

Component specific Hf-W dating of Allende and Vigarano CV3 chondrites

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The formation of chondrules, matrix and other components of chondrites is not yet fully understood. Knowing their relative formation ages and genetic relationships can provide crucial information on their formation conditions. Short lived radionuclides can provide new insights into the chronology of the formation of early solar system materials. In the past, the ²⁶Al-²⁶Mg system has been mainly used for this purpose, but recently the ¹⁸²Hf-¹⁸²W system emerged as a promising tool to date chondrule formation. Thus, components of chondrites that never underwent high temperature metamorphism, like CV3 chondrites, are well suited candidates for Hf-W investigations. Earlier studies of Allende chondrules with the Al-Mg und Pb-Pb systems indicate that they formed up to 3.2 Ma after CAI formation¹⁻⁴.

We prepared 23 Allende and 13 Vigarano separates for Hf and W isotope measurements, covering both reduced and oxidized CV chondrites. These include pure handpicked chondrule and matrix fractions as well as magnetic separates and bulk aliquots. The separates all define isochrons which indicates a contemporaneous formation of all components. The ages defined by the isochrons suggest formation of Allende and Vigarano components within 3 Ma after CAI formation. These ages are consistent with chondrule formation ages obtained from other isotopic systems.

Notably, W and Hf concentrations in chondrule and matrix fractions from Allende and Vigarano vary considerably. Chondrules from Allende exhibit high Hf/W ratios (2.5 to 3.0), whereas matrix and strong magnetic fractions exhibit low Hf/W ratios (0.5 to 0.9). Unlike in Allende, Vigarano contains chondrules with extremely low Hf/W ratios. As suggested from petrological observations, these low ratios can be attributed to the presence of metal inclusions within the reduced Vigarano chondrules.

[1] Bizzarro *et al.* (2004) *Nature* **432**, 275-278; [2] Connelly *et al.* (2008) *Astroph. Journal* **675**, L121-L124; [3] Connelly & Bizzarro (2009) *Chem. Geol.* **259**, 143-151; [4] Amelin & Krot (2007) *Meteor. & Plan. Sci.* **42**, 1321-1335.

Actinide redox processes on iron sulfides: an electrochemical, microscopic, and computational approach

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Little is known about the reaction mechanism of actinyl complexes on mineral surfaces, i.e. the role of the redox potential, the nature of the reductant, the importance of minerals in terms of providing catalytic surfaces, the role of anions in solution that polarize a mineral surface to promote or inhibit electron transfer, and the activated states that may slow down the kinetics of the redox process.

In order to resolve these, electrochemical studies using a micropowder electrode technique were performed in combination with a quantum-mechanical and microscopic (AFM) approach. The electrochemical approach allows us to determine the specific redox potential of actinide reduction on a given mineral surface. For example, uranyl reduction takes place at -0.22 V on hematite, -0.17 V on magnetite, and at -0.14 V on pyrite. Further electrochemistry experiments were performed on machinawite, in order to be able to compare these with quantum-mechanical calculations on the thermodynamics, charge and spin transfer, and electrochemical potential for reduction and oxidation to occur. The calculations show that the energy gain of the co-adsorption of hydroquinone (as an analogue for microbial reduction) and uranyl is on the order of 0.5 eV (≈ 50 kJ/mol) as compared to the separate adsorption of uranyl and hydroquinone. Similar co-adsorption on FeS (mackinawite) reveals that Fe(II) cations in the mineral surface become high spin (Fe(II) in bulk mackinawite is low spin), thereby increasing its potential for electron transfer.