

Sulfide Stability of Planetary Basalts. C. M. Caiazza¹, K. Righter², E. K. Gibson Jr.², J.T. Chesley³ and J. Ruiz³
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Introduction: The isotopic system, ^{187}Re – ^{187}Os , can be used to determine the role of crust and mantle in magma genesis. In order to apply the system to natural samples, we must understand variations in Re/Os concentrations. It is thought that low [Os] and [Re] in basalts can be attributed to sulfide (FeS) saturation, as Re behaves incompatibly to high degrees of evolution until sulfide saturation occurs [1]. Previous work has shown that lunar basalts are sulfide under-saturated, and mid-ocean ridge, ocean-island and Martian (shergottites) basalts are saturated [2,3]. However, little is known about arc basalts.

In this study, basaltic rocks were analyzed across the Trans-Mexican Volcanic Belt (Fig. 1). These basalts formed in a volcanic arc produced by the subduction of the Rivera and Cocos Plates beneath the North American Plate. The resulting East to West-trending belt has produced thousands of volcanoes. Approximately 50 basalt samples were analyzed for S abundances. Temperature, oxygen and sulfur fugacity ($f\text{O}_2$, $f\text{S}_2$) were calculated using published and new bulk and mineral composition data [4]. Using T, $f\text{O}_2$, $f\text{S}_2$ and bulk compositions, the amount of sulfur expected at sulfide saturation conditions was calculated for each sample. Comparison of the measured and calculated S contents allowed us to determine whether the basalts are sulfide saturated or undersaturated. This information was then used to interpret the behavior of Re and Os during arc magma evolution, and compare to other planetary basalts.

Experimental: Concentrations of S were determined using a LECO IR-32 total sulfur analyzer (Fig. 2). Approximately 0.3 g of each sample, along with V_2O_5 and low S accelerator reagents (Fe), were placed in a crucible and burned in the presence of O_2 . These conditions allowed S in the basalt to be released as SO_2 gas, and measured by an infrared Luft-cell detector. Working curves for S standards were first constructed, and then unknown samples were run.

Mineral grains in the basalt samples were also analyzed using a CAMECA SX100 electron microprobe. Polished thick sections were made by mounting small rock pieces in epoxy, followed by slicing with a rock saw and/or grinder. Samples were then polished and carbon coated for imaging and electron microprobe analysis of olivine, sulfide and spinel.

Results: According to S analyses, the basaltic samples have [S] ranging from 60 to 1190 ppm. High concentrations (1190 and 568 ppm) were found in two samples, both of which are unusual alkaline compositions (minette and hornblende lamprophyre).

There is no correlation between FeO and S content in any of the individual basalt suites. Forsterite (Fo) contents of selected olivines were also calculated and determined to be between 70%-80%. Spinel analyzes yielded Cr_2O_3 concentrations ranging from 4-45 wt%, and in all cases also contained significant Al and Fe components.

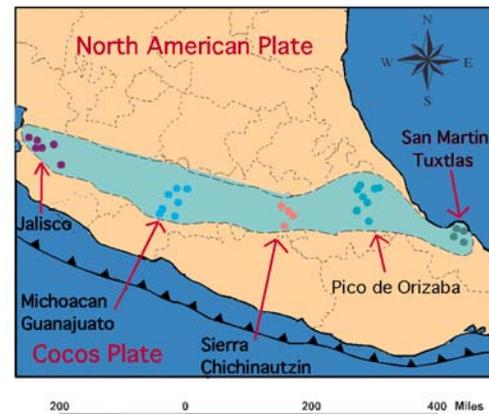


Figure 1. Map of the Trans-Mexican Volcanic Belt. Samples were collected from the area shaded in green.

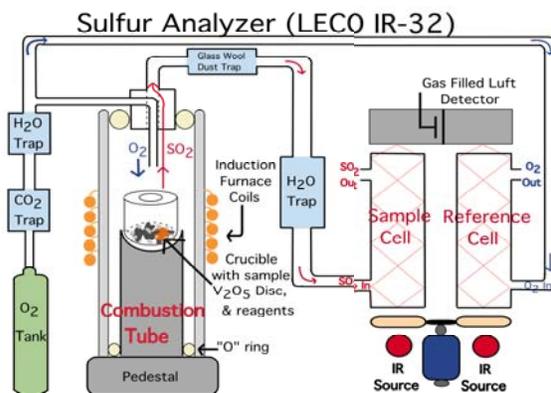


Figure 2. Schematic diagram of sulfur analyzer used to determine sulfur concentrations of basalts.

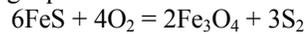
Discussion: A main focus of this study was to determine whether or not these arc-basalts are sulfide saturated. Temperature, $f\text{O}_2$, $f\text{S}_2$, and composition can be used to calculate the S content of a liquid at sulfide saturation during differentiation [2,5,6], according to: $\ln X_S = a \ln f\text{S}_2 - b \ln f\text{O}_2 + c \ln X_{\text{FeO}} + d/T + e + \sum f_i X_i$, where X_S is the mole fraction of dissolved S; a, b, c, d, e and f_i are constants; and the summation is over melt components, i [2].

A) The liquidus temperature ($^{\circ}\text{C}$) of phenocryst-poor basalts can be calculated using magnesia content [7]:

$$T = 948.5 + 48.59\text{MgO} - 2.771(\text{MgO})^2 + 0.0882(\text{MgO})^3$$

B) Oxygen fugacity, or the O_2 pressure at which the magma equilibrated, was determined using an equation from [8] that correlates $f\text{O}_2$ with the $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio of a silicate liquid, bulk composition, and temperature. $\text{Fe}_2\text{O}_3/\text{FeO}$ ratios were calculated from olivine-liquid equilibria. A small and negligible pressure effect on $\text{Fe}_2\text{O}_3/\text{FeO}$ was ignored.

C) Calculations of $f\text{S}_2$ were obtained from the following equilibrium:



and

$\Delta G = -RT\ln K = -RT\ln [(a_{\text{Fe}_3\text{O}_4})^2(f\text{S}_2)^3]/[(a_{\text{FeS}})^6(f\text{O}_2)^4]$. Gibbs free energy data for Fe_3O_4 and FeS were taken from [9], and temperature and $f\text{O}_2$ were calculated as explained above. Here, the activity of FeS was assumed to equal one, and the activity of Fe_3O_4 in the spinel was calculated using the activity model of [10].

Using the temperature, $f\text{O}_2$, $f\text{S}_2$, and composition determined for each basalt, S contents were calculated for the condition of sulfide saturation.

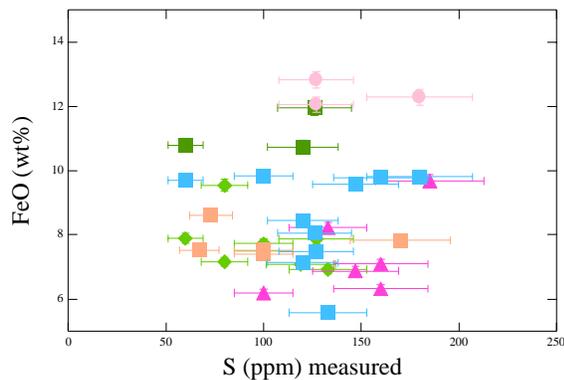


Figure 3. Plot of S measured concentrations vs. FeO abundances (symbols the same as Figure 4). Note that two samples have much higher S concentrations (that plot off the diagram to the right).

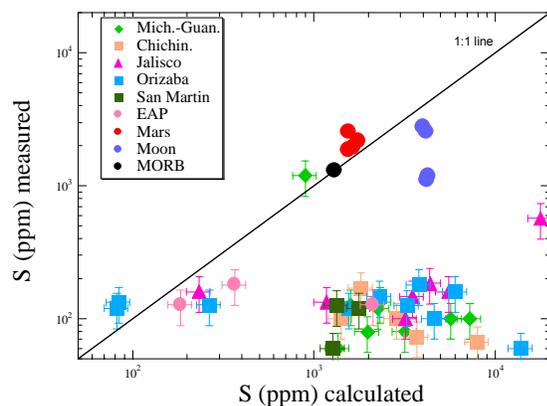


Figure 4. A plot of calculated vs. measured [S].

Discussion

Calculated and measured S concentrations are compared in Figure 4. The samples closest to the 1:1 line are sulfide saturated, while those further from the line are sulfide under-saturated. The majority of the basaltic samples are sulfide under-saturated (Fig. 4). However, six samples remain close to the line of saturation. Several different scenarios may explain these data.

In the first case, magma in a magma chamber may be initially sulfide saturated. As magma ascends in the volcanic plumbing and erupts onto the surface, it does not degas significantly and retains or preserves S contents indicative of sulfide saturation.

In another scenario, the basaltic magma begins as sulfide saturated, but as it sits within the magma chamber, S is lost through degassing. Once erupted onto the surface, the samples no longer have the original S compositions, and thus appear to be under-saturated.

A last possibility to consider is that the basaltic magmas were never saturated to begin with. Degassing would not have made a difference. They would still remain under-saturated once collected from the surface. This last scenario is one to keep in mind when studying lunar and Martian basalts. Martian basalts appear to be saturated, yet lunar basalts are under-saturated [3]. The lunar basalts may have lower S contents due to either degassing events or simply a lunar mantle with lower S contents, causing under-saturation.

Conclusions: Preliminary assessment indicates a connection between Re content and sulfide saturation or under-saturation in several of the Mexican basalts. However, a detailed study of Re, Os, and S in all basaltic samples awaits further analysis. Future plans include comparing S contents of planetary basalt suites, including lunar basalts, shergottites, and oceanic basalts.

References:

- [1] Shirey, S.B. and Walker, R.J. (1998) *Ann. Rev. Earth Plan. Sci.* 26, 423-500;
- [2] Wallace, P. and Carmichael, I.S.E. (1992) *Geochim. Cosmochim. Acta* 56, 1863-1874;
- [3] Righter, K. (2000) LPS XXXI, abstract no. 1281;
- [4] Righter, K., Chesley, J.T. and Ruiz, J. (2002) *Geology* 30, 619-622;
- [5] Haughton, D.R., Roeder, P.L., and Skinner, B.J. (1974) *Econ. Geol.* 69, 451-467;
- [6] Li, C. and Naldrett, A.J. (1993) *Econ. Geol.* 88, 1253-1260;
- [7] Jones, J.H. (2003) *Lunar Planet. Sci.* XXXIV, 1130.
- [8] Kress, V.C. and Carmichael, I.S.E. (1991) *Contrib. Mineral. Petrol.* 108, 82-92;
- [9] Robie, R.A., Hemingway, B.S. and Fisher, J.R. (1978) *US Geol. Survey Bull.* 1452;
- [10] Sack, R.O. and Ghiorso, M.S. (1990) *Contrib. Mineral. Petrol.* 106, 474-505.