

Incorporation of Uranium and Other Trace Elements in Lacustrine Tufa Calcite

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Beamline(s): X26A

Introduction: We used in situ micro X-ray fluorescence (XRF) and X-ray absorption near edge spectroscopy (XANES) to continue our characterization of U and other trace element concentrations and U oxidation state in natural tufa calcite. Samples are from the Barstow Formation, California. Tufa occurs as meter-scale towers with smaller tube-like concretions that appear to be associated with the plumbing system of springs that fed into an alkaline lake. The morphologies and association of these deposits with lacustrine conglomerate shoreline deposits suggest that they formed in a similar manner to more modern tufa towers at nearby Mono Lake. Previous work on the Barstow Fm. has shown that U concentrations can be high and that U is present as U(IV) [1].

Methods and Materials: Analyses were conducted in situ on five polished slabs of tufa. Three samples analyzed for trace element concentrations with XRF and all samples were analyzed for U oxidation state with XANES. The incident beam was tuned to 17.2 keV, just below the U L_3 edge, using a Si(111) channel cut monochromator. The collimated beam was then focused to ~15 μm in diameter using Rh coated Kirkpatrick-Baez mirrors. XRF compositional data and fluorescence mode XANES were collected using a Canberra SL30165 Si(Li) detector. Elemental concentrations were determined by the “standardless” XRF technique.

Results: XRF analyses show that trace element concentrations vary within and between samples. Ca concentrations are homogeneous throughout the samples and bulk X-ray diffraction analyses indicate that the tufa is predominantly calcite. Ranges and averages for notable trace elements are listed in Table 1. Of particular interest are relatively high concentrations of Mn, Sr, Au, and U. Maximum concentrations of almost 600 ppm U, 1.3 wt.% Sr, and 44 ppm Au were measured in the samples. High concentrations of other elements (Cu, Fe, Pb, and Zn) were observed in isolated “hot spots,” which may reflect small inclusions of a sulfide mineral (such as chalcopyrite). Elemental concentrations for these hot spots are excluded from Table 1.

Consistent with our previous results [1], U is present as U(IV) in all four tufa samples analyzed. One other study has shown U(IV) in calcite [2]. That calcite precipitated in association with zinc ore deposits, presumably from basinal brines. Studies of carbonates formed at Earth’s surface such as coral aragonite [3] and paleosol calcite [4] have documented U(VI).

Conclusions: High concentrations of U, Au, and other trace elements have been incorporated in tufa calcite from the Barstow Fm. XANES studies have shown that U is present as U(IV). More work is needed to understand how these elements are complexed in the fluid from which they precipitated and to understand how they were ultimately incorporated in the calcite structure. Both U and Au can be reduced to their insoluble forms by bacteria [5,6]. We suggest that microbes may have played a role in the enrichment of U and Au in the Barstow Fm. tufa.

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(ppm)	Mn	Fe	Cu	Zn	Sr	Au	Pb	U
Low value	1112	298	10	7	4039	13	7	122
High value	4729	2346	61	99	12982	44	80	598
Mean	2646	802	29	20	6009	20	23	340

Table 1. Ranges and means for trace elements in three tufa samples as determined by XRF.