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A contribution to the surface characterization of alkali metal sulfates

Marzia Fantauzzi, Americo Rigoldi, Bernhard Elsener, Davide Atzei, Antonella Rossi*

Dipartimento di Scienze Chimiche e Geologiche, INSTM Research Unit, Centro Grandi Strumenti Università di Cagliari, I-09042 Monserrato, Cagliari, Italy

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ABSTRACT

The analytical characterization of surfaces of sulfur-bearing samples that present sulfides, polysulfides and/or elemental sulfur as reaction products can be difficult by simply relying on the binding energy of the S2p X-ray photoelectron signals, due to the small chemical shifts. In such cases the Auger parameter concept can be used to distinguish among different chemical states, but this requires a model to curve fit complex Auger SKLL signals in order to resolve the contributions arising from sulfur in different chemical states on the surface. With this scope a detailed X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES) surface analytical study of the group IA sulfates is presented in this paper. Sulfates were chosen as model compounds for curve fitting the X-ray induced SKLL spectra since in these compounds sulfur is present in a unique chemical state.

For the first time the multicomponent SKLL spectra are fitted with model functions consisting of an intense ^{1}D and a low intensity ^{1}S contribution with constant energy difference of 8 eV. It was found that the kinetic energy of the $SK_{2,3}L_{2,3}$ (^{1}D) line increases from 2105.1 ± 0.1 to 2107.5 ± 0.2 eV whereas the corresponding $S2p_{3/2}$ binding energy decreases from 169.5 ± 0.1 eV for Li_2SO_4 to 167.8 ± 0.1 eV for Cs_2SO_4. Shifts to lower binding energy values are observed also for S2p, S2s and O1s peaks. In the chemical state plot the alkali sulfates fall on a line with an Auger parameter of ca. 2275 eV whereas elemental sulfur is found at 2277 eV. A shift of 0.6 eV in the calculated Auger parameter α' is observed from 2274.7 ± 0.1 eV for Li to 2275.3 ± 0.2 eV for Cs sulfate.

These results are discussed with respect to the influence of the cation using fundamental data and concepts such as ion radius, oxidation state and ionization energy, and separating intra-atomic and inter-atomic effects. All the information show a relatively small interaction between the sulfate anion and the cations as a consequence of the strong group localization of the valence states over the sulfate tetrahedron.

The sulfur SKLL spectrum of sulfates and elemental sulfur consisting of an intense ^{1}D and a low intensity ^{1}S contribution with constant energy difference of 8 eV can be considered a first step toward curve fitting of multicomponent sulfur SKLL spectra and the interpretation of complex mechanisms of oxidation and dissolution that involve sulfur.

1. Introduction

Sulfur speciation, the identification of the oxidation state, the chemical environment, and the coordination of sulfur are important in many different fields of research such as geology [1,2], glass technology [3], coal and oil industry [4,5], air pollution [6] and its remediation [7] in processing and degradation of sulfide minerals [8,9], in corrosion [10] and in tribology [11,12]. As long as bulk speciation is required sulfur K-edge X-ray absorption near-edge structure (XANES) is used [1–6]. Chemical speciation at the solid–liquid interface is of crucial importance to describe and understand the mechanisms of adsorption [13,14], dissolution and formation of the electrical double-layer or the interaction of sulfide minerals with the environment [8,9,15–18]. For these surface-related properties X-ray photoelectron spectroscopy (XPS) with its high surface sensitivity is state of the art.

Both techniques rely on the energy position of the sulfur K-edge in XANES and S2p photoelectron peak in XPS, respectively. The peak positions not only depend on the oxidation state (a chemical shift of 14 eV exists between S^{2-} and S^{6+} in sulfur K-edge, while the chemical shift for S2p in sulfides and sulfates line is ca. 8 eV) but also on the chemical environment; for example the associated cations [19] and the energy position might not be straight-forward for sulfur speciation.

The problem of sulfur speciation has been discussed in the literature in the context of chemical reactions occurring at the surface of sulfide minerals where the sulfur species at the surface are important in ore beneficiation [15,16,20] and in oxidation/dissolution of sulfide minerals accompanied by the release of several eco-toxic

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* Corresponding author at: Dipartimento di Scienze Chimiche e Geologiche, SS 554 Bivio per Sestu, 09100 Cagliari, Italy. Tel.: +39 070 6754464; fax: +39 070 6754456.
E-mail addresses: rossi@unica.it, antonella.rossi@mat.ethz.ch (A. Rossi).

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species such as heavy metals and arsenic [15–18]. This paper starts from a wider research on sulfur chemical state identification on the surface of sulfide minerals.

There is consensus that a sulfur enriched layer is formed on sulfide surfaces upon dissolution, but the assignment of chemical state to the S2p components is controversial: according to some authors elemental sulfur is formed [21,22], while according to [23] the sulfur enriched layer is constituted by polysulfides or by a metal-deficient sulfide layer [24]. Our research on enargite (Cu_3AsS_4) oxidation in Fe (III) bearing solutions has indicated a metal deficient sulfide layer [17,18].

The identification of the exact chemical state of sulfur on the basis of the S2p peak can be very difficult when sulfide, polysulfide and/or elemental sulfur are present on a sample surface due to small differences on the S2p binding energies, ranging between 162.0 and 164.4 eV. Since the chemical shift of the X-ray induced SKLL Auger peak between S^{2-} and S^{6+} compounds is higher (ca. 12 eV) than S2p chemical shift the use of SKLL peak can be helpful for sulfur speciation, especially in combination with photoelectron peak by means of the so-called Auger parameter α' and of the chemical state plot, introduced by [25]. The Auger parameter allows to obtain information on the local chemical environment of core-ionized atoms and the Wagner chemical state plots contain information on the initial state effects (Madelung potential and ground state valence atomic charge at the core-ionized atom) and on the final state effects (relaxation energy).

Correlations between Auger parameter shifts and catalytic activity, refractive index, and electronic properties in oxides and interface layers were found [26] and Auger parameter was found to be effective for describing chemical state of elements in geological samples and in sulfur containing minerals [27].

In previous papers [17,18,27] the authors calculated the Auger parameter of sulfur in different compounds taking into account the different components of S2p peaks but no attempts of curve fitting were performed on SKLL peaks and the kinetic energy of the centroid of the most intense component of SKLL peak was considered, even if S2p peak showed more than one component in the binding energy range sulfide–elemental sulfur.

For more accurate results the SKLL peak should be resolved in its components. In this paper, for the first time, a detailed XPS and XAES analysis of alkali metal sulfates is presented, together with the curve fitting of SKLL signal: since high purity commercial sulfates are available and due to the fact that sulfur in such compounds has a unique oxidation state (S^{6+}), alkali metal sulfates were chosen to resolve the complex line shape of SKLL signal into its components by means of synthetic curves. The obtained peak fitting parameters will be useful for the investigation of more complex signals, and so they could be applied to resolve the SKLL peaks of S^{2-}, S_n^{2-} and S_8 bearing samples.

Furthermore, a deepened study on the influence of the cation among the alkali metal sulfates is presented: the cation seemed to influence the binding energy of photoelectron S2p peak, kinetic energy of SKLL peak and Auger parameter of sulfur and the shifts will be discussed in term of initial and final state effects. Moreover the effect of the ionicity of the compound on the X-ray induced Auger SKLL signal cross-section is presented.

Table 1
Details of the sulfate samples used in this work.

Molecular formula	Purity	Supplier
$Li_2SO_4*H_2O$	99%	Merck
Na_2SO_4	99% min.	Riedel de Haën
K_2SO_4	99%	Merck
Rb_2SO_4	99.8%	Aldrich
Cs_2SO_4	99.99%	Aldrich

2. Experimental

2.1. Sample preparation

Details on the alkali metal sulfates samples used in this work are provided in Table 1. The moisture sensitive compounds were purchased in sealed containers under nitrogen. All containers were opened in the glove box (UNILAB manufactured by MBraun), under argon atmosphere. Residual oxygen and water in the glove box were monitored and resulted to be always lower than 1 mg/kg. Together with alkali metal sulfates a sample of elemental sulfur was analyzed after grinding in an agate mortar in glove box. All the powders were pressed into a disk such as is used for infrared spectroscopy. The pellets were then mounted on a standard sample holder (Fig. 1) with a double-sided adhesive tape. The transfer of the sample to the fast-entry air lock of the XP-spectrometer was accomplished using a bell-device (Fig. 1) that allows the transfer of the sample without contact to air [28]. The samples were cooled at the liquid nitrogen temperature during the measurement to avoid secondary decomposition effects and to maintain the residual pressure below 10^{-6} Pa. In order to verify the purity of the sulfate samples X-ray diffraction spectra were performed using a powder diffractometer STOE STADI P (STOE & Cie GmbH, Darmstadt, Germany) equipped with an image-plate detector and a Cu Kα X-ray source. X-ray diffraction data are reported in supplementary materials (Fig. S1): no other phases were detected on the sulfate samples.

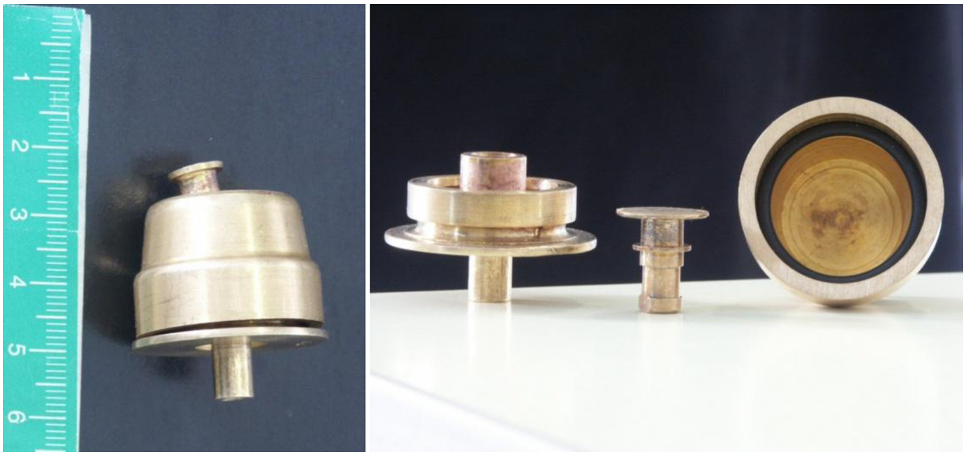

Fig. 1. Bell-device for transferring the sample from the glove box to the fast entry air lock of the XP-spectrometer [28].