

U-Pb and trace elements in xenotime from sediment-hosted Co-Cu-Au and Cu-Ag deposits, ID-MT

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SHRIMP U-Pb geochronology of hydrothermal xenotime can reveal the timing of mineralization for ores that have historically proven difficult to date. Hydrothermal xenotime may occur as isolated grains, intergrowths with ore minerals, or epitaxial overgrowths on detrital zircon. Dates for Precambrian xenotime are obtained from weighted averages of ²⁰⁷Pb/²⁰⁶Pb ages. For Phanerozoic xenotime, ²⁰⁶Pb/²³⁸U ages require correction for matrix differences between standards and unknowns due to large compositional variability.

In the Blackbird Co-Cu-Au district, east-central ID, xenotime has a complex association with cobaltite. Oscillatory-zoned (o-z) cores of xenotime, which also occur as rare inclusions in unzoned cobaltite, are 1371 ± 4 Ma, possibly related to intrusion of nearby megacrystic granite (1377 ± 4 Ma). A second generation of xenotime formed ca. 1300 Ma as unusually large (100-200 μ m) symplectic grains, and as smaller overgrowths on o-z cores. Most cobaltite occurs as euhedral, o-z grains intergrown with unzoned xenotime grains or unzoned rims on o-z cores. U-Pb dating suggests that both cobaltite and xenotime were remobilized and reprecipitated in the Cretaceous. The types of xenotime are distinguishable by REE patterns.

At the Spar Lake Cu-Ag deposit, western MT, xenotime forms discontinuous overgrowths (1-30 μ m) on detrital zircons within the Revett Fm. (Belt Supergroup). SHRIMP dating of this xenotime yields ages of 1409 ± 8 Ma (the time of Cu-Ag mineralization), and 1310 ± 14 Ma. REE, As, U, and Th/U can be used to discriminate hydrothermal xenotime from other types of xenotime. The 1410-Ma age indicates that this xenotime did not grow during diagenesis of the Revett (~1.45 Ga), but rather formed ~40 m. y. after sedimentation during the hydrothermal ore-forming process.

Method to estimate the contribution of molecular U(IV) to the product of U(VI) reduction

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The reduction of soluble hexavalent uranium to tetravalent uranium can be catalyzed by bacteria and minerals in the subsurface. A reported end-product of this reduction is the mineral uraninite (UO₂), which is desirable because of its low solubility. Although uraninite was long assumed to be the only product of U (VI) reduction, our present work indicates the formation of an adsorbed U (IV) species—dubbed molecular U (IV)—under certain geochemical conditions. The presence of this species was confirmed using X-ray absorption spectroscopy (XAS). High resolution transmission electron microscopy (HRTEM) with electron diffraction further confirmed a non-crystalline uranium reduction product. The discovery of molecular U (IV) is an important development because this species is likely to be more labile and susceptible to reoxidation than uraninite. Thus, current conclusions about the stability of reduced uranium in the subsurface may need to be reassessed.

Here, we propose a wet chemical method to differentiate between molecular U (IV) and uraninite in environmental samples which may contain a mixture of the two. The method utilizes a concentrated bicarbonate solution to extract molecular U (IV) from *Shewanella oneidensis* MR-1 cells, biogenic and chemogenic Fe (II) solid phases, and contaminated sediments over the course of several hours. To calibrate the method, U (IV) is extracted from known mixtures of uraninite and monomeric U (IV). Our results show that molecular U (IV) is efficiently removed from biological cells and Fe (II) phases by bicarbonate extraction, without affecting uraninite stability. Both extracted and unextracted samples were analyzed using XAS to validate the results of the extraction. Our extraction method provides a rapid alternative to XAS analysis to estimate molecular U (IV) in environmental samples.