Differential changes in Ni^{2+}, Co^{2+} and Fe^{2+} coordination in silicate melt with pressure

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It is currently debated whether siderophile element abundances in the Earth's mantle reflect single-stage metal-silicate equilibration at high pressure at the base of an extensive magma ocean (homogeneous accretion), or the mixing of differentiated protoplanets each with a core formed at low pressures (heterogeneous accretion). This question has been addressed by parameterizing metal/silicate partition coefficients of siderophiles such as Ni, Co and Fe as a function of pressure, temperature and other variables, and extrapolating these parameterizations to determine P-T conditions that reconcile observed mantle abundances. Implicit in these parameterizations is that the partial molar volumes vary monotonically with pressure. XANES spectroscopy shows that the average coordination of Ni^{2+} in silicate glasses recovered from melts quenched at pressure, changes from tetrahedral to octahedral between 1 and 4 GPa, while that of Co^{2+} and Fe^{2+} remain unchanged. The effects of this transition are clearly mirrored in the distribution coefficients between iridium metal and silicate melt measured over the same range, showing that the quenched glasses reflect the liquid state at P and T. The partitioning can be modelled using different values of the partial molar volume of tetrahedral and octahedral NiO in the silicate melts. Changes in coordination environment of each siderophile in silicate melts will generally occur over different pressure intervals, preventing simple extrapolation of metal/silicate partitioning. The results enable an improved parameterization of the pressure dependence of Fe-Ni-Co partitioning, which excludes the simple single-stage magma-ocean hypothesis.

Martian magmatic volatiles recorded in olivine-bearing melt inclusions and matrix of shergottite Y-980459

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Martian basaltic meteorites [shergottites] contain a wealth of information about Mars. Of particular interest is the geochemical record contained in melt inclusions from the most primitive shergottite, Yamato 980459 (Y98). Using polished sections of Y98 mounted in indium to avoid volatile contamination from epoxy, our ion- and electron-microprobe study aims to constrain the volatile contents of primary Martian magmas generated by mantle melting. This record is also used to track the subsequent melt evolution of shergottite magmas. We report preliminary results for volatile abundances (H_2O, CO_2, S, Cl, F) in olivine-hosted melt inclusions (MI) and groundmass glasses (GG).

Unlike other shergottites, MIs in Y98 have remained glassy because of rapid cooling following eruption. Volatile concentrations of MI and GG in Y98 were analyzed by a Cameca ims-6f at DTM following the techniques of [1]. MIs contain distinctly higher contents of H_2O (~200 ppm) and CO_2 (600-1600 ppm) than GGs (<100 ppm H_2O and <20 ppm CO_2). In contrast, the MIs contain lower amounts of F (~15 ppm) and S (~900 ppm) than those in the GGs (~25 ppm F and 2200-3000 ppm S). Cl contents are almost constant among the MIs and GGs (~50 ppm). The CO_2 solubility in basaltic magmas suggests that the MIs were trapped at a depth of ~3 kbar. The pre-erupted magmatic water contents recorded in the Y98 MIs are ~2 orders of magnitudes lower than those proposed by the wet shergottite magma hypothesis (e.g. 1.8 % [2]), although the absolute water abundances in the MIs may have been changed by post-entrapment modifications. By using Na as an indicator of the degree of crystal fractionation (mainly olivine + pyroxene), the degree of degassing between pre-erupted (MI) and erupted (GG) Y98 melts are estimated as follows: CO_2 (~100 %) > H_2O (>80%) > Cl (50-70 %) > F (~0 %) ≈ S (~0 %, probably saturated with sulfide). Likewise, we estimate that the bulk Y98 liquid contained <30 ppm H_2O, 200-500 ppm CO_2, ~20 ppm Cl, ~5 ppm F, and ~300 ppm S.

[1] Hauri *et al.* (2002) *Chem. Geol.* **183**, 99-114. [2] McSween *et al.* (2001) *Nature* **409**, 487-490.