

EXPERIMENTAL CONSTRAINTS ON THE CHEMICAL DIFFERENTIATION OF MERCURY'S MANTLE. A. Boujibar¹, K. Righter¹, K. Pando², L. Danielson³, ¹NASA Johnson Space Center, 2101 Nasa Parkway, Houston, TX 77058, ²UTAS – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, ³Jacobs JETS, NASA Johnson Space Center, 2101 NASA Pkwy, Houston, TX 77058 (asmaa.boujibar@nasa.gov).

Introduction: Mercury is known as being the most reduced terrestrial planet with the highest core/mantle ratio. Results from MESSENGER spacecraft have shown that its surface is FeO-poor (2-4 wt%) and S-rich (up to 6-7 wt%) [1-2], which confirms the reducing nature of its silicate mantle [3]. In addition several features suggest important melting stages of the Mercurian mantle: widespread volcanic deposits on its surface [4], a high crustal thickness (~10% of the planet's volume) [5] and chemical compositions of its surface suggesting several stages of differentiation and remelting processes [6]. Therefore it is likely that igneous processes like magma ocean crystallization and continuous melting have induced chemical and mineralogical heterogeneities in the Mercurian mantle.

The extent and nature of compositional variations produced by partial melting remains poorly constrained for the particular compositions of Mercury (very reducing conditions, low FeO-contents and high sulfur-contents). Melting experiments with bulk Mercury-analogue compositions are scarce and with poorly controlled starting compositions. Therefore additional experimental data are needed to better understand the differentiation processes that lead to the observed chemical compositions of Mercury's surface.

Methods: Partial melting experiments have been conducted with a piston cylinder apparatus at NASA JSC using enstatite chondrites (EH4) with variable oxygen fugacity and sulfur content at 1 GPa and temperatures between 1400°C and 1650°C. The f_{O_2} of the experiments was controlled by varying the Si/SiO₂ ratio of the starting composition. Indeed it has been previously shown that the addition of Si metal allows the reduction of the samples. However, the reaction of the sample with the assembly leads usually to partial oxidation of Si, that can yield a SiO₂-enrichment of the silicate [7]. Therefore, instead we chose to vary the Si/SiO₂ ratio, in order to control the f_{O_2} without affecting the elemental ratios of the bulk starting compositions.

We used two starting compositions: the first one with 2 bulk wt% S, 5wt% Si in the starting metal and a 62/38 silicate/metal mass ratio and the second one more reduced with 6 bulk wt% S, 12wt% Si in the starting metal and a 50/50 silicate/metal mass ratio. Experimental run products were analyzed with Cameca and the JEOL EPMA's at NASA JSC. The new data are combined with previous work, and then compared to

the chemical composition of Mercury's surface in order to better understand mantle mineralogy, chemical differentiation processes and evaluate the bulk composition of the planet.

Results:

Oxygen fugacity. The oxygen fugacity of the samples was calculated relative to the IW buffer as a function of the activity coefficients of FeO and Fe in the silicate melt and in the liquid metal respectively. We found f_{O_2} comprised between IW-4.5 and IW-3. FeO content in the silicate melt is found very low (comprised between 0.24 to 0.78 wt%). However its concentration does not present notable differences between the runs performed with the moderately and highly reduced compositions, despite significantly different Si-content of the metals (2-3 wt% Si_{metal} against 12-13 wt% Si_{metal} in the most reduced samples). This can be attributed to the solubility of FeS in the silicates melts at very reducing conditions, as shown in recent studies of [8-9].

Phase proportions. Run products from the SiO₂-poor and the SiO₂-rich compositions are composed of orthopyroxene, silicate melt and liquid metal at high temperature but at low temperature (<1450°C), quartz is also present in the runs synthesized with the SiO₂-rich starting composition. No sulfide phases were observed in all samples, which can be due to sulfur volatilization during the heating of the samples. Indeed mass balance calculations show that at least half the initial content of sulfur was volatilized during sample heating. In addition the samples synthesized with the most S-rich composition are also very reduced, so that S is highly partitioned to the silicate melt (with S-concentrations up to 9 wt% and S partitioning coefficients between metal and silicate of 0.07 to 0.1). Moreover liquidus temperature is lower with the S-rich SiO₂-poor composition (1500°C) in comparison to the S-poor SiO₂-rich composition (1650°C).

Evolution of the melts compositions. The evolution of Al₂O₃ and alkali elements (Na₂O and K₂O) is similar with the two types of compositions. The CaO and MgO are more enriched in the S-rich silicate melts in contrast to SiO₂ which is more depleted in the melts relative to the S-poor samples (**Fig. 1**). This could be due to MgS and CaS solubility in the silicate melts and to the high starting SiO₂ concentration of the S-poor samples.

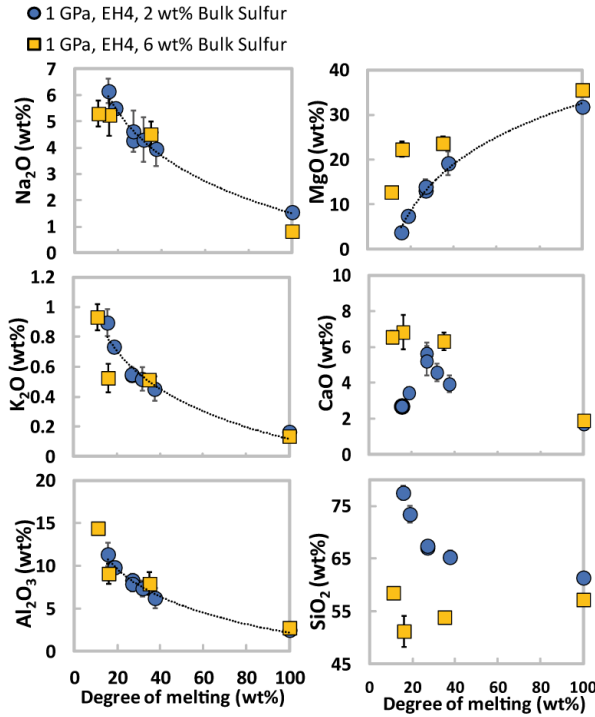


Fig. 1 Chemical composition of the silicate melts as a function the degree of melting of the S-poor SiO_2 -rich EH-like composition (blue circles) and S-rich SiO_2 -poor EH-like composition (yellow squares).

Comparison with previous data and Mercury's surface:

Ca/Si, Mg/Si and Al/Si element ratios of our silicate melts and that of previous studies [7-10] are compared to that of Mercury's surface in **Fig. 2**. We found that the melts produced with the S-poor composition and that previously synthesized at 1 GPa with EH4 Indarch composition [7] have lower Al/Si and Ca/Si ratios than Mercury's surface. This can be originated by the high SiO_2 of both compositions. Indeed, in [7], as stated above, the oxygen fugacity of the samples was controlled by adding Si in the starting metals. However during the equilibration at high pressure and temperature, Si can be oxidized and can yield high SiO_2 concentrations.

In contrast, the compositions of Mercury's surface are in a good match with our silicate melts synthesized with the S-rich starting material and the samples run at 1 bar by [10] with EH4 chondrites. In these run products, the $f\text{O}_2$ was controlled by varying the Si/ SiO_2 ratio. In the present study, this was done directly in the starting powder and in [10] with an external buffer within the gas-mixing furnace.

These results show that the ultramafic surface of Mercury can simply be explained by partial melting of EH chondrites at pressures comprised between 1 bar and 1 GPa and very reducing conditions. The melts observed on the surface of Mercury could have been formed by melting of a chondritic mantle at depths of up to 55 km. Therefore, it is not required to invoke several stages of differentiation and remelting processes to explain the Mercurian surficial compositions derived from MESSENGER results [2] as previously proposed [6]. Further studies to better determine the effect of pressure, S and SiO_2 contents on phase relations and melting processes are underway and will provide better constraints on the physical and chemical properties of the Mercurian mantle.

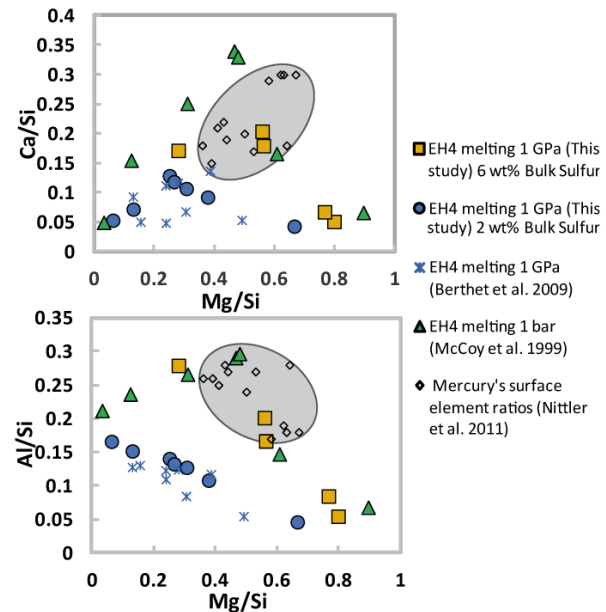


Fig. 2 Comparison between Ca/Si, Al/Si and Mg/Si ratios of Mercury's surface compositions [2] (grey area and diamonds) with the silicate melts obtained in this study (blue circles and yellow squares) and that of [10] (green triangles) and [7] (blue crosses).

References: [1] McClintock W. E. et al. (2008) *Science*, 321, 62-65. [2] Nittler L. R. et al. (2011) *Science*, 333, 1847-1850. [3] Zolotov M. Y. et al. (2013) *JGR*, 118, 138-146. [4] Solomon S. C. et al. (2011) *Planet Space Sci.*, 59, 1827-1828. [5] Padovan S. et al. (2014) *AGU*, P21C-3938. [6] Charlier B. et al. (2013) *Earth & Planet. Sci. Let.* 363, 50-60. [7] Berthet S. et al. (2009) *GCA*, 73, 6402-6420. [8] Malavergne V. et al. (2014) *Earth & Planet. Sci. Let.* 394, 186-197. [9] Boujibar A. et al. (2014) *Earth & Planet. Sci. Let.* 391, 42-54. [10] McCoy T. J. et al. (1999) *Meteoritics & Planet. Sci.*, 34, 735-746.