

SPECIAL SAM ARTICLES**THERMAL EFFECTS OF MINORITY CHALCOGENIDE MINERALS: DTA-TG, IR SPECTROSCOPY AND SEM ELECTRON MICROSCOPY STUDIES**V. L. BARONE¹, I.L. BOTTO¹ and I.B. SCHALAMUK²

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Abstract— Aspects related to the thermal behaviour of minority chalcogenides containing Bi, Sb, Pb, Cu and Ag, associated with massive binary sulfides of economical importance, have been analyzed and compared. Selected samples proceed from different Argentine ore deposits. DTA-TG measurements of jamesonite ($\text{FePb}_4\text{Sb}_6\text{S}_{14}$), eucairite (CuAgSe) and tetradymite (Bi_2STe_2) have been registered in oxidant atmosphere. The binary mineral chalcocite (Cu_2S) has been also analyzed and employed with comparative purposes. The study was carried out with the aid of X-ray diffraction (XRD), IR spectroscopy and scanning electron microscopy (SEM) with microprobe chemical analysis (EDAX). Mass and energy changes during the thermal treatment can be associated with the increase of the metallic character of chalcogen and subsequently with the reactivity of the intermediate dioxide or oxocompound.

Keywords— Chalcogenides, thermal behaviour, jamesonite, tetradymite, eucairite.

I. INTRODUCTION

The roasting process of metal sulfide to produce the metal is the basis of an important process used industrially on a large scale. Basically, it implicates an oxidation process to remove sulfur as volatile oxide.

So, over the centuries, lead and copper metals have been produced from galena and chalcopyrite, massive sulfide minerals, by this pyrometallurgical route. For long time, the extractive metallurgy of these metals has been directed towards energy economy (Habashi, 1985). In this respect, the presence of impurities originated by minority minerals namely sulfosalts and metal chalcogenides has been a problem very difficult to solve. This type of compounds, usually associated with common massive sulfides, affects

not only the energetic efficiency of the process but also the quality of the raw metals. In fact, it is well known that certain metalloids, e.g. antimony and bismuth, contaminate the copper and for this reason they must be removed previously by selective and expensive leaching processes. New technologies (e.g. hydrometallurgical route) have been developed in the last decades to reduce not only the dangerous evolution of SO_2 and the undesirable presence of impurities but also the energetic cost of the process. In spite of these disadvantages, the thermal conversion of sulfide is even employed as extractive metallurgy for lead and copper.

Sulfosalts show a complex composition and structure (Makovicky, 1989) and the insufficient characterization of the starting materials in which these minority phases are included can affect the thermal reaction path. Hence, the assignment of the thermal effects of the massive sulfide can be made on a speculative basis. In the last years the characterization of the samples has been improved with a large amount of techniques (as spectroscopy and microscopy), which allow to assign more confidence to each thermal event (Dunn, 1997).

The oxidation occurs as a sequence of solid-gas and solid-solid reactions although it is usually controlled by the oxygen diffusion. This mechanism is observed as the first step. Thus, the evolution of chalcogenide dioxides with the temperature increase is related to the respective atomic weight.

The formation of oxocompounds followed by their decomposition as well as solid-solid and/or solid-gas reactions can be overlapped with ionic diffusional processes.

This work is a comparative analysis of the thermal oxidation of three minority species. We intend to demonstrate the behaviour of chalcogenides in the process. For this reason, we have selected the complex sulfide $\text{FePb}_4\text{Sb}_6\text{S}_{14}$ (jamesonite), a selenide of composition CuAgSe