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Sommario

During the interaction of sulphide minerals with the environment many reactions may occur. The knowledge of sulphur chemical state is important in order to clarify the mechanisms of oxidation/dissolution and precipitation reactions also in biotic conditions on the surface of these minerals. To date different hypotheses have been proposed for identifying the sulphur compounds that may form but no consensus is reached so far because the identification has been carried out either only on the basis of the photoelectron signals or combining the photoelectron signal with the centroid of the X-ray induced SKLL Auger line.
The objectives of this thesis are: the development of an analytical strategy for the unambiguous identification of sulphur chemical state in nanometer thick layers that form on mineral surfaces after leaching. To this purpose the acquisition of detailed spectra of a series of metal sulphides and of model systems made of mixtures of sulphur and polysulphides prepared under controlled conditions is necessary. Second objective was the establishment of the curve-fitting procedure to allow the separation of the different components present on the surface (sulphide, polysulphides, sulphates) not only of the S2p XP-spectra but also of the SKLL spectra. Based on these results the Auger parameter values will be determined and will be used together with the chemical state plot to distinguish the chemical state of sulphur species formed on the mineral surfaces

after different surface treatments. In this way, the surface reactivity of sulphide minerals and more in general, of sulphur âbearing particles will be determined

The present work is organized in six chapters: the first one presents a short overview on the environmental problems that may occur when sulphide minerals, especially, those bearing eco-toxic elements such as arsenic, are exposed to the acidic mine drainage in the presence of oxidants and/or of microorganisms which enhance oxidation kinetics. It then outlines the analytical strategy that was adopted in this work for the identification of the sulphur chemical state.

In the second chapter a literature survey is provided: it underlines the role of sulphur in sulphide bearing minerals: Section 2.1 reports information about the mineral enargite and the chemical state of sulphur on its surface as it is available to date. Section 2.2 deals with the literature on the possibility of using the KLL Auger transition. In chapter 3 a brief description of X-ray photoelectron and X-ray excited Auger electron spectroscopy is given while the materials and methods used in the present work are presented in chapter 4.

In chapter 5 â results and discussion - the X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES) analyses on alkaline and transition metal sulphide and sulphates, polysulphides and sulphide minerals are presented. In particular the spectra recorded on the S2p and S KLL lines of the sulphides and sulphates are shown: they were collected for getting the peak fitting parameters and apply them to the model systems obtained by mixing sulphur with sodium tetrasulphide and to investigate the composition of mineral surfaces. Minerals were analysed freshly cleaved, ground and after air exposure. The chemical state of sulphur in sulphates, sulphides (alkali- and transition metal compounds, minerals) and polysulphide is then discussed. For the first time the X-ray excited Auger SKLL lines were fitted with parameters based on standards. In this way, which can be considered as an extension of previous work, a separation of the different components and a more precise determination of their kinetic energy were achieved. The Auger parameter and the chemical state plot were obtained by combining the S2p photoelectron lines and the SKLL Auger lines. On this basis a clear distinction of the chemical state of sulphur in sulphates, in alkali sulphides and in transition metal sulphides was possible. The chemical state of sulphur in the bulk of minerals such as enargite or pyrite was determined. The chemical state of sulphur that formed on the surface of compounds after exposure to air or after grinding was found to vary according the coordinating metal and its concentration.

It can be assessed that the analytical approach developed in the presented thesis and based on the curve â fitting procedure applied to the X-ray induced Auger electron spectroscopy appears to be a very promising method for identifying the chemical state of sulphur and for providing a new insight in the surface chemistry of sulphide minerals.

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