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Dissolution of the (001) surface of galena: An in situ assessment of surface speciation by fluid-cell micro-Raman spectroscopy

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Abstract

The chemical evolution of the galena (001) cleavage surface dissolving in oxygen-saturated solutions was investigated by fluid-cell micro-Raman Spectroscopy (μRS) and solution chemistry. In this novel design of μRS apparatus, the solution in the fluid cell is continuously renewed. A fairly thick (several tens to hundreds of nanometers) layer forms at the galena surface in solutions with pH between 1 and 5.8. This surface layer is composed of Pb oxides, sulfates, and metastable species of sulfur. Native sulfur forms at pH 1 and 4.6, but is not a predominant surface species at pH 5.8. Dissolution rates, measured by solution chemistry, decrease with pH and reaction time. The formation of Pb oxides in these experiments at such low pH values contrasts with thermodynamic predictions based on properties at the macroscale (bulk solution).

The in situ assessment of surface speciation confirms that sulfur can partially oxidize at the interface, and indicates that this process of sulfur oxidation depends on pH. We propose that sulfur oxidation may take place, at least partially, during the reaction of dissolved molecular oxygen with S atoms at the galena surface, or in the immediate vicinity. After this first step of reaction, oxygen combines with Pb ions to form Pb oxide at the interface.

Keywords: Surface speciation, in situ investigation, galena, surface dissolution