Essential aqueous geochemistry of Pb(II) solid formation

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Lead is a biologically non-essential toxic metal whose biogeochemical cycle has been affected considerably by anthropogenic activities [1]. Its mobility in aqueous environments is determined by its abillity to form soluble complexes with organic matter [2], adsorbed complexes on Fe, Mn and Al oxide surfaces [3], and most of all a great variety of solids with major anions such as O^{2-}, hydroxyl, carbonate, sulfate, and nitrate [4]. However, the essential aqueous geochemistry of lead has serious gaps of knowledge. In particular, a dubious $Pb(OH)_2$ solid phase has been proposed [4,5], but never identified, and solubility product constant values with up to four orders of magnitude differences have been reported [6] and incorporated in the databases of the different geochemical speciation codes available. The goal of this work was to test the existence of this hydroxide phase and the validity of its solubility constants.

The solids formed in perchlorate and nitrate electrolyte systems, under closed and open atmospheric CO_2 conditions, were identified by X-ray diffraction and other spectroscopies. We show that no solid phase of $Pb(OH)_2$ is formed at any pH value, and thus the concentrations of aqueous Pb(II) are controlled by the solubilities of solid oxide phases and combinations of carbonates and hydroxi-carbonates, depending on the conditions imposed on the system. Therefore, widespread geochemical databases must be corrected to exclude $Pb(OH)_2$ as an actual Pb(II) solid phase forming, to yield more accurate aqueous Pb(II) solubility behavior predictions.

[1] Boutron et al. (1983) Geochim. Cosmochim. Acta 47, 1355-1368. [2] Pinheiro et al. (1999) Environ. Sci. Technol. 33, 3398-3404. [3] Mckenzie et. al. (1980) Aust. J. Soil Res. 18, 61-73. [4] Elkhatib et al. (1991) Environ. Pollut. 69, 269-276. [5] Liu et al. (1989) J. Colloid Interface Sci. 130, 101-111. [6]Liu et al. (2003) J. Colloid Interface Sci. 268, 266-269.

Evaporation of Mg- and Si-rich melts: evolution of chemical and isotopic compositions of FUN CAIs

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Extremely large mass-dependent fractionations of Si, Mg and O isotopes in FUN CAIs suggest that their precursors lost significant amount of matter by evaporation. Chemical and Mg, Si and O isotopic compositions of the residues produced by evaporation of forsterite-rich melts (FUN1 and FUN2) in vacuum at 1900ºC suggest that the evaporating component is Mg_2SiO_4 [1]. The evaporation trajectories of FUN1 and FUN2 pass close to the compositions of C1 and Vig1623-5 FUN CAIs, and the measured Mg and Si isotopic compositions of most natural FUN CAIs also plot close to the correlation lines established by the evaporation residues [1].

To test if evaporation of melts with compositions different from the forsteritic melts would result in residues with chemical and isotopic compositions of C1 and 1623-5, we conducted new sets of experiments in which FUN3 and FUN5 melts were evaporated at the same conditions as earlier. Starting FUN3 and FUN5 compositions were obtained by adding MgO and SiO_2 to the C1 (FUN3) and 1623-5 (FUN5) in the amounts required by enrichments in heavy Mg and Si isotopes in these CAIs.
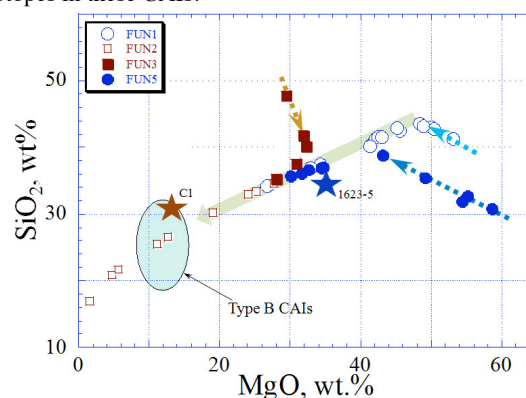
After initial predominant loss of Si (FUN3) or Mg (FUN5), further evaporation results in loss of Si and Mg in forsteritic proportions (constant a_{MgO}/a_{SiO_2} in the melt) and the evaporation trajectories are the same as established by FUN1 and FUN2 melts.

[1] Mendybaev et al. (2013) 44th LPSC, Abstract #3017.