

ARE SMALL DIFFERENCES IN PHOSPHOROUS CONTENT RESPONSIBLE FOR LARGE DIFFERENCES IN THE COMPOSITION OF TERRESTRIAL AND MARTIAN MAGMATIC ROCKS?

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Introduction: The composition of magmatic rocks from Mars is constrained by three distinct but complementary sources of information. These are, *in-situ* analyses at the hand-sample scale performed by landers or rovers at the Martian surface (e.g. Viking, Pathfinder, MER), orbital measurements at the planetary scale (e.g. the Gamma Ray Spectrometer onboard Mars Odyssey, or the OMEGA instrument onboard Mars Express) and the Shergottite-Nakhlite-Chassignite (SNC) group of meteorites generally accepted to be of Martian origin. The quantity and quality of the data available has increased dramatically over the past few years, providing unprecedented insight into the details of the chemistry and mineralogy of Martian rocks. When all data are considered, it is immediately apparent that rocks from Mars show many important differences compared to their Terrestrial counterparts. For example, one of the most striking features of volcanic rocks from Mars is that they are significantly richer in iron and poorer in silica than lavas produced by partial melting of the Earth's mantle. The iron-rich nature of Martian volcanics has been attributed to a higher FeO content of the Martian mantle compared to that of the Earth [1], while the low silica content has no widely accepted explanation. It is also of note that the SNC meteorites generally show superchondritic Ca/Al, an observation which contrasts with most terrestrial basalts, and which places constraints on the composition of the mantle source which produced the SNC's [2].

A phosphorous-rich silicate Mars. In addition to these differences in major-element chemistry, the available analyses of Martian rocks suggest that the sampled silicate portion of Mars is significantly richer in phosphorous than the Earth's crust/ upper mantle. Although the difference in absolute concentration is modest (<0.2 wt% P₂O₅), if P-content is compared to that of titanium (another incompatible high field-strength element), it is found that both SNC meteorites [3] and *in-situ* analyses of the MER rovers [4] show a P₂O₅/TiO₂ ratio of ~1, a value 10 times greater than that of typical Terrestrial mid-ocean ridge basalts. This difference may be perfectly explained by the fact that P is a moderately siderophile element which will be partitioned between its metallic form (in the core) and its oxidized form (in the mantle). Given the stoichiometry of the reaction governing this partitioning ($2P + 2.5O_2 \rightleftharpoons P_2O_5$) thermodynamic consid-

erations imply that the P₂O₅ content of the mantle will be a sensitive function of oxygen fugacity (fO₂). Indeed, variations in the P-content of the mantle will be far more sensitive to variations in fO₂ than elements of lower valence, such as Fe, because of the different number of O₂ involved in the oxidization reaction. A rapid calculation shows that if the Martian mantle is enriched in Fe relative to the Earth's mantle by a factor of 2.5 [1], and that this difference is due exclusively to a difference in oxygen fugacity (Mars being more oxidized), a ten-fold increase in the P₂O₅ content of silicate Mars relative to silicate Earth is to be expected.

What implications of a P-rich silicate Mars? The idea that the Martian mantle is P-rich compared to that of the Earth is not new. On the other hand, no particular importance has been attached to this observation, and it is the aim of this contribution to make the case that this difference may have far reaching consequences, from both a chemical and physical perspective. Published experimental data and the thermodynamic calculator p-MELTS developed by Ghiorso and co-workers [5] are used for this purpose. The validity of this latter approach has been assessed based upon comparison of predicted and experimental results of [6] for an iron-rich bulk composition.

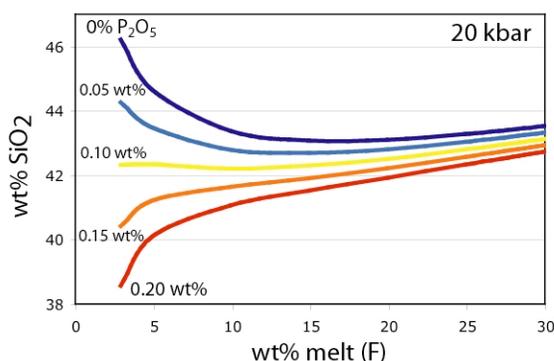


Figure 1. Predicted variation of silica content (using pMELTS) of liquids produced by partial melting at 20kb of the bulk composition of Dreibus and Wänke [1]. The bulk wt% P₂O₅ of the system was varied as shown by curves of different color.

Liquids produced by partial melting. One of the most dramatic influences of the addition of small amounts of phosphorous to a peridotite assemblage concerns the compositions of liquids produced by partial melting. At fixed pressure and in the absence of phosphorus low degree partial melts are enriched in

silica, increasing degrees of melting leading to decreasing silica content, as long as Cpx remains in the residue (see Fig. 1). This behavior is well known in the Terrestrial mantle, and is the consequence of low-degree partial melts being rich in alkalis [7]. However, with increasing phosphorous content in the bulk system, low degree partial melts become increasingly poor in silica for a given degree of partial melting, this effect being greatest for small melt fractions (Fig. 1). This effect may be understood in terms of the fact that phosphorous is known to dramatically affect the silica activity of silicate melts because of its unusual structural role [8] as elegantly demonstrated by the experimental results of [9]. Given that the bulk Martian mantle contains an approximated 0.17wt% P_2O_5 [1], consideration of Fig. 1 suggests that, in contrast to the case of the Earth, low degree partial melts on Mars will be particularly silica-poor, and that increasing degree of partial melting will tend to increase the silica content of liquids produced. The difference in silica content between liquids produced from a mantle with 0 and 0.2 wt% P_2O_5 is almost 10wt% SiO_2 when the degree of partial melting is 3%, a value more or less independent of pressure (Fig. 2). Furthermore, the addition of P_2O_5 is also found to increase the Ca/Al ratio of liquids significantly, as illustrated in Fig. 3.

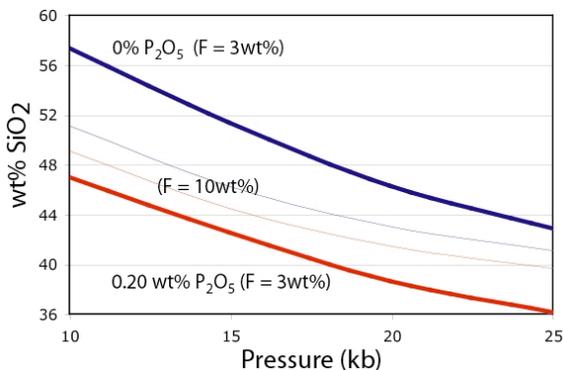


Figure 2. Predicted variation of silica content (using pMELTS) of liquids produced by partial melting of bulk compositions containing 0% (blue curves) and 0.2wt% P_2O_5 (red curves) as a function of pressure. Thick lines are for liquids produced by 3% melting and thin lines for 10%.

Crystallization sequences. In addition to the importance of phosphorous during partial melting, experimental studies have shown that P is a highly efficient flux, suppressing the crystallization of a variety of silicate and oxide minerals [10]. In this respect the fact that P strongly inhibits the crystallization of magnetite [10] may contribute to the fact that Martian volcanics can reach very high FeO contents. Furthermore, the increase in silica activity caused by the presence of P has been demonstrated to stabilize low-Ca pyroxene (pigeonite) rather than olivine on the liquidus [10], an

effect which may have important bearing on the relative proportions of mafic minerals in the Noachian crust [11].

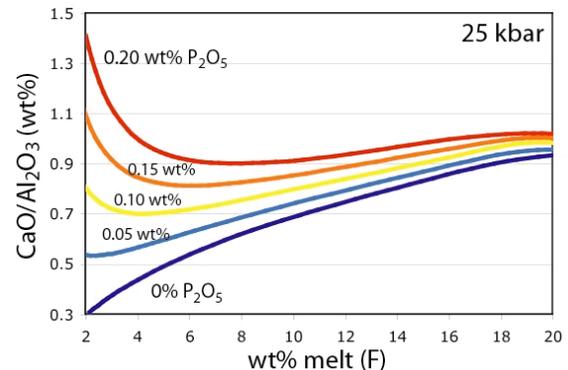


Figure 3. Predicted variation of CaO/Al₂O₃ (using pMELTS) of liquids produced by partial melting at 25kbar of the bulk composition of [1] (see Fig. 1).

Implications for the transport of magmatic liquids. Further to the chemical consequences discussed above, the difference in P-content between the Earth and Mars may also lead to very different transport mechanisms of magmatic liquids. For example, in the Martian mantle, low degree partial melts will have viscosities significantly lower than comparable terrestrial liquids, leading to more efficient transport (a difference of almost an order of magnitude is calculated for a 3% melt). At the surface, the fluxing effect of P may inhibit crystallization and be a significant factor contributing to the morphology of Martian lava flows.

Conclusions. There is little doubt that the Martian mantle is significantly richer in P_2O_5 than that of the Earth, an observation which may be explained in terms of a difference in oxidation state. This difference may have fundamental consequences for the generation and crystallization of magmatic liquids, and may explain many of the first-order differences between the composition and mineralogy of the rocks near the surface of Mars and the Earth.

References: [1] Dreibus G. and Wänke H. (1985) *Meteoritics*, 20, 267-381. [2] Agee C.B. and Draper D.S (2004) *EPSL*, 224, 415-429. [3] Lodders K. (1998) *MAPS*, 33, A183-190. [4] Gellert R. et al. (2005) *JGR*, 111, E02S05. [5] Ghiorso M.S. et al. (2002) *G3*, 3, doi 10.1029/2001GC000217. [6] Bertka C.M. and Holloway J.R. (1994) *Contrib. Mineral Petrol.*, 115, 323-338. [7] Hirschmann M.M. et al., (1998) *GCA*, 62, 883-892. [8] Gan H. and Hess P.C. (1992) *Am. Mineral.* 77, 495-506. [9] Kushiro I. (1976) *AmJSci.*, 275, 411-431. [10] Toplis M.J. et al. (1994) *GCA*, 58, 797-810. [11] Mustard J.F. et al. (2007) *7th Mars Conf.* Rogers A.D. and Christensen P.R. (2007) *JGR*, 112, E01003. Poulet F. et al. (2008) *LPSC* this volume. Pinet P.C. et al. (2007) *7th Mars Conf. abstract 3146*.