

AN INVESTIGATION INTO SULFUR CONCENTRATIONS AT SULFIDE SATURATION IN SILICATE MELTS UNDER REDUCING CONDITIONS: IMPLICATIONS FOR THE PLANET MERCURY.

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Introduction: With the data returned from the MErcury Surface, Space ENvironment, GEochemistry, and Ranging (MESSENGER) mission, there are now numerous constraints on the physical and chemical properties of the planet Mercury, including surface composition [e.g., 1]. The high S and low Fe contents observed from MESSENGER suggest a low oxygen fugacity (fO_2) of the present materials on the planet's surface. Estimates of the fO_2 for Mercurian magmas are approximately 3.2-4.3 log units below the Iron-Wüstite (ΔIW) oxygen buffer [2], several orders of magnitude more reducing than other terrestrial bodies we have data from such as the Earth, Moon, or Mars [3-5]. In addition, it has been demonstrated that sulfur solubility in silicate melts increases as fO_2 decreases [e.g., 6 and references therein], which is significantly different than what is observed on Earth and in other fairly oxidized environments [7-9]. The goal of this study is to determine the sulfur concentration at sulfide saturation (SCSS) as a function of temperature (T), pressure (P), fO_2 , and silicate melt composition through high PT experiments. The results of these experiments will aid in our understanding of the fate of elements during the differentiation and thermal evolution of the planet Mercury and provide guidance for the geochemical interpretations of other highly reduced planetary bodies.

Methods: Experiments were conducted at 1 GPa and 4 GPa from 1500°C to 1850°C on synthetic starting materials under reducing conditions.

Starting materials. Starting materials consisted of synthetic diopside ($CaMgSi_2O_6$) or monticellite ($CaMgSiO_4$) produced from high purity reagent grade oxides, mixed with either elemental sulfur or troilite (FeS). The silicate mixes were produced by combining the reagents in the appropriate proportions and grinding under ethanol for up to two hours in a Fritsch Pulverisette 2 automated mortar and pestle. These compositions were chosen for two reasons. First, the geochemical information collected from the MESSENGER XRS and GRS indicate high Si, Mg, and Ca abundances and low Fe abundances [e.g., 1]. Second, although there is a correlation on the mercurian surface between Ca and S [1], it has been shown experimentally that Mg partitions more strongly than Ca into sulfide phases [10]. Therefore, the main benefit of using these starting compositions is that they will allow us to assess

Ca and Mg exchange equilibria between a diopside melt and a sulfide melt as a function of sulfide composition (i.e., Fe abundance of the sulfide) and temperature at mercurian fO_2 .

Experimental. For each experiment, a graphite capsule was used to minimize any reactions of the sulfur-bearing samples with the sample capsule and assemblies. Since graphite capsules are unable to control fO_2 below the GCO (graphite-CO-CO₂) oxygen buffer, silicon metal was added directly to the experimental charges to decrease the fO_2 of the system to below that of the mercurian interior [2]. Some graphite capsules were filled by packing the silicon metal, sulfur or sulfide, and silicate in layers, while others were filled by first mixing all components in varying proportions using a hand held mortar and pestle under ethanol before drying at least 8 hours at or above 100°C in a drying oven then loading this mixture into the graphite capsule.

Low pressure (1 GPa) experiments were completed in Depths of the Earth QUICKpress piston cylinder (PC) apparatuses fitted with 13 mm and 10 mm pressure plates using barium carbonate cells as the pressure transmitting medium. High pressure (4 GPa) experiments were completed in an 880-ton Rockland Research press (MA), fitted with a Walker style multi-anvil module utilizing the COMPRES 14/8HT and 14/8G2 sample assemblies [11]. Run durations ranged from 10 minutes to 4.5 hours. Experiments were quenched by cutting power to the system and allowing the samples to slowly decompress.

Analytical. Experimental charges were set in epoxy and dry-sectioned with diamond wafering blades on a slow speed saw before dry-polishing in hexagonal boron nitride and alumina powders to prevent the loss of sulfide phases soluble in water or oil [12]. Experimental run products were analyzed via wavelength-dispersive X-ray spectroscopy Field Emission Electron Probe Microanalysis on a JEOL JXA-8530F at NASA's Johnson Space Center. All phases present including silicate glass, metals, and sulfides were analyzed with an accelerating voltage of 15 keV. A beam current of 15 nA was used for silicates, whereas a beam current of 20 nA was used for metals and sulfides. A broad beam (10-20 μm) was used for glass analyses and a focused beam (1-5 μm) was used for metals and sulfides. Standards for

the silicate analyses included diopside (Mg, Si, Ca), troilite (S), olivine (Mg, Si, Fe), and various glass standards (Mg, Si, Ca, Fe, Al). Standards for the metal and sulfide analyses included Si metal, Fe metal, diopside (Mg, Ca), Re metal, and troilite (S). Benitoite was used as the standard for Ba and provided a check on contamination from the cell assembly. Peak count times ranged from 30-60 seconds and background count times ranged from 15-30 seconds. The fO_2 of each experimental charge was calculated for all experiments that contained an Fe-rich metal phase using the same method as [10].

Table 1. Experimental run conditions. Values denoted by * were calculated with respect to the $\Delta Si-SiO_2$ oxygen buffer and then converted to approximate ΔIW values because no Fe-rich metal phase was present.

Exp#	T (°C)	P (GPa)	fO_2 (ΔIW)	S (wt.%)	SS?
002	1850	4	-6.24	8.49	N
009	1850	4	-5.68	12.29	N
012	1850	4	-7.35*	20.45	N
019	1700	1	-6.95	13.10	N
020	1700	1	-8.10*	20.63	N
022	1700	1	-6.35	8.85	N
023	1700	1	-6.57	9.37	N
024	1700	1	-6.32	8.03	N
027	1500	1	-4.44	7.26	Y
032	1600	1	-3.27	1.12	Y
036	1500	1	-4.55	6.26	Y
037	1600	1	-5.76	3.51	N
038	1500	1	-4.55	5.29	N
039	1500	1	-4.19	5.88	Y
041	1500	1	-4.53	6.12	Y

Results: In this study, 15 experiments were conducted; 12 in a PC and 3 in a MA (Table 1). Experiments run at 1 GPa in the PC were conducted at temperatures ranging from 1500°C to 1700°C, with fO_2 ranging from -3.27 to -8.10 $\log_{10} \Delta IW$ and S concentration in the silicate melt phase ranging from 1.12 wt.% to 20.63 wt.%. Only 5 of these runs were saturated with respect to sulfides. The major sulfide phase present was troilite (FeS), with minor amounts of CaS and MgS, except for experiment 027 which had both FeS and CaS present as the major sulfides with minor amounts of MgS. Experiments run at 4 GPa in the MA were all conducted at 1850°C, with fO_2 ranging from -5.68 to -7.35 $\log_{10} \Delta IW$ and S contents ranging from 8.49 wt.% to 20.45 wt.%. None of the MA runs were saturated with respect to sulfides.

Discussion: While only 5 of the 15 experimental runs completed in this study have been determined to be at sulfide saturation, the S contents of the unsaturated experiments can be used as minimum SCSS values. All data have been plotted in Figure 1, showing general agreement with the SCSS model proposed in [13], though direct comparison is difficult because the experiments in this study were run at higher temperatures (up to 1850°C) than the model accounts for, and many of our experiments were S unsaturated. These data also generally agree with previously published literature values summarized in [14]. While [14] determined that fO_2 , P , and T were the dominant controls of SCSS in silicate melts, our results here imply that melt composition may have a measurable impact upon SCSS as well. The results of this work imply that if the planet Mercury formed under reduced conditions inferred by present surface composition, the elevated sulfur and other volatile abundances measured at the surface may have been transported by reduced silicate melts generated from partial melting of the interior.

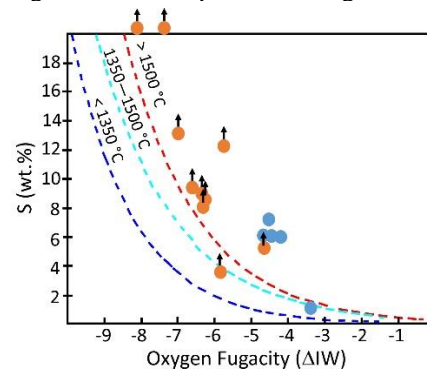


Figure 1. Sulfur wt.% concentrations versus $\log_{10} fO_2$ (relative to the ΔIW oxygen buffer) for experiments in this study, compared to the SCSS models proposed in [13]. Blue circles are experimental runs at sulfide saturation; orange circles with arrows are experimental runs undersaturated with respect to sulfides.

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