The oxidation state of uranium in zircon

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U-Pb dating of zircon, $ZrSiO_4$, is the most common tool in geochronology. It is generally assumed that U occurs entirely as U^{4+} and that it substitutes directly for Zr^{4+}, although there is a mismatch in the size of the ionic radii. On the other hand, the ionic radius of U^{6+} is almost identical to that of Zr^{4+} and the difference in charge could be compensated for by the presence of other commonly occurring cations such as P and the REE. If both U^{4+} and U^{6+} are incorporated by zircon, then the oxidation state ratio should relate to that of the original melt from which the zircon crystallised. In this case, zircon may have a role to play as an indicator of the redox conditions of ancient magmas.

Oxidation states may be determined by X-ray absorption near edge structure (XANES) spectroscopy. U L_{III}-edge XANES spectra were recorded in fluorescence mode at beamline I18 of the Diamond Light Source. A suite of U-bearing glasses quenched from melts equilibrated over 20 log units in oxygen fugacity (fO_2) were used as standards. The XANES spectra of these samples exhibit systematic trends in both the absorption edge energy and white line intensity that correspond to a change in oxidation state from U^{4+} to U^{6+}. For natural zircons, spectra were recorded from individual crystals mounted in epoxy using a 4 μm analysis spot. Spectra were also recorded for one free-standing crystal, with a well defined morphology, mounted on a rotation stage to determine if spectral features vary with crystallographic orientation.

The spectra of zircons from a wide range of geological settings display variability that is much greater than that due to differences in crystal orientation. With reference to the glass standards, the range of edge energies suggests that the oxidation state may vary continuously between U^{4+} and U^{6+}. Relationships between the XANES spectra and U content, age, Eu and Ce anomalies, and trace element composition are being investigated.

Groundwater hydrogeochemical anomalies in São Paulo State, Brazil

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Groundwater has a special social, economic and strategic value in São Paulo State, the most industrialized and developed region in Brazil, supplying totally or partially about 70% of its municipalities through private and public wells. Groundwater chemical quality is an object of great concern, since the number of known cases of aquifer pollution is rising. Among these cases, there are chemical anomalies of natural origin, such as Cr^{6+}, Ba^{2+} and F^- occurrence in various aquifers. The aim of this research group is to investigate inorganic geochemical anomalies in aquifers, in order to assist the public authorities in the management of groundwater resources and contaminated areas. The techniques that are being used for the research projects include chemical analyses of water, chemical and mineralogical analyses of solid phase (XRF, XRD, SEM, microprobe analysis, sequential extraction analysis) and stable (^{18}O, D) and radiogenic ($^{86}Sr/^{87}Sr$) isotopes analyses in these phases.

One of the projects that are under development investigates the anomalous natural concentrations of Cr^{6+} in the groundwater of a wide region of the Western portion of São Paulo State. As part of a geochemical investigation of rock-water interaction, chemical and mineralogical characterization of sandstone samples from deep boreholes perforated in the city of Urânia was conducted. The results of this investigation indicated that: (1) the average concentration of chromium in the sandstones is anomalous (221 ppm); (2) chromium concentrations reached values of up to 6000 ppm in diopside, which is one of the main heavy minerals of the sandstones; (3) chromium concentrations on clay minerals and iron hydroxides are also relatively high (>650 ppm). Besides, from multilevels monitoring wells, stratified groundwater samples were collected for chemical analyses. The results indicated the occurrence of a hydrochemical stratification of the aquifer: waters from the base of the aquifer are alkaline (pH >10), whereas in the shallow zone of the aquifer, pH is neutral to mildly acid. Cr^{6+} prevails in the aquifer and a maximum concentration of 0.139 mg/L was obtained. The release of chromium from the solid phase to the water probably evolves the dissolution of Cr^{3+} minerals (like diopside), followed by a redox reaction that oxidizes Cr^{3+} to Cr^{6+} and reduces manganese oxide minerals. Additionally, adsorption reactions may also take place and desorption and mobilization of Cr^{6+} may be favored in some portions of the deep aquifer where pH is anomalously alkaline.