

Constraints on the source of mantle plumes from the first picrites erupted Ethiopian flood basalt province

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The earliest basalts erupted by largest mantle plumes are typically 200-300°C hotter than those derived from convecting upper mantle at mid-ocean ridges. They originate from a thermal boundary layer deep in Earth that is assumed to be the core-mantle boundary. Consequently the first plume-derived basalts provide constraints on Earth structure and differentiation history. The first picrites erupted by the Iceland plume have a high proportion of primordial He ($^3\text{He}/^4\text{He} \sim 50 R_a$) yet a range in radiogenic isotope and incompatible trace element ratios that overlap the global mid-ocean ridge basalt range [1]. This is difficult to reconcile with pristine mantle dominating the plume head. The simplest interpretation is that the convecting mantle has been polluted by primordial He either at the core-mantle boundary or during ascent, thus still requires the existence of primordial volatile reservoir.

In an attempt to provide better constraints on the deep mantle source of plumes we have analysed the He-Sr-Nd-Pb isotopic composition of the earliest high-Ti picrites (HT2) from the Dilb section of the ~30 Ma Ethiopian flood basalt province. The basalts are characterized by high Fe and Ti contents for MgO = 14-15% that implies the parent magma was derived from a high temperature small melt fraction, likely the plume head. The basalts are characterized by a narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70396–0.70412) and $^{206}\text{Pb}/^{204}\text{Pb}$ (18.82-19.01). $^3\text{He}/^4\text{He}$ of olivine never exceeds 21 R_a . The Afar plume was sourced in a discrete mantle reservoir that is less degassed and more enriched than the convecting upper mantle. The source region is significantly more degassed than the mantle sampled by the proto-Iceland plume and more homogenous. Clearly the largest mantle plumes are not initiated in a single deep mantle domain with the same depletion/enrichment history and they do not mix with convecting mantle to the same extent.

[1] Starkey *et al.* (2009) *Earth Planet. Sci. Lett.* 277 91-100.

Oxidative corrosion of uraninite (UO₂) surfaces

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Uraninite (UO₂) is the most abundant uranium ore mineral, the product of proposed bioremediation strategies for uranium-contaminated soils and aquifers and its synthetic analog is the primary constituent of most nuclear fuels. It incorporates interstitial oxygen up to a stoichiometry of UO_{2.25} without disruption of the uranium lattice, but the structural details of the process are the subject of ongoing study and debate. Because the solubility and dissolution kinetics of uraninite depend heavily on the oxidation state of uranium, understanding the mechanisms of UO₂ surface oxidation and corrosion is essential to predicting its stability in the environment throughout the nuclear fuel cycle. To date, however, no study has addressed this process at the molecular scale at atmospheric pressure and room temperature.

We present crystal truncation rod (CTR) x-ray diffraction studies of pristine and oxidized UO₂ (111) and (100) surfaces. The clean (111) surface shows minimal contraction of the uppermost atomic layers and a layer of oxygen or hydroxyl group adatoms above the vacuum-terminated surface. Upon exposure to oxygen, an oxidation front proceeds into the crystal, interstitial oxygen atoms penetrate to depths of 30 Å or more, surface-normal layer distances contract (consistent with bulk uraninite oxidation) and an ordered superlattice forms, commensurate with the underlying bulk. Similar oxygen surface penetration and layer contraction are observed upon oxidation of the (100) surface. These results demonstrate that the solid state diffusion of oxygen into UO₂ and UO_{2+x} surfaces is facile and that ordering kinetics are relatively rapid, even at room temperature.

Ab initio thermodynamics, which combines density-functional theory calculations with macroscopic thermodynamics, provides insight into the energetics, bonding and oxidation processes that occur as oxygen reacts with the surfaces and diffuses into the solid. Subsurface oxidation is predicted to contract surface-normal layers, consistent with experimental observations.