

## Infrared spectroscopic identification of aqueous uranium(VI) species

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Migration of uranium(VI), the most stable form of uranium in environmental waters, is largely controlled by its geochemical reactions, both in solution and at the mineral-water interface. Current knowledge about U(VI) speciation is mainly based on thermodynamic calculations using data obtained by non-structural experiments, i.e. potentiometric titration [1]. A spectroscopic verification of the speciation of aqueous U(VI) is still insufficient. For the identification of different molecular species previous studies applied primarily EXAFS and Raman spectroscopy at very high uranyl concentrations (>100 mM) unreasonably in an environmental context [2-4].

In this study we used Attenuated Total Reflectance Fourier-transform Infrared (ATR-FTIR) spectroscopy, that allows the direct measurement of liquid samples. Our aim was to obtain additional vibrational spectroscopic information on the U(VI) species and especially to verify the U(VI) speciation throughout a wide pH range (pH 2-10) at a micromolar concentration level. The obtained spectral information was compared to previously reported thermodynamic data [1].

ATR-FTIR spectra were recorded at  $\text{UO}_2^{2+}$  concentrations ranging from 5 to 0.005 mM at pH 4. The spectroscopic results indicate distinctly that dimer and trimer hydroxo complexes become dominant upon lowering the uranyl concentration at pH 4. The thermodynamic data predict an absolute predominance of the free uranyl species  $\text{UO}_2^{2+}$  until pH 5 at these conditions.

At the micromolar concentration level the calculations predict the dominance of the uncomplexed uranyl ion until pH 5 and the formation of uranyl hydroxo complexes at neutral pH. Uranyl complexes with atmospheric carbonate in alkaline solutions are proposed above pH 6.5. However, the obtained ATR-FTIR spectra of low concentrated 0.02 mM uranyl solutions already show the coexistence of free and hydroxo complexed uranyl at pH 2.5. The appearance of carbonate complexes in solution becomes noticeable at the spectra of solutions at pH 7. Since the results are partially contradictory to previous predictions of U(VI) speciation a critical review of the present knowledge of uranium migration in the environment is required.

### References

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## Crystal size distribution (CSD) of periclase in marbles from the southern Adamello Massif, Italy

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Crystal size distributions (CSD) of periclase are presented for two profiles near the Cima Uzza summit, located in the southern Adamello massif (Italy). The data base was combined with geochemical and petrologic information to deduce the controls that acted on the periclase forming reaction.

Contact metamorphic dolomite marbles are exposed as xenoliths surrounded by mafic intrusive rocks. Periclase was retrograded to brucite. Periclase growth is the consequence of limited high temperature fluid infiltration. Stable isotope data show depletion for <sup>13</sup>C and <sup>18</sup>O in a narrow region (~40cm) near the igneous contact, whereas the periclase forming reaction front extends up to 4m into the host rock. A similar median grain sizes for periclase crystals was found over the entire profiles, but a larger proportion of bigger grains with increasing distance from the contact was observed. Textural analyses are combined with geochemistry data in a qualitative model that describes the dynamic nucleation and crystallization of periclase in this infiltration driven system. We attribute variations in grain sizes to changing reaction affinities along a dispersed infiltration front. This study highlights the need to invoke disequilibrium processes for metamorphic mineral growth and expands the use of CSD's to systems of mineral formation driven by fluid-infiltration.