

Isotopic evidence for an activity of the early Sun studied from the isotopic measurements of Kapoeta

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The Kapoeta meteorite (howardite) is a regolith breccia meteorite, and is known to be a highly gas-rich meteorite that experienced early irradiation by cosmic rays, however, its irradiation history is complicated and still disputed with respect to evidence of early solar irradiation. Our previous study on neutron capture history of Kapoeta suggests the existence of preirradiation materials migrating into the meteorite parent body [1]. The existence of space-weathered rims in several regolith grains in the Kapoeta meteorite is resulted from the irradiation of cosmic-ray on the regolith parent body [2]. In this study, Sr, Ba, Ce, Nd, Sm and Gd isotopic compositions of the sequential acid-leachates from the Kapoeta meteorite were determined to find systematic and correlated variations of their p-process isotopic abundances and to understand the neutron capture record due to cosmic-ray irradiation.

Significantly large isotopic excesses of ⁸⁴Sr, ¹³⁰Ba, ¹³²Ba, ¹³⁶Ce, ¹³⁸Ce and ¹⁴⁴Sm were observed particularly in the first leaching fraction (L1). Interestingly, a large isotopic shift of ¹⁵⁰Sm/¹⁴⁹Sm and ¹⁵⁸Gd/¹⁵⁷Gd due to neutron capture reactions was also found in the first fraction, corresponding to the neutron fluence of 2.6×10^{16} n cm⁻², which is more than 10 times higher than those in the other fractions. The large difference of neutron capture records of L1 from the other three suggests the existence of preirradiation materials migrating into the Kapoeta parent body.

Systematic isotopic data in this study reveal the enrichment of several p-process isotopes of the fraction L1 leached probably from a very surficial part of regolith grains of Kapoeta, suggesting the production of p-process isotopes resulted from the interaction of SCR during the regolith process of the Kapoeta parent body. The result provides isotopic evidence for an activity of the early Sun.

[1] Hidaka and Yoneda (2009) *EPSL* **285**, 173–178. [2] Noble *et al* (2011) *MAPS* **45**, 2007-2015.

Fulvic and Humic Acid interaction with Phosphate at synthetic and natural oxide surfaces

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Fulvic acid (FA) and humic acid (HA) have a large variability in binding to metal (hydr)oxides and interact differently with oxyanions, as studied experimentally for goethite, phosphate, and a series of soil HAs that cover the large natural variation in molecular charge and size. A surface complexation approach has been developed that aims to describe the pH-dependent competitive behaviour of natural organic matter (NOM) in soil as well as model (hydr)oxide systems, using variable inner and outer-sphere complexation as well as protonation of RCOO ligands.

Modelling shows that the competition of phosphate with various HAs is linearly related to the HA charge. Expressed per unit charge, HA competes as well as FA (or even better), which is unexpected since the various humics highly differ in molecular size (~1-10 nm) suggesting variation in mean distance of approach [1]. Modelling suggests that at low loading, both FA and HAs are predominantly adsorbed in the Stern layer domain which points to a strong change of the molecular conformation of the humic acids. Our calculations suggest that the metal (hydr) oxide surfaces are efficiently covered by an ultra-thin layer of NOM. Therefore, realistic surface complexation modeling of natural systems should account for this pervasive NOM surface coverage.

From the perspective of global carbon sequestration, adsorption of NOM is also important since minerals may protect adsorbed carbon against oxidation. In soils, the reactive metal (hydr)oxide fraction consists of nanoparticles, typically representing ~3-30 m² g⁻¹ soil [2]. When covered by an ultra-thin layer of NOM, it may represent at least 0.2-2% NOM. Surface-associated NOM may be even three times higher. In our competition study, we have also included pyrogenic HA since it will be released to the environment in case of large-scale application of biochar, potentially creating Dark Earths or Terra Preta soils. Terra Preta soils are fertile, rich in carbon as well as phosphate. Our charge distribution model for NOM predicts a more than 10-fold increase in dissolved phosphate for soils rich in black carbon. This is due to the relatively high molecular charge of pyrogenic HA.

[1] Weng *et al* (2007) *J. Colloid Interf. Sci.* **314**, 107-118. [2] Hiemstra *et al* (2010) *Geochim. Cosmochim. Acta* **74**, 41-58.