

Computer Simulation of Uranyl Adsorption on Montmorillonite Clay

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Introduction and Methods

We performed computer simulations to study the adsorption characteristics of the aqueous uranyl ion (UO_2^{2+}) near the siloxane surface of montmorillonite, a smectite clay. Our goal is to better understand the fate of uranium waste products in groundwater and soil sediments, a problem of increasing importance in environmental geochemistry.

We used the Monte Carlo simulation methodology and clay potential parameters of Skipper et al. (1995). Potential parameters for the aqueous uranyl ion yield a coordination geometry consistent with experimental data (Gilbaud et al., 1996). In our simulations, we have investigated the clay $d(001)$ spacing and uranyl coordination structure as a function of water content. The simulation supercell consisted of approximately 8 unit cells of the mineral, 3 UO_2^{2+} ions, and N interlayer water molecules.

Results

We examined the interlayer structure as the water content (N) was increased from 0 (dry clay) to 96 (300 mg $\text{H}_2\text{O}/\text{g}$ clay). The table below shows layer spacing and average U–O and U–Si distances (obtained from radial distribution functions). The uranyl ions are oriented with the O–U–O axis tilted slightly from the surface normal. Even at low water content ($N = 30$), the U–Si distance indicates that the uranyl ions do not form inner-sphere surface complexes. The first U–O peak at 2.45 Å is comprised exclusively of water oxygen atoms with a coordination number of 5. The second broader peak at 4.25 Å is due to both water and surface oxygen atoms. Two distinct water layers are seen at $N = 60$, with a $d(001)$ spacing of 14.72 Å. This layer spacing agrees well with the experimental value of 14.81 Å (Giaquinta et al., 1997).

N	$d(001) / \text{Å}$	U–O dist. / Å	U–Si dist. / Å
0	11.45 ± 0.07	2.60, 4.95	3.10
30	13.15 ± 0.14	2.45, 4.25	4.80
60	14.72 ± 0.09	2.45, 4.35	4.95
90	16.87 ± 0.13	2.45, 4.70	4.85

References

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Carbon and oxygen isotope compositions of carbonatite complexes from the Kola Peninsula, Russia

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The Kola-Karelia Region of Russia and Finland contains many carbonatite complexes, most of which are part of the Palaeozoic Kola Alkaline Province. Stable carbon and oxygen isotope compositions from published data (Khibina et al.) and new data (Sallanlatvi et al.) are compared here in order to find general patterns in the nature of their mantle source. The samples investigated contain several carbonate minerals and also several stages of carbonatite crystallization in order to have a complete view on carbonatite genesis and evolution.

Original (mantle) compositions are often modified in carbonatites by processes of fractional crystallization, degassing, and hydrothermal alteration. Careful consideration has been given to eliminating these processes before comparing the remaining primary compositions. For example, a recent study of REE-rich carbonatites at Khibina and Vuorijarvi, involving a combination of detailed mineral chemical investigation, stable (C,O) and radiogenic (Sr, Nd) isotopes, showed that each has a pegmatitic stage where a REE mineral (burbankite) and calcite or dolomite are co-genetic. Subsequent alteration caused much wider variation in stable isotopic values.

The primary oxygen isotope compositions are uniform (7 to 8 ‰) but there are large variations in $\delta^{13}\text{C}$ from normal mantle compositions (~ -6 ‰) to rather high $\delta^{13}\text{C}$ values (~ -2 ‰) which are independent of the age of the complex. The data are best explained by mantle heterogeneity caused by CO_2 metasomatism. In the Khibina and Vuorijarvi REE-rich carbonatites which are very similar as described above, the $\delta^{13}\text{C}$ ranges of primary carbonatites with low (unaltered) $\delta^{18}\text{O}$ values are different from each other but are correlated with their radiogenic isotope compositions. Interestingly, the Khibina complex with normal mantle $\delta^{13}\text{C}$ values have higher Sr isotope ratios than the Vuorijarvi carbonatites with relatively high $\delta^{13}\text{C}$. This difference is even more pronounced if other complexes (e.g. Kovdor and Turij) are also included in the comparison. The relationship between $\delta^{13}\text{C}$ and radiogenic isotope compositions is opposite to what would be expected in case of mantle contamination by subducted sedimentary carbonate. The data appear best explained by subduction-related source contamination facilitated by CO_2 metasomatism that caused $\delta^{13}\text{C}$ variations in the different mantle components.