

Methane solubility under reduced conditions in a haplobasaltic liquid, applicable to degassing of magma ocean

P. ARDIA^{1*}, A.C. WITHERS¹, M.M. HIRSCHMANN¹ AND R.L. HERVIG²

¹University of Minnesota, Dept. of Earth Sciences, 108 Pillsbury Hall, Minneapolis, MN 55455
(*correspondance: pardia@umn.edu);

²Arizona State University, School of Earth and Space Exploration, Tempe, AZ 85287, USA

Oxygen fugacity (fO_2) may have a critical influence on the solubility of volatiles in silicate liquids, which in turn influences fluxes of volatiles from planetary interiors to their atmospheres. Carbon dissolves in oxidized basic melts as carbonate but under reduced conditions is limited by precipitation as graphite or diamond. At conditions where melt is in equilibrium with Fe alloy, the carbonate solubility will not exceed few ppm [1], limiting volcanogenic transport of C to the atmosphere. Therefore, dissolved C-H species may dominate C solubility and transport at low fO_2 [2][3].

We investigated the solubility of C-O-H fluid in a haplobasaltic melt ($Di_{40}An_{42}Ab_{18}$), adding C as $Si_5C_{12}H_{36}+H_2O$ to produce $SiO_2+CH_4+H_2$ and H_2O . Experiments were performed at 0.7, 1.5, 2.0 and 3.0 GPa at 1400°C and the fO_2 was buffered using a double Pt-capsule technique, where the external buffer (e.b.) fixed the fH_2 by transport across a H-permeable Pt barrier, and the internal buffer (i.b.) set the fO_2 of the silicate charge. We used three buffer combinations: 1) e.b. with Fe-FeO-Fe₃C-H₂O and i.b. with graphite; 2) e.b. with Fe-FeO-H₂O and i.b. Si^0 ; 3) e.b. with Ni-NiO-H₂O and i.b. Si^0 . We examined resulting glasses by optical and SEM microscopy to establish equilibrium coexistence of the melt with a fluid phase and verified glass compositions with EMPA. Dissolved volatile species were identified by microRaman spectroscopy and OH and C concentrations were quantified by FTIR and SIMS, respectively. Results show that C dissolves as methane together with OH and H₂ in equilibrium with a volatile phase composed chiefly of CH₄ and H₂. At IW to IW-2 (buffer 1) the dissolved C increases linearly with pressure from 70 ppm at 0.7 GPa to 360 ppm at 3.0 GPa. Methane may therefore be the dominant C species outgassed from reduced planetary mantles.

[1] Hirschmann and Withers 2008, *EPSL* **270**, 147-155. [2] Mysen *et al.*, 2009, *GCA* **73**, 1696-1710. [3] Kadik *et al.*, 2010, *Geochemistry Int.* **48**, 953-960

Mobilization of Pb from weathered shots at a firing range in Athens, Greece

A. ARGYRAKI^{1*}, A. GODELITSAS¹, N. PETRAKAKI¹, J.M. ASTILLEROS² AND A. KARAGEORGIS³

¹University of Athens, 15784 Zographou, Athens, Greece
(*correspondance argyraki@geol.uoa.gr)

²Univ. Complutense Madrid, E-2804 Madrid, Spain

³HCMR, PO Box 712 Anavyssos, Greece

The dispersion and accumulation of Pb and other heavy metals in soil depends on their source as well as interactions between the soil solution and mineral components, resulting in dissolution and precipitation of new solid phases which incorporate the metals. This research focused on mobilization of Pb from shots exposed to weathering within a recreational area in Athens, Greece. Parts of the study area were used in the past as firing ranges. Lead in surface soil was measured by AAS after dissolution with aqua regia and concentration values reached a maximum of 2400 mg g⁻¹ with a median of 114 mg g⁻¹. Samples were subsequently collected from two vertical soil profiles located close to the areas with the highest measured Pb concentrations and analyzed by XRF in order to produce Pb profiles up to a depth of 0.5 m and investigate the downwards migration of Pb. The analytical results were interpreted in conjunction with XRD data and SEM observations on soil samples. An abrupt, ten-fold decrease of Pb soil content was observed within the upper 10 cm at both profiles. The fate of metallic Pb in soil was further studied through two experiments. The first, involved burial of unused Pb shots in uncontaminated soil at the wider area of the studied site which lithologically consists of carbonate and ophiolite rock. After a period of 4 months the shots were removed from soil. Study by SEM confirmed the formation of hydrocerussite crystals on their surface. The second experiment involved in-situ AFM in contact mode to directly monitor changes in surface microtopography of metallic Pb reacting with an aqueous solution of CO₂ at pH = 4. Data from this experiment indicated a rapid growth of Pb hydroxycarbonate phase from about 7 min to about 11 min from exposure.

In conclusion, the combination of chemical analyses and microscopic techniques contributed to the understanding of Pb mobilization process during weathering of Pb shots. This includes rapid formation of Pb carbonate phases on the surface of shots and their subsequent dissolution under surface soil conditions. Lead starts migrating downwards and is effectively immobilized through formation of secondary Pb hydroxycarbonate phases within the upper 10 cm of soil.