Oxidative corrosion of the uraninite (111) surface

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Uraninite (UO_2) 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 (1-3). This material is known to incorporate 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 (e.g., 4-5). Because the solubility and dissolution kinetics of uraninite depend heavily on the oxidation state of uranium, understanding the mechanims of UO_2 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 results of a crystal truncation rod (CTR) x-ray diffraction study of the UO_2 (111) surface. This hard x-ray technique is ideally suited to such studies, because it can probe the structures of interfaces at atmospheric conditions and buried below liquids and solids. The single-crystal surface was prepared under anoxic conditions, measured under dry helium, then exposed to dry O_2 gas and measured at several time points over the course of two weeks. The pristine surface is characterized by minimal contraction of the uppermost atomic layers and the addition of an oxygen layer above the vacuum-terminated surface. Following exposure to dry O_2, an oxidation front proceeds into the crystal, intersitial oxygen atoms penetrate to depths of 30 Å or more, U-U layer distances contract (consistent with bulk uraninite oxidation), and an ordered superlattice, which is commensurate with the underlying bulk, forms. These results demonstrate that the solid state diffusion of oxygen into UO_2 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 surface and diffuses into the solid. Surface oxidation results in formation of a U^{+6} cation triply bonded to single oxygen adatoms. Subsurface oxidation is predicted to contract U-U layers consistent with experimental observations.

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A COMPARISON OF GLASS AND MINERAL INCLUSIONS IN QUARTZ AND ZIRCONS FROM KEWEENAWAN RHYOLITE FLOWS

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Melt inclusions (MI) and a wide-variety of mineral inclusions are well preserved in quartz phenocrysts and zircons from porphyritic rhyolite flows of the Midcontinent Rift System. The inclusions and their host minerals have been examined using EPMA, cathodoluminescence microscopy (CL), SEM/EDS, and LA-ICP-MS. Rhyolite from the North Shore Volcanic Group, the Porcupine Mountains, the Portage Lake Volcanics, and the Michipicoten Island Formation were utilized in this study. Inclusions hosted by quartz and zircons were studied in thin sections and grain mounts, respectively.

The MI were categorized based on their phase assemblages and preservation style [1]. CL images of the host quartz phenocrysts reveal multiple stages of growth and dissolution. Ti contents (measured by EPMA and LA-ICP-MS) in the quartz vary widely and range from <15 to 280 ppm. Using a modified TitaniQ method [2], this corresponds to a temperature change of more than 250 °C in individual samples (using $aTiO_2=1$ and isobaric conditions). Presently there are still too many variables to constrain the absolute crystallization temperatures. The MI were analysed by LA-ICP-MS for major oxides and trace elements including Zr and Ti. The ranges in zircon saturation temperatures calculated using the model described by [3] agree with the TitaniQ temperature ranges. Unfortunately, it has been difficult to confidently constrain the Ti content (for TiO_2 activity calculations) in the MI using LA-ICP-MS analyses. This is due to the complex nature of the Ti distribution in the surrounding host quartz. The occurrence and distribution of zircon as inclusions in the quartz does suggest coeval crystallization of both phases.

An examination of SEM/EDS spectra of inclusions in zircon revealed at least 18 different minerals. They include K-spar, plagioclase, pyroxene, quartz, Fe-Ti oxides, apatite, monazite, and several different sulphides. Mineral inclusion assemblages in the zircons are distinct in each of the rhyolite samples that were studied. The mineral inclusions occur as isolated grains within zircon and inside glass bearing MI in zircon. While the majority of the inclusions appear to be primary and pristine, some of mineral and MI show evidence of modification by secondary processes. Utilization of the trace element chemistry of the mineral and MI trapped in zircon can potentially be used to better constrain the activity of TiO_2 in the melt during crystallization. This approach can lead to a more accurate estimate of quartz crystallization temperatures for Keweenawan rhyolite.

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