Study of Pb isotopic compositions during metallurgical slags leaching experiments

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Chemical leaching of both Lead Blast Furnace (LBF) and Imperial Smelting Furnace (ISF) slags were conducted at different pH (4, 5.5, 7, 8.5 and 10) under open air and nitrogen atmospheres. LBF and ISF slags contain 3.62 wt% and 1.26 wt% of Pb, as metallic droplets embedded in CaO-SiO-FeO matrix. According to total acid digestion, ISF slag exhibits a more radiogenic composition ($^{206}Pb/^{207}Pb$: 1.1479 ± 0.0018) than LBF ($^{206}Pb/^{207}Pb$: 1.0733 ± 0.0018) for which the ratios are comparable to previous studies [1].

Dissolved Pb constantly increases with time in ISF (and to a lesser extend LBF) leaching solutions under open-air atm., which is consistent with SEM imaging of weathered slags, showing the increasing weathering of slag's surface over the long term period, releasing Pb included in metallic droplets. On the contrary, dissolved Pb quickly reaches a plateau under N₂ atm. This difference may be related to Pb precipitates formed in both cases: few Pb(OH)₂ were formed for both LBF and ISF under N₂ atm. at pH 8.5, whereas PbO₂, PbCO₃ and Pb₃(CO₃)(OH)₂ are controlling the dissolved Pb under open-air atm. for both slags. Furthermore, the Pb concentration remains higher at pH 10 than at pH 8.5 in both slag leachates, with 4 mg L⁻¹ and 1 mg L⁻¹, resp.

Globally, ISF slag dissolution under open-air atm. is related to a more radiogenic Pb isotopic composition in the leachates, compared to N₂ atmo. experiments: ²⁰⁶Pb/²⁰⁷Pb in leaching solution was typically 1.1569 \pm 0.006 and 1.1378 \pm 0.002, resp. at pH 10. Moreover, ²⁰⁶Pb/²⁰⁷Pb remains close to the bulk slag value at pH 8.5, with values of 1.1495 \pm 0.002 and 1.1477 \pm 0.002, under N₂ atm and open-air atm., resp. Under N₂ atmosphere the ²⁰⁶Pb/²⁰⁷Pb ratio in LBF slag leachate displays extremely radiogenic values compared to initial bulk ratio (i.e. i.e. 1.0806 \pm 0.002 and 1.0785 \pm 0.001 at pH 8.5 and 10, resp. against 1.0733 \pm 0.002). Thus, assuming an homogeneous isotopic composition of lead included in metallic droplets, such results would indicate an isotopic fractionation during dissolution and/or sorption processes. Allende Chondrule Chronology Revisited: Eroding Age Gap between CAIs and Chondrules

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We have recently suggested [1-3] that carbonaceous chondrites, as undifferentiated primitive objects formed in the protoplanetary disk, were accreted very early, within the first 1 Ma at the beginning of the Solar System. We have further suggested that the current ⁵³Mn-⁵³Cr data for bulk carbonaceous chondrites [1-3] imply that chondrules in them must also have formed early, given the logical necessity of forming chondrules first before accreting chondrites (we need "sand grains" first to form the cosmic "sandstone"). This argument was supported by examination of Allende chondrules with ultra high precision Mn-Cr isotope systematics [2]. This simple temporal relationship is at odds with the currently accepted paradigm of chondrule chronology of ²⁶Al-²⁶Mg and some Pb-Pb ages [e.g., 4, 5], which at face value requires a minimum age gap between CAIs and chondrules by 2-3 Ma. However, a younger chondrule age poses a serious dynamic problem for the early solar nebula, known as the "storage problem" [6], namely, how could CAIsized particle float in the protoplanetary disk for over 2-3 Ma until chondrules form, then accrete together to form chondrite, without facing head wind and spiraling into the Sun rapidly. Gas drag would efficiently remove the CAI-sized dust particles in the solar nebula in a timescale far less than 2-3 Ma. Although some new theoretical models were subsequently developed to solve the long term storage problem of CAIs [e.g. 7], new high precision U-Pb ages once again supported chondrule formation started contemporaneously with CAIs [8]. Since our initial report [2], ²³⁵U/²³⁸U isotope composition was shown to be no longer a constant [e.g. 9], thus some of the relative age anchors require readjustment. We will reexamine the emerging stories in the light of new measurements.

 Moynier et al. (2007) ApJL, 671, L181. [2] Yin et al.
(2009) LPSC 40th, A2006. [3] Jenniskens et al [2012] Science, 338, 1583. [4] Kurahashi et al. (2008) GCA, 72, 3865. [5] Connelly et al. (2008) ApJL, 675, L121. [6] Cameron (1995) Meteorit., 30, 133. [7] Ciesla (2009) Icarus, 200, 655. [8] Connelly et al. (2012) Science, 338, 651. [9] Brennecka et al (2010) Science, 327, 449.

[1] Komárek et al. (2008) Environ. Int. 34(4), 562-577.