

An EXAFS study of Pd²⁺ solvation in aqueous media and chloride complexing to 340 °C at saturated vapour pressure

T.M. SEWARD¹, C.M.B. HENDERSON², AND J.M. CHARNOCK²

¹Institut für Mineralogie und Petrographie, ETH Zentrum, CH-8092 Zürich, Switzerland.

²CCLRC Daresbury Laboratory, Warrington WA4 4AO, United Kingdom.

With increasing temperature to the critical point, the decrease in hydrogen bonding in liquid water gives rise to fundamental changes in ion-solvent interaction. These effects are manifested by changes in ion-oxygen (water) bond lengths with associated changes in ion-water coordination numbers with increasing temperature. As part of our ongoing studies of ion-hydration and complexation in aqueous solutions at elevated temperatures and pressures, we have been studying the aquated Pd²⁺ ion and its complexation by chloride using X-ray absorption spectroscopy.

EXAFS measurements on 0.005m Pd(NO₃)₂ in 1.000m HClO₄ from 25 to 202 °C at equilibrium vapour pressures were performed in fluorescence mode using a high temperature cell containing silica glass windows. At 25 °C, Pd²⁺ is coordinated by four oxygens at a distance of 2.00 Å. When temperature is increased to 202 °C, the number of coordinated water oxygens remains at four and the distance is unchanged at 2.00 Å. These results are in contrast to other cations such as Ag⁺ and Sr²⁺ which "dehydrate" with increasing temperature as the cation-oxygen (water) bond distance contracts. Chloride-containing solutions show extensive complexation. For example, EXAFS measurements on 0.010m PdCl₂ in 0.010m HCl from 25 to 340 °C indicated a mixture of complexes in four-fold (square planar) configuration. At 25 °C, Pd²⁺ is coordinated by 2.5 chlorides and 1.5 oxygens at a distance of 2.28 and 2.04 Å, respectively. At 340 °C, 3.0 chloride ligands and 1.0 oxygens coordinate Pd²⁺ at 2.26 and 2.14 Å respectively. The formation of square planar PdCl₄²⁻ in 0.010m Pd(NO₃)₂ / 0.100m HCl solutions from 100 °C to 340 °C is characterized by a Pd²⁺ - chloride distance of 2.28 Å. The results will be discussed with relation to high temperature ion hydration and complexation for other systems.

On the importance of the microstructure for understanding U-Pb ages of dating minerals

A.-M. SEYDOUX-GUILLAUME¹, R. WIRTH², A. DEUTSCH¹ AND U. SCHÄRER³

¹Institut für Planetologie, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany (seydoux@uni-muenster.de)

²GFZ-Potsdam, Div. 4, Telegrafenberg, 14473 Potsdam, Germany

³UMR 6526 Géosciences AZUR, Université de Nice-Sophia Antipolis, Parc Valrose, 06108 Nice, France

The U-Pb method is most commonly used for high precision age dating. Minerals suitable for application of this method contain substantial quantities of U and Th, thus receiving intense auto-irradiation doses during their geologic history. During an alpha decay event a radionuclide liberates its energy by ejecting an α-particle while the remaining nucleus is recoiled in the opposite direction. Most of the atomic displacements leading to amorphization of a crystal lattice are caused by alpha-recoil nuclei. Physical properties of an amorphous mineral differ significantly from those of a crystalline mineral. It is discussed, for example, that an amorphous lattice will retain radiogenic Pb to a lesser degree than a perfect one, yielding discordant ages. Microstructural investigations are therefore of fundamental importance to better understand U-Pb ages of dating minerals.

Using Transmission Electron Microscopy (TEM), we investigate the microstructure of U-Pb dating minerals, amongst them natural monazites that have concordant U-Pb ages. Ages were from 474 Ma to 1900 Ma and radionuclide contents up to 13 wt.% ThO₂, 1600 ppm UO₂, and 7000 ppm PbO. In a first step, thin sections of single crystal fragments were analysed using Scanning Electron Microscope and Electron Microprobe, to look at possible zonations and to obtain reliable analyses. Then, samples were prepared for TEM investigations (JEOL3010), either with normal Ar-milling or with Focus Ion Beam milling.

Our results show that although they are old, high in radionuclides, and also having suffered high radiation doses during geological histories, these monazites are not metamict. We only report nm-isolated domains, where the lattice is distorted. Even for the oldest monazite (1900 Ma) we observed only small regions with some dislocations. We conclude that radiation damages do not accumulate in monazite because during self-annealing defects are healed faster than the lattice is damaged. It will be quite impossible for Pb to diffuse out of the monazite lattice. This explains why monazite is mostly concordant in the U-Pb concordia diagram.

References

- Schärer U. and Deutsch A. (1990), *Geochim. Cosmochim. Acta* **54**, 3435-3447.
 Seydoux-Guillaume A.M., Wirth R., Nasdala L., Gottschalk M., Montel J.M. and Heinrich W. (2002), *Phys. Chem. Minerals* **29**, 240-253.