

Study of diatoms/aqueous solution interface. II. Interaction of trace metals (Zn, Cu, Cd, Pb, Cr, Al) with freshwater and marine diatoms.

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In this study a thermodynamic approach is applied to model the interaction in aqueous solution of the surfaces of living diatoms with various trace metals. Four different diatoms were used: two marine planctonic species (*Thalassiosira weissfloggi*, *Skeletonema costatum*) and two freshwater periphytic species (*Achnantes minutissima*, *Navicula minima*). Metal adsorption experiments (Cd, Pb, U, and Al) performed on viable diatoms in batch reactors evidenced very fast and reversible processes similar to those reported for bacterial surfaces (Fein et al., 1997). Adsorption of Cd and Pb follows a typical adsorption edge with 100% saturation at pH ≥ 6 whereas Al adsorption exhibits a maximum at pH 7-8. Metal sorption is only weakly affected by varying ionic strength but is significantly reduced in the presence of diatom organic exudates and aqueous carbonate and chloride that form complexes with these metals. A high-resolution, reversible titration of diatoms with Cd, Cu, Pb and CrO_4^{2-} using ion-selective electrodes in a wide range of pH and metal concentration allowed to generate a set of thermodynamic constants for the surface complexation reactions between these metals and various surface sites. The effect of complexation by dissolved organic matter in solution was taken into account by measuring total and free metal concentration using anodic stripping voltametry. Change of diatom surface potentials in the presence of adsorbed metals and their organic complexes has been evidenced using electrophoretic mobility (ζ -potential) measurements. These results allowed to construct a rigorous thermodynamic model of metals-algae interactions which can be used for various environmental applications. A study of copper and zinc stable isotope fractionation generated by the sorption of these metals on diatoms during their growth in laboratory was performed using a multicollector ICP-MS. Moderate isotopic fractionation was noticed for Zn, however, all four diatom species exhibit the same isotopic signature for copper.

Understanding CL in natural zircons

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Cathodoluminescence of zircons

Cathodoluminescence (CL) is widely used in zircon geochronology for the identification and interpretation of internal structures in zircon. The contrast in CL images of natural zircons reflects structural phenomena of the crystals, originating, for example, from magmatic growth or differential recrystallisation due to fluid interaction. However, the mechanism of CL generation in natural zircons is not completely understood. In order to gain a thorough understanding of the origin of CL in natural zircon, we combined pan- and monochromatic CL investigations on natural and experimentally heat-treated (870-1620 K) partially metamict zircons from Sri Lanka with Raman spectroscopy, powder X-ray diffraction (XRD) and high precision ion microprobe trace element analyses.

Results

The investigated zircons were weakly luminescent in panchromatic mode, with monochromatic CL spectra that does not show any fine structure, which is typical for amorphous solids. Raman and XRD spectra documented the highly metamict state of these zircons. Heat treatment of these crystals caused an increase of the CL intensity. However, during the first recovery stage, which corresponds to the recombination of point defects in disordered crystalline remnants, as seen by a decreasing unit-cell volume, only a little increase in the CL intensity was observed. At higher annealing temperatures CL intensity increases dramatically and extrinsic luminescence bands become visible in the spectra. At this stage the crystalline domains start to grow at the expense of the amorphous material, as can be seen by decreasing crystallite size broadening effects in the XRD and Raman spectra. SIMS analyses show that the REE concentrations within the annealed grains do not show significant variations.

Conclusions

The results suggest that the CL intensity of natural zircons is mainly determined by the amount of crystalline material in those zircons that underwent a transformation to a metamict structural state. The extrinsic luminescence centers plays a lesser role in determining the CL contrast in panchromatic images of natural zircons.