COMPOSITION AND DIFFERENTIATION OF 'BASALTS' AT THE SURFACE OF MERCURY.

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Introduction: Images of the surface of Mercury by the Mariner 10 and MESSENGER spacecraft reveal that volcanism was widespread and produced kilometer-thick deposits [1-3]. However, Mercury remains heavily cratered and preservation of a pristine upper crust cannot be completely ruled out. Whatever surface rocks represent a primary crust, products of partial melting of the planet's interior, crystallized from a magma ocean [4], or impact melts of these superficial materials, they are the record of early differentiation processes, crust and mantle formation and their evolution through time.

The first MESSENGER measurements of surface elemental abundance ratios by the X-Ray Spectrometer (XRS; [5]) and the Gamma-Ray Spectrometer (GRS; [6]) produced surprises based on expectations and understanding of Mercury prior to MESSENGER's arrival. Volatiles are not depleted and the low FeO content points to highly reduced materials. In this study, elemental ratios obtained by XRS are used to calculate absolute abundances of major elements for surface materials. Melting experiments have been performed on average compositions to constrain their emplacement temperature and the potential mineralogy at the surface of Mercury.

Surface compositions: XRS measurements acquired during solar flares by the MESSENGER spacecraft allow detection of fluorescent signals of elements with atomic numbers up to Fe. Elemental ratios for Mg/Si, Al/Si, S/Si, Ca/Si, Ti/Si and Fe/Si can thus be accurately determined because there are independent of the measurement geometry and the total composition [5]. The elements Si, Ti, Al, Fe, Mg and Ca constitute virtually all the silicate part of the surface material, and element ratios can thus be converted to oxides weight percent with a single possible solution when normalized to 100%. Alkalis (Na and K) and phosphorous are minor elements in these MgO-rich compositions. The ratio S/Si is high and calculated S abundances range from 1.4 to 3.9 wt% S.

Calculations of absolute abundances from element ratios measured by XRS require some assumptions. Major elements are usually considered as oxides in a silicate material. However, under reducing conditions that prevails on Mercury [7], iron mainly occurs as a metal phase. Low-pressure partial melting experiments on the Indarch enstatite chondrite, a potential building block of Mercury, have shown the occurrence of immiscible metallic and sulfide melts associated with the silicate melt [8]. In the temperature range 1200-1450°C relevant for surface basalts of Mercury, a Fe-Ni-Si-rich metal liquid may contain up to 7.7 wt % Si and 80-90 wt % Fe. A sulfide melt dominated by Fe and S also occurs with up to 12 wt % Ca and 12 wt % Mg. Lithophile elements can thus behave partly as chalcophiles and partitioned into iron and sulfur immiscible melts. The speciation of each element should thus be carefully inspected before performing detailed interpretation of silicate melt compositions for Mercury.

'Basalt' compositions: As a first approximation, the partitioning of Si, Fe, Ca and Mg to immiscible metallic and sulfides melt is not considered. Calculated compositions have low iron contents from 0.6 to 4.9 wt% FeO. SiO_2 is high and ranges from 52 to 60 wt%, but the main common characteristic of surface compositions is the high MgO content, from 18 to 27 wt%. Such high MgO is similar to the high-temperature ultramafic komatiites emplaced on Earth, but consideration of all measured elemental abundances point to a composition transitional between basaltic and komatiitic rocks [5]. Two compositional groups are discriminated (Table 1), based primarily on their calcium and alumina contents. Group 1 is characterized by low Al_2O_3 (ca. 8 wt%), high CaO (10 wt%) and high MgO (25-27 wt%). Group 2 contains more Al_2O_3 (12-14 wt%), and less CaO (6-8 wt%) and MgO (18-23 wt%). The normative mineralogy recalculated from bulk analyses shows that Group 1 is essentially made of orthopyroxene, clinopyroxene, plagioclase and minor olivine. Group 2 contains orthopyroxene, plagioclase and quartz. These two compositions are thus separated by the quartz saturation plane, and Group 2 is notably devoid of a clinopyroxene component.

Table 1: Composition of basalts at the surface of Mercury calculated using elemental ratios from XRS measurments of [5].

	Group 1	Group 2
SiO_2	53.6	56.6
TiO_2	0.4	0.6
Al_2O_3	8.3	13.2
FeO	1.4	3.4
MgO	25.9	19.3
CaO	10.3	6.9
Sum	100.0	100.0
Mg#	0.96	0.94

Group I corresponds to the average of measurements 4 and 5 of [5]; Group II is the average of measurements 6, 7, 8 and 10 of [5]. Data are expressed as weight percent.

Low-pressure phase equilibria: Melting experiments have been conducted on calculated average compositions for Group 1 and 2 (Table 1). Compositions of Group 1 are located in the olivine stability field and crystallize olivine as the liquidus mineral at 1440°C. Olivine crystallization is followed by protoenstatite (1322°C) and orthoenstatite (1300°C), which are different structural types of low-Ca pyroxene. Diopside appears at 1250°C. Plagioclase has been observed at 1200°C. Compositions of Group 2 are slightly quartz normative and located in the protoenstatite stability field which starts crystallizing at 1350°C. Orthoenstatite follows at 1224°C and plagioclase and quartz appear together on the liquidus at 1200°C. Group 2 does not crystallize clinopyroxene. The two compositional groups cannot be related to each other by any fractionation process at low or high pressures.

The role of sulfur: The concentration of S is correlated with that of Ca. This suggests the potential occurrence of minerals such as oldhamite (Ca,Mg)S at the surface of the planet. The two different groups we identified (mainly based on the presence or not of a clinopyroxene component in the bulk composition) might simply be related by various oldhamite proportions. In this case, both basaltic compositions would lack a significant clinopyroxene component. If the abundance of (Ca,Mg)S minerals is the main factor of compositional variations of basalts, the surface of the planet would then seem relatively homogeneous with basalts composed of orthopyroxene, plagioclase and minor quartz components. Alternatively, if S occurs in immiscible sulfide melts that contain a lower amount of Ca (maximum 12% Ca in [8]), the difference between the two types would persist.

Melt viscosities: Chemical and thermal characteristics of lavas at the surface Mercury have direct implications for the dynamics of eruption and lavas flows. Calculations of viscosities [9] for surface basalts at the liquidus temperature, 1455°C for Group 1 and 1372°C for Group 2, range from 0.8 to 1 Pa.s which is at the lower limit of any measured silicate melt. This is consistent with the high-temperature low viscosity emplacement styles observed on Mercury [3].

Conclusions: In order to estimate the composition of basaltic rocks at the surface of Mercury, the speciation of the different elements should be investigated in detail. Understanding the distribution of Ca (and Mg) between the silicate melt and immiscible sulfur melts or sulfur minerals such as oldhamite is particularly critical. The presence of different types of basalts at the surface of Mercury could be an indicator of a differentiated interior and could inform us on the composition of the elemental building blocks, their early history of

melting and transport, and implications for Mercury's internal structure [10].

References: [1] Robinson M. S. and Lucey P. G. (1997) *Science*, 275, 197-200. [2] Head J. W. et al. (2008), *Science,* 321, 69-72. [3] Head J. W. et al., *Science,* 333, 1853-1856. [4] Brown S. M. and Elkins-Tanton L. T., *EPSL*, 286, 446-455. [5] Nittler L. R. et al. (2011), *Science,* 333, 1847-1850. [6] Peplowski P. N. et al. (2011), *Science,* 333, 1850-1852. [7] Malavergne V. et al. (2010), *Icarus*, 206, 199-209. [8] McCoy T. J. et al. (1999), *Meteoritics & Planet. Sci.*, 34, 735-746. [9] Giordano D. et al. (2008), *EPSL*, 271, 123-134. [10] Smith D. E. wr al. (2011) submitted to *Science.*