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Phase equilibria of ultramafic compositions on Mercury and the origin of the compositional dichotomy

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ABSTRACT

Measurements of major element ratios obtained by the MESSENGER spacecraft using x-ray fluorescence spectra are used to calculate absolute element abundances of lavas at the surface of Mercury. We discuss calculation methods and assumptions that take into account the distribution of major elements between silicate, metal, and sulfide components and the potential occurrence of sulfide minerals under reduced conditions. These first compositional data, which represent large areas of mixed high-reflectance volcanic plains and low-reflectance materials and do not include the northern volcanic plains, share common silica- and magnesium-rich characteristics. They are most similar to terrestrial volcanic rocks known as basaltic komatiites. Two compositional groups are distinguished by the presence or absence of a clinopyroxene component. Melting experiments at one atmosphere on the average compositions of each of the two groups constrain the potential mineralogy at Mercury's surface, which should be dominated by orthopyroxene (protoenstatite and orthoenstatite), plagioclase, minor olivine if any, clinopyroxene (augite), and tridymite. The two compositional groups cannot be related to each other by any fractional crystallization process, suggesting differentiated source compositions for the two components and implying multi-stage differentiation and remelting processes for Mercury. Comparison with high-pressure phase equilibria supports partial melting at pressure < 10 kbar, in agreement with last equilibration of the melts close to the crust–mantle boundary with two different mantle lithologies (harzburgite and lherzolite). Magma ocean crystallization followed by adiabatic decompression of mantle layers during cumulate overturn and/or convection would have produced adequate conditions to explain surface compositions. The surface of Mercury is not an unmodified quenched crust of primordial bulk planetary composition. Ultramafic lavas from Mercury have high liquidus temperatures (1450–1350 °C) and very low viscosities, in accordance with the eruption style characterized by flooding of pre-existing impact craters by lava and absence of central volcanoes.

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1. Introduction

Images of the surface of Mercury by Mariner 10 (e.g. Strom et al., 1975; Robinson and Lucey, 1997) revealed plains materials whose origin was debated, and not until additional, higher resolution images were acquired by the Mercury Surface, Space Environment, Geochemistry, and Ranging (MESSENGER) spacecraft did it become apparent that surface volcanism was widespread and produced kilometer-thick deposits (Head et al., 2008, 2011). Many pyroclastic deposits have also been identified (Rava and Hapke, 1987; Kerber et al., 2011). The crater deficiency of Mercury compared to the Moon even suggests that most of its surface has been volcanically resurfaced by intercrater plain emplacement (Fassett et al., 2011, 2012). Therefore, a substantial

portion of the crust did certainly originate volcanically (Denevi et al., 2009). However, there are also some areas of Mercury that are heavily cratered and these might represent ancient surfaces, so that local preservation of a pristine upper crust cannot be completely ruled out. Surface rocks may thus represent a primary crust, possibly crystallized from a magma ocean (Brown and Elkins-Tanton, 2009), impact melts of superficial crustal materials, or products of partial melting of the planet's interior. Composition and origin of surface rocks thus provide a direct record of early planetary differentiation, crust and mantle formation, and evolution of these chemical reservoirs through time.

The first measurements of surface elemental abundance ratios by MESSENGER's X-Ray Spectrometer (XRS; Nittler et al., 2011) and the Gamma-Ray Spectrometer (GRS; Peplowski et al., 2011) produced surprises based on expectations and understanding of Mercury prior to the satellite's arrival. Some volatile elements (K and S) are not depleted and the low FeO content of the surface points to highly reduced conditions (Wadhwa, 2008; Malavergne

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et al., 2010; Zolotov, 2011; McCubbin et al., 2012). This suggests that chondritic materials are probably the building blocks of the planet, possibly either enstatite chondrite or bencubbinite (Wasson, 1988; Taylor and Scott, 2003; Malavergne et al., 2010).

In this study, XRS elemental ratios presented by Nittler et al. (2011) are used to calculate absolute abundances of major elements for surface materials. Data treated in this study do not include the northern volcanic plains described by Head et al. (2011). The ten XRS measurements discussed here have been acquired at high altitudes and thus cover large areas averaging the composition of various units (Fig. 1a), essentially a mixture of high-reflectance plains and a low-reflectance material (Head et al., 2008; Denevi et al., 2009). We discuss calculation methods and assumptions to take into account the speciation of major elements under reduced conditions relevant for Mercury. We evaluate the partitioning of major elements between silicate, metallic and sulfide melts and the nature and abundance of sulfide minerals at the surface of the planet. Calculated compositions are compared to terrestrial ultramafic compositions and the appropriate nomenclature for lavas on Mercury is presented. Two compositional groups have been identified and one-atmosphere melting experiments are presented for each average composition to constrain their emplacement temperature, crystallization paths and the potential mineralogy at the surface of Mercury. We also explore the physical properties of magmas on Mercury and discuss the implications of these compositional groups for the differentiation and melting processes on Mercury.

2. Surface compositions: calculations and assumptions

XRS measurements acquired during solar flares by MESSENGER allow detection of fluorescent signals of elements with atomic numbers up to that of Fe. The X-ray spectrum corresponds to the very surface with a maximum sampling depth of 100 μm . Elemental ratios for Mg/Si, Al/Si, S/Si, Ca/Si, Ti/Si and Fe/Si have been determined because ratios are largely independent of the measurement geometry and the total composition (Schlemm et al., 2007; Nittler et al., 2011).

Calculation of the absolute abundances from element ratios requires some assumptions. In silicate materials, major elements are usually considered to occur as oxides. However, under the reducing conditions that prevail on Mercury, estimated to be between 2.6 and 6.5 log units below the iron–wüstite buffer (Malavergne et al., 2010; Zolotov, 2011; McCubbin et al., 2012), iron occurs mainly as a

metal phase or as a sulfide. Low- and high-pressure partial melting experiments at low $f\text{O}_2$ on the Indarch enstatite chondrite (McCoy et al., 1999; Berthet et al., 2009), a potential building block of Mercury (Wasson, 1988; Brown and Elkins-Tanton, 2009), have shown that immiscible metallic and sulfide melts are in equilibrium with the silicate melt. These iron and sulfide immiscible melts contain significant amounts of Si, Ca and Mg, showing that lithophile elements behave partly as siderophile and chalcophile elements under reducing conditions. The speciation of each element should thus be carefully evaluated before performing detailed interpretation of silicate melt compositions for Mercury.

2.1. Calculations on an oxide basis

The silicate part of the surface material of Mercury mainly contains the elements Si, Ti, Al, Fe, Mg, Ca and O. Consequently, element ratios relative to Si measured for these elements can be converted to oxides weight percent with a single possible solution when the total is normalized to 100% and oxygen is assumed to be the only anion. Alkalis (Na and K), manganese and phosphorous are first considered as minor elements in these MgO-rich compositions (see later for the potential effect of sodium). For example, MESSENGER's gamma-ray spectrometer measured an average of 0.28 ± 0.05 wt% K_2O in surface materials (Peplowski et al., 2011). This initial estimate considers only the silicate component of the XRS measurements. The effects of partitioning of Si, Fe, Ca and Mg between a silicate and immiscible metallic and sulfide melts are then considered and discussed.

Calculated compositions have low iron and titanium contents, from 0.6 to 4.9 wt% FeO and 0.3–1.3 wt% TiO_2 (Table 1). The low iron content confirms previous interpretations based on multispectral images (Blewett et al., 1997; McClintock et al., 2008) but the low titanium contents do not support a significant contribution by Ti-oxides in producing low-reflectance materials (Denevi et al., 2009; Riner et al., 2009, 2010, 2011; Sprague et al., 2009; Lawrence et al., 2010). The SiO_2 content is high and ranges from 52 to 60 wt%. Two compositional groups are distinguishable, mainly based on their calcium and aluminum contents (Fig. 1b). Group 1 (G1) has low Al_2O_3 (ca. 8 wt%), high CaO (10 wt%) and high MgO (25–27 wt%). Group 2 (G2) contains more Al_2O_3 (12–14 wt%), and less CaO (6–8 wt%) and lower MgO (18–23 wt%). Average compositions have been calculated for these two groups using XRS data that also include measurements for Ti/Si and Fe/Si ratios (Table 1).

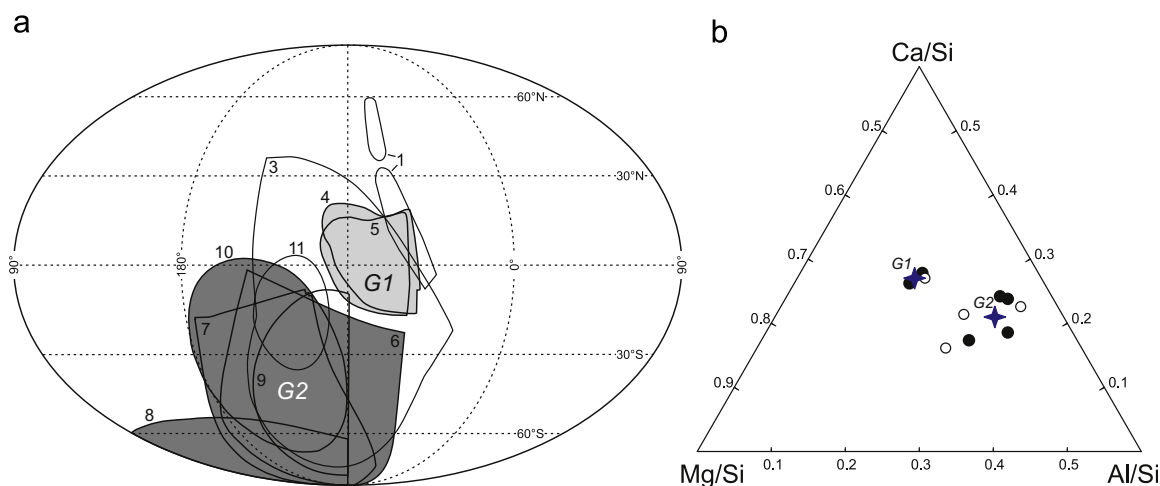


Fig. 1. XRS data from Nittler et al. (2011) for surface composition of Mercury. (a) Footprints sampled by XRS during measured solar flares, numbered according to Table 1. Light grey corresponds to the region for average composition G1 (data 4 and 5), dark grey is for average composition G2 (data 6, 7, 8 and 10). (b) Ternary diagram with Mg/Si, Ca/Si and Al/Si mass ratios. Black circles are data used to calculate average compositions (stars) for Group 1 (G1) and Group 2 (G2). White circles are data for which Fe/Si and Ti/Si were not acquired (data 1, 3, 9 and 11 of Table 1).

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