1. Sorption-reduction of aqueous $U^{VI}$ by ferrous micas

The primary objective of our work in the present grant period was to extend our earliest results to a wider range of solution and mica compositions, and reaction times. These objectives were pursued through a series of systematic, batch sorption experiments, performed under argon at 25°C. Single crystal run products were analyzed by transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The use of large single crystals and high water/rock ratios had advantages, but precluded changes in solution composition. The bulk of the data was determined by XPS of edge and basal plane orientations. Some of our results have been reported in Ilton et al. (2003) and Ilton and Simmons (2003). However, we made three unexpected discoveries that have expanded the possible pathways for sorption-reduction: 1) XAS has shown that uranyl may be reduced in the interlayer region, 2) XPS yielded evidence that pentavalent uranium is stabilized on the mica edge orientations, and 3) HRTEM recorded the presence of U/Fe-rich nano-scale zones on interior basal surfaces. All of our results are briefly summarized here.

1.1 XPS analyses: Crystal chemical and solution controls. Much of latest work was made possible by using a third mica specimen (nearly end-member Fe and low F) that was very reactive (Ilton et al., 2003). Consequently, $U^{VI}$ sorption-reduction was detectable at much lower uranyl concentrations (down to 0.5 $\mu$M) and shorter reaction times. In addition, higher uranium sorption allowed us to track subtle features, such as satellites and the 5f valence level, that are more diagnostic of uranium oxidation (Figure 1).

![Figure 1](image-url)

**Figure 1.** XP spectra of the U4f region of annite edge orientations reacted with 5 $\mu$M $U^{VI}$. The purpose of this figure is to correlate certain feature, such as satellites and U5f signal intensity that are diagnostic of uranium oxidation state with changes in core level U4f peak shapes and positions. These particular 5 and 25 mM Na experiments were chosen because nearly equivalent amounts of uranium were sorbed on both samples. Figure 12a shows a strong association between $U^{V}$ satellite and the low binding component, whereas a $U^{VI}$ satellite is associated with the high binding energy component. Combining information from Figure 12a and 12b demonstrates that increased U5f intensity is also associated with the low binding energy component. As discussed in the text, these observations confirm that the low and high binding energy components are $U^{V}$ and $U^{VI}$, respectively. Binding energies were adjusted to Cls at 284.6 eV.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
This work has confirmed the results of our initial study which was the first to show that ferrous micas can heterogeneously reduce uranyl to \( U^{IV} \), and that reduction occurs on edge not smooth exposed basal surfaces. However, we can now put constraints on the effectiveness of sorption-reduction as a function of mica composition and a broad range of solution parameters. For example, micas with \( \text{Fe} / (\text{Mg} + \text{Fe}) \) less than 0.5 showed no detectable reductive capacity at uranyl concentrations less then 0.5 mM. In contrast, the high Fe, low F bioite (annite) actively reduced uranyl at concentrations as low as 0.5 \( \mu \)M. Moreover, the effect of alkali cations on the reaction is greatly amplified for the annite, where the addition of 25 mM \( \text{NaCl} \) improved reduction efficiency, as measured by sorbed \( \text{U}^{IV}/\text{U}^{VI} \) to ratios as high as 2:1, whereas 25 mM \( \text{KCl} \) essentially blocked the reaction. The effect of Na on reduction of uranyl by the low Fe micas was not detected until uranyl reached 0.5 mM. For the annite experiments, sorption-reduction occurred from pH 4.5 to 9.5, and the Na effect occurred at all pH values studied. In sum, annite strongly exaggerated tendencies first noted for the lower Fe biotites, such as the effect of Na and the strong anisotropic reactivity of edge orientations versus smooth exposed basal surfaces.

Based on our data and spectral modeling ferrous micas reduce \( U^{VI} \) to \( U^{IV} \) with the degree of reduction also controlled by crystallography, mineral composition, and the type of alkali cation in solution. Electron transfer from \( \text{Fe}^{II} \) in biotite to sorbed \( U^{VI} \) occurs at edge sites, is blocked by the siloxane layer and by K in solution and, as expected, is dependent on the Fe and \( \text{Fe}^{II} \) concentration in biotite. The effect of alkali cations is consistent with our work on \( \text{Cr}^{VI} \) reduction by micas (Ilton and Veblen 1994a; Ilton et al. 1997; Ilton et al. 2000).

Perhaps the most significant new finding is evidence for a sorbed species with the intermediate oxidation state \( U^{V} \). Under certain conditions, in particular at high pH, it became apparent that a third core level peak was required to adequately model the composite \( \text{U}4f \) spectrum. This additional component is nearly midway between \( U^{VI} \) and \( U^{IV} \). Further, it is correlated to the appearance of a new satellite feature at 8 eV above the core peak. The 8 eV satellite has been assigned to either \( U^{V} \) (e.g., Bera et al., 1998, and references therein) or an oxygen defect cluster (e.g., Guilbert et al., 2000, and references therein). That the 8 eV satellite is associated with a distinct peak which has a binding energy between \( U^{IV} \) and \( U^{VI} \) bolsters the evidence for \( U^{V} \). At first glance the result is surprising because it is well known that \( U^{V} \) is highly unstable and will readily disproportionate in aqueous solution. If \( U^{V} \) is ultimately proven to exist in our experiments, then this could shed new light on heterogeneous reduction mechanisms and pathways for \( U^{VI} \) in the environment. We plan to continue working on this discovery and outline strategies for doing so in the proposed work section of this renewal proposal.

We found additional support for the existence of \( U^{V} \) by applying factor analysis to a series of variably reduced \( \text{U}4f \) spectra to extract component peaks and their parameters. The results of this study were submitted to the Journal of Nuclear Materials (Ilton and Simmons, 2003). Factor analysis isolated three components, one was clearly \( U^{VI} \), the second was consistent with \( U^{V} \) and the third was a mixed valent species. Further, factor analysis can yield valuable information concerning the initial state of \( U^{VI} \) standard material. This is important because \( U^{VI} \) reduces under the X-ray beam during XPS. Although this phenomenon is often duly noted (e.g. Allen et al., 1993), it is not usually considered when interpreting analyses. By applying factor analysis to a series of beam reduced uranium spectra one can, in theory, extract an end-member \( U^{VI} \) standard peak without any a priori assumptions concerning the initial state of the material, peak parameters or background shape. We did just that and derived, what we consider to be the best estimate of \( U^{VI}4f \) peak parameters in the literature.

Another important contribution from the present grant period was the demonstration that sorption-reduction is not an artifact of preparation. In one test, pre-leached micas showed similar
reactivity to freshly cut edge orientations. In a second test, step edges on basal surfaces, uncovered by or produced by splitting micas along 001, also demonstrated appreciable reduction activity. We suggest that the step terminations on basal surfaces more closely mimic natural mica edges than cut edges. In any case, three different preparation methods yielded similar results and we are confident that the reaction will occur in nature, given appropriate solution and mica compositions.

1.2 XAS measurements. A limited number of annite thick sections were analyzed by XAS methods (XANES and X-ray fluorescence). Figure X ... The results are important because they indicate, for the first time, that uranyl may be reduced in the interlayer region, although the amounts may not be quantitatively important. This highlights an apparent paradox: why will uranyl reduce in the interlayer region, but not on exposed basal planes? This is an area of ongoing research, and will be discussed in the Proposed Work section of this renewal proposal.

Figure 2. X-ray spectroscopy of annite thick section (100 µM thick). The annite was reacted for 5 hours at pH 5 in a solution containing 5 µM UVI and no added alkalis. Basal planes are oriented perpendicular to the page and the reacted edge is pointed north. Relative signal intensity is color coded and keyed to the vertical bar to the right of each figure. The spatial scale on the left side of the figures and is given in microns. The figure on the right side gives total absorption and is proportional to sample thickness. The left figure shows the fluorescence image of uranium. Uranium is concentrated in a 10 µM thick fringe at the reacted edge. The enhancement of uranium signal at the left edge of the sample is an artifact of sample orientation relative to the X-ray beam (see text.)

1.3 TEM observations. High-resolution transmission electron microscopy (HRTEM) and analytical electron microscopy (AEM) of micas with low uranium coverage showed no detectable uranium. Uranium was detected on annites that had high concentrations of sorbed uranium. HRTEM/AEM of these annite interior basal surfaces reveal nano-sized U/Fe-rich zones (Figure 3). These zones are the subject of continued investigation.
Figure 3. TEM image of U/Fe rich zones on interior basal surfaces. The U/Fe zones are the dark patches. Note that the sample edge points north, but this edge might have been created during preparation and may not represent an edge that interacted with solution.

2.2 Interpretation of Cr X-ray photoelectron spectroscopy data

2.1 Theoretical studies. Our theoretical work is motivated by the need to better distinguish between inter and intra atomic features in the XP spectra of transition metals. For example, the bonding environment can confuse interpretations of oxidation states (e.g. Ilton et al. 2000). We have made significant progress in determining the effect of bonding environment on the XP spectra of Cr$^{3+}$ (Ilton, Bagus and DeJong 2003). Our initial theoretical work is distinguished from other studies (e.g., Gupta and Sen, 1975) by containing no empirical fits or assumptions and by incorporating relativistic, core hole, and spin-orbital coupling effects on the multiplet structure of the free Cr$^{3+}$ ion. These calculations included all possible angular momentum couplings and recouplings (e.g., Bagus et al., 2000) that could be made for the p shell ions keeping 5 electrons in the open p shell and 3 electrons in the open 3d shell. They do not include the redistribution of the 3p electrons into the 3d shell considered by Pierloot, Tsokos, and Roos (1993) for neutral transition metal ions. However, for the Cr$^{3+}$ ion, these effects change the d$^3$ multiplet splittings by only ~0.3 eV, Pierloot et al. (1993); other many electron effects, as noted below, may be more important for the relative energies of the ionic final states for the 3p XPS. The results of Ilton and Bagus (2003) are broadly similar to those of Gupta and Sen, but significant differences are apparent. We believe that our results provide a better representation of intra-atomic effects than previous work. This establishes a more reliable benchmark for distinguishing inter-atomic affects on the XP spectra of Cr$^{3+}$ in solid phases.

For example, in Figure 4 (from Ilton, Bagus and Dejong 2003) we compare a synthetic spectrum based on our calculations, to that of α-Cr$_2$O$_3$. Note that the Cr2p$_{3/2}$ doublet, the Cr2p$_{1/2}$ shape, and the spin-orbital splitting for Cr$_2$O$_3$ are nearly reproduced by theory. However, appreciable differences occur, and it is likely that inter-atomic effects are influential. As expected, there is an even greater discrepancy between theory and the Cr3p spectrum of Cr$_2$O$_3$. We speculate that this larger discrepancy arises because the 3p-3d exchange coupling and the splittings of the Russell-Saunders terms for the different angular momentum couplings of the (3d)$^3$ sub-shell are more important for the 3p holes than for the 2p holes and a relevant discussion is in Appendix A.
Figure 4. Comparing theoretical spectra (smooth lines) for the free Cr\(^{3+}\) ion to an experimental spectra for Cr\(_2\)O\(_3\) (from Ilton, Bagus, and DeJong, 2003)

Embedded cluster theoretical studies have been initiated for a CrO\(_6\) model of Cr\(_2\)O\(_3\). Preliminary results indicate that there are ~3.5 3d electrons associated with Cr rather than the nominal count of 3 for the Cr\(^{3+}\) cation indicating a modest extent of covalency in the initial state before ionization of a core electron. The consequences of this initial state covalency and of possible core ion CT for the XPS will be determined with our continuing theoretical studies.

2.2 Experimental studies. Our experimental XPS studies have been extended to uvarovite (a Cr\(^{3+}\) containing garnet), and variably hydrated and crystalline Cr\(_2\)O\(_3\). The Cr2p spectra for uvarovite is similar to those for Cr\(^{3+}\)-chlorites and Cr sorbed to micas, but appreciably different than for Cr\(_2\)O\(_3\) (Figure X1). Interestingly, if one were to use Gupta and Sen’s (1975) multiplet calculations to model Cr2p for Cr in or on silicates, Cr\(^{4+}\) not Cr\(^{3+}\) would be the best fit (Ilton et al., 2000). In contrast, we have shown that Cr2p for Cr sorbed to Mn\(_2\)O\(_3\) (manganite) is best modeled by Gupta and Sen’s multiplet structure for Cr\(^{3+}\), which was the expected oxidation state for Cr (Weaver, Hochella, and Ilton, 2002). We have also demonstrated that the Cr2p spectra for Cr\(_2\)O\(_3\) varies with the degree of hydration and/or crystallinity; the low binding energy multiplet appears to increase with decreasing hydration and increasing crystallinity.

A number of authors have used Gupta and Sens calculations to model Cr2p spectra for sorbed Cr and Cr\(_2\)O\(_3\); Banerjee and Nesbitt 1999; Weaver et al. 2002) and in all cases, the authors altered the original multiplet features-whether by a lot or a little depends on the eye of the beholder-to accommodate the experimental XP spectra. We suggest that this practice is premature. Thus, one of our intents in this renewal period is to establish, by comparison of detailed theoretical analyses and experiments, the relative importance of intra-atomic and inter-atomic contributions to the XP spectra of Cr cations in various bonding environments. Our continued efforts will strengthen interpretations of XP spectra for Cr and other transition metals in both the geochemistry and, more generally, materials chemistry communities.
3. Bibliography


