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

INTRODUCTION

Galena (PbS) is a mineral of both economic and environmental importance. Its dissolution has been extensively studied (e.g., De Giudici et al. 2005, and references therein) by means of several diverse techniques such as bulk reaction, atomic force (AFM) and scanning tunneling (STM) microscopy, electrochemistry, X-ray photoelectron spectroscopy (XPS), and Fourier-transform (FTIR) and attenuated total reflection (ATR) infrared spectroscopy. Evidence from these studies, ranging from bulk to micro- and nanoscale, from morphological to compositional, from ex situ to in situ, and from surface to bulk, is partly equivocal and open to debate (e.g., Chernyshova 2003). For instance, XPS investigations indicate that microscopic secondary products can correspond to sulfate, Pb hydroxides, Pb oxides, and Pb-deficient galena surfaces (e.g., Fornasiero et al. 1994). On the other hand, during the process of oxidation from sulfide to sulfate at galena surfaces, several thermodynamically unstable species can be kinetically favored, namely polysulfides and sulfoxy anions. However, these chemical species have short lifetimes and are sensitive to experimental conditions (Nowak and Laajalehto 2000). Fluid-cell atomic force microscopy (AFM) gives clear evidence for the appearance of nanometer-sized phases at a galena surface dissolving in acidic and oxygen-saturated solutions (De Giudici and Zuddas 2001; Cama et al. 2005; Stack et al. 2004; Mikhlin et al. 2005; and references therein). Despite this fairly large body of literature, both the structure and the composition of galena surface coatings are still poorly constrained.

In an early investigation based on factor-group analysis, Ferraro (1975) predicted that galena (and other rock-salt structure minerals) should have no Raman active vibrational modes, and therefore cannot be analyzed by Raman spectroscopy. More recently, several experimental investigations determining Raman spectra of metal sulfides supported this idea (Mernagh and Trudu 1993; Shapter et al. 2000). In contrast, however, a growing body of literature provides evidence for first-order and second-order Raman spectra of galena (Smith et al. 2002, and references therein). Most of these Raman investigations of the galena surface are dominantly of a technical nature, dealing, for example, with flotation problems (see Andreev and Barzev 2003; Chernyshova 2003, and literature therein).

A novel experiment using in situ micro-Raman spectroscopy (μRS) is presented in this work. The surface speciation at the galena (001) surface was investigated during dissolution in an oxygen-saturated solution at different pH values (ranging from 1 to 5.8, in HCl). The overall rates of galena dissolution in the μRS-fluid-cell are measured by solution chemistry. Results are compared with those obtained by previous AFM, bulk solution, and XPS studies on the same mineral (De Giudici and Zuddas 2001; De Giudici et al. 2005). The in-situ assessment of surface speciation is then compared to other literature data.