{Ag}$ , but these data are excluded due to problematic overlapping interferences in the spectra at 107 mass, which possibly involve  $^{75}\text{As}^{32}\text{S}$  or  $^{63}\text{Cu}^{12}\text{C}^{32}\text{S}$ . In session C2, we determined that the  $^{139}(\text{AgS})$  peak is better resolved from isobaric interferences and has sufficient count rates in our sulfides. Error corresponding to the reproducibility of sulfide reference materials increased linearly with increasing concentration, hence error for the unknowns was calculated using this linear correlation.

### 3.4. Antimony

We calculated the Sb working curve on the basis of UQAC-MSS1, MSS-1, and MSS-5 (calibrations for FeS1 and FeS8 are not available) with a line fit through the origin. The concentrations reported for these reference materials range from 0.12-61.3 ppm. The calibration defines a linear trend in both sessions, but the MSS-1 reference standard appears to be systematically low in session C2.

### 3.5. Tellurium

The Te working curve was calibrated using UQAC-MSS1, MSS-1, and MSS-5, whereas Te concentrations are unknown for FeS1 and FeS8. The three reference materials were calibrated by LA-ICPMS using MASS-1 as a standard, which has a certificate value for Te of 15 ppm (Barnes, pers. comm. 2017). The reported Te concentrations range from 0.15 – 32 ppm. In session C1, low count rates (0-2 total counts) in UQAC-MSS1 at 0.15 ppm indicate that it was at the detection limit and the calibration curve was forced through the origin. For session C2, improved tuning produced higher sensitivity and the detection limit is estimated to have been 0.2 ppm based on counting statistics of the standards. Among unknowns, all values <0.5 ppm were estimated to be below detection. We do not have high confidence in the accuracy of sulfides with <4 ppm Te due to >70% error, which is due to scatter in the replicate analyses of the lowest concentration reference material. However, as counts were detected above background levels, indicating that these grains contain some Te, these analyses are reported as containing <4 ppm in Table S4.

### 3.6. Gold

The Au concentration for sulfide reference materials ranges from 1.2-1610 ppm, but most sulfides in this study contain <1 ppm Au. We did not include FeS1 or FeS8 in the Au calibration curve, because their concentrations are >180 ppm and not representative of the unknowns. In session C1, the peak-position was not accurately set, resulting in erroneous measurements and this data is not reported. In session C2, we accurately located the Au peak at the beginning of the session, but the peak position shifted overnight due to instrument instability and subsequent data are omitted. The lowest concentration reference material contains 1.2 ppm Au and the calibration curve was through the origin, therefore the detection limit was unconstrained. Improved analysis of Au concentrations requires reference materials with <1 ppm Au.

### 3.7. Chlorine

We measured a concentration of  $50 \pm 20$  ppm Cl in FeS8 by electron microprobe and used this measurement to calibrate Cl/S<sub>2</sub> ratios. As our reported Cl numbers are derived from a one point calibration, the detection limit is unconstrained. More reference materials with both low and high Cl concentrations are needed to improve the precision and accuracy of Cl analyses.

### 4. Sulfide major element concentrations by SHRIMP-RG

In addition to major element analyses by EMPA (Table 2), major element ratios were determined by SHRIMP-RG. During O<sub>2</sub><sup>-</sup> sessions, Fe/Ni ratios were measured, while Cu/S<sub>2</sub> ratios were measured during the second Cs<sup>+</sup> session (Tables 3-4). These measurements provide a useful indication of composition within the volume of the sputter pit. Absolute concentrations of Fe, Ni, and Cu measured by SHRIMP-RG are not accurate because the calibrations for major elements tend to be non-linear and are not well constrained by the available reference materials. Fe/Ni ratios, however, measured on SHRIMP-RG are consistent with EMPA results measured on the same grains (D'Errico, 2016).

### 5. References for Supplemental Methods and Table S1

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