New Constraints on the Magnitude and Timing of Late Accretion

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Late accretion is defined as continued planetary growth subsequent to the cessation of core segregation. Late accretion was evidently a common, final step in the formation histories of rocky planetary bodies, regardless of size [1]. Evidence for this comes from estimates of planetary mantle compositions for various bodies, projected to contain raised, and broadly chondritic relative abundances of the highly siderophile elements (HSE). Although a ubiquitous process, the proportions of late accretionary mass additions, relative to planetary mass, may have ranged considerably. For example, current estimates suggest the Earth and Mars received proportionally much more late accreted mass than the Moon, perhaps reflecting stochastic late accretionary processes [2]. The timing of late accretion must also have varied considerably, with late accretion evidently occurring on asteroidal-sized bodies within the first 10 m.y. of solar system formation [1], but also acting on late-formed bodies, such as the Moon.

The nature and timing of late accretion to Earth is a particularly important issue, as this process could have delivered considerable water and organics to the mantle. One possibility is that the putative giant impact that generated the Moon was a major clearinghouse event for HSE, and thus, an event that heralded in a final stage of terrestrial late accretion. The long-term preservation of ^{182}W isotopic heterogeneities in the mantle [3-4], however, likely indicates that the terrestrial mantle was never completely homogenized, and possibly that the cumulative effects of terrestrial late accretion commensed well before the Moon-forming event. The presence of small enrichments in ^{182}W in some early-Earth rocks (Isua [3] and Nuvvuagittuq), coupled with depletions in HSE abundances estimated for their mantle sources, provides some evidence for uneven mixing of late accreted materials into the mantle, although other options to explain the enrichments are also possible. Of note, the magnitudes of ^{182}W enrichments are consistent with the mass addition proportions suggested by HSE abundances [3].

[1] Day *et al.* (2012) *Nature Geoscience* **5**, 614-617, [2] Bottke *et al.* (2010) *Science* **330**, 1527-1530, [3] Willbold *et al.* (2011) *Nature* **477**, 195-198, [4] Touboul *et al.* (2012) *Science* **335**, 1065-1069.
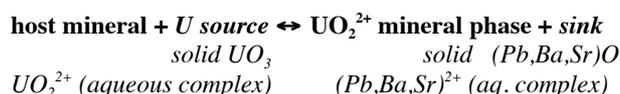
A first principles study of uranyl and neptunyl incorporation into sulfate minerals

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Solid solution formation at the mineral/water interface occurs when an ion in solution replaces an ion in the lattice; however, experimental observations have not fully decoupled the factors that control this process (*e.g.* ionic radius of foreign ion, coordination environment, molecular orbital interactions, charge compensation). In order to examine the thermodynamics of incorporation, the energies of incorporation of uranyl (UO_2^{2+}) into anhydrous sulfate minerals, anglesite ($PbSO_4$), barite ($BaSO_4$), and celestine ($SrSO_4$), are calculated using a quantum mechanical approach. For each mineral, source and sink reference phases are chosen to facilitate the substitution of the uranyl ion with a cation from the host mineral as described by the general equation:

host mineral + *U source* ↔ **UO_2^{2+} mineral phase +** *sink*
            solid UO_3   *solid (Pb,Ba,Sr)O*
UO_2^{2+} *(aqueous complex)*   *(Pb,Ba,Sr)$^{2+}$ (aq. complex)*

Of the three sulfate minerals, the energy of uranyl incorporation into anglesite was the lowest for solid state oxide reference phases (ΔE_{rxn} = 1.57 eV). Anglesite also provided the lowest energy of incorporation of an aqueous species ($UO_2^{2+}{}_{aq}$ with the release of $Pb^{2+}{}_{aq}$). Using aqueous species as source and sink phases but solid incorporation hosts required the combination of periodic and cluster quantum mechanical methods. Incorporation of uranyl was then compared with incorporation of $Np(VI)O_2^{2+}$ and $Np(V)O_2^+$ aqueous neptunyl complexes.

Since these static incorporation energies are most closely representative of the enthalpy of incorporation, the free energy was estimated using vibrational entropy values from empirical force field calculations in order to curtail computational expense. These vibrational entropy data tend to make incorporation energy values less energetically uphill. The limits of U- and Np-incorporation were also calculated to predict solid solution behavior.