



# Characterization of the sulphate mineral coquimbite, a secondary iron sulphate from Javier Ortega mine, Lucanas Province, Peru – Using infrared, Raman spectroscopy and thermogravimetry



Ray L. Frost<sup>a,\*</sup>, Željka Žigovečki Gobac<sup>b</sup>, Andrés López<sup>a</sup>, Yunfei Xi<sup>a</sup>, Ricardo Scholz<sup>c</sup>, Cristiano Lana<sup>c</sup>, Rosa Malena Fernandes Lima<sup>d</sup>

<sup>a</sup> School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

<sup>b</sup> Institute of Mineralogy and Petrography, Department of Geology, Faculty of Science, University of Zagreb, Horvatovac 95, 10000 Zagreb, Croatia

<sup>c</sup> Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil

<sup>d</sup> Mining Engineering Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil

## HIGHLIGHTS

- We have studied the mineral coquimbite.
- Using SEM with EDX, thermal analytical techniques and Raman and infrared spectroscopy.
- Chemical formula was determined as  $(\text{Fe}_{1.37}^{3+}, \text{Al}_{0.63})_{\Sigma 2.00}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ .
- Thermal analysis showed a total mass loss of  $\sim 73.4\%$  on heating to 1000 °C.

## ARTICLE INFO

### Article history:

Received 19 November 2013

Received in revised form 30 January 2014

Accepted 30 January 2014

Available online 3 February 2014

### Keywords:

Coquimbite

Amarantite

Raman spectroscopy

Sulphate

Infrared spectroscopy

## ABSTRACT

The mineral coquimbite has been analysed using a range of techniques including SEM with EDX, thermal analytical techniques and Raman and infrared spectroscopy. The mineral originated from the Javier Ortega mine, Lucanas Province, Peru. The chemical formula was determined as  $(\text{Fe}_{1.37}^{3+}, \text{Al}_{0.63})_{\Sigma 2.00}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ . Thermal analysis showed a total mass loss of  $\sim 73.4\%$  on heating to 1000 °C. A mass loss of 30.43% at 641.4 °C is attributed to the loss of  $\text{SO}_3$ . Observed Raman and infrared bands were assigned to the stretching and bending vibrations of sulphate tetrahedra, aluminium oxide/hydroxide octahedra, water molecules and hydroxyl ions. The Raman spectrum shows well resolved bands at 2994, 3176, 3327, 3422 and 3580  $\text{cm}^{-1}$  attributed to water stretching vibrations. Vibrational spectroscopy combined with thermal analysis provides insight into the structure of coquimbite.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Coquimbite is an iron (III) sulphate mineral of ideal formula  $\text{Fe}_2^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , which derives its name from the Coquimbo region, Chile [1]. Coquimbite is found as secondary mineral developed in the oxidized portions of weathering iron sulphide deposits in arid regions, although it could be also found associated with fumarolic activity [1]. The mineral was first described from Tierra Amarilla near Copiapó, Chile [2–5], and other occurrences were reported in Quetena, Chuquicamata, Alcaparroso, Chile; Concepción mine, Huelva, Spain; Skouriotisa, Cyprus; Rammelsberg, Hartz, Germany, among others [1,3,6–8].

Coquimbite was recently found in Peru, at the Javier Ortega mine, Lucanas Province, Departamento Ayacucho [9]. Main ore mineral in Javier Ortega mine is chalcopyrite and secondary ore minerals are sphalerite and galena [9]. Coquimbite occurs in the oxidized portions of this iron sulphide deposit, together with other secondary sulphate minerals like alunogen, chalcantite, copiapite, halotrichite, jarosite, krausite, römerite and with sulphur. Coquimbite in Javier Ortega mine occurs in well developed violet crystals up to 5 cm long [9].

Coquimbite is a hexagonal mineral [10,11] with  $a = 10.922(9)$ ,  $c = 17.084(14)$  Å, space group  $P\bar{3}1c$  and  $Z = 4$  [12]. Ideal formula of this mineral is  $\text{Fe}_2^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ , but there is often a replacement of  $\text{Fe}^{3+}$  by  $\text{Al}^{3+}$ , so the formula of this mineral should be written  $\text{Fe}_{2-x}^{3+}\text{Al}_x(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  [6,12]. There are three outstanding features of the coquimbite structure. The dominant structural

\* Corresponding author. Tel.: +61 731382407; fax: +61 731381804.

E-mail address: [r.frost@qut.edu.au](mailto:r.frost@qut.edu.au) (R.L. Frost).

feature is a discontinuous chain, composed of alternating Fe octahedra and S tetrahedra, parallel to, and approximately one-half the length of, the *c* axis. The symmetry causes the chain to be repeated in the upper one-half of the cell. The individual chain segments (i.e. two centrosymmetrically related clusters of six  $\text{SO}_4$  tetrahedra and three Fe octahedra in each unit cell) are linked through hydrogen bonds only. The second structural feature is the geometrical arrangement of these chains which gives rise to “channels”, paralleling the  $a_1$  and  $a_2$  axes, which are occupied by water molecules linked to the chains by hydrogen bonds. The third structural feature are independent (Al, Fe) octahedra located at the origin and at the centre of the *c* edges surrounded by six  $\text{H}_2\text{O}$  molecules. There are three crystallographically different iron atoms octahedrally coordinated to six O and/or Ow (= oxygen atom of an  $\text{H}_2\text{O}$  molecule) forming  $\text{Fe}1\text{O}_4\text{O}_6$ ,  $\text{Fe}2\text{O}_3\text{Ow}_3$ , and  $\text{Fe}3\text{Ow}_6$  octahedra. Two of in total three crystallographically independent  $\text{H}_2\text{O}$  molecules, Ow1 and Ow3 are bonded to one iron atom, whereas Ow2 is not bonded to any cation. The mean (Fe–O) distance of Fe3 site differ from distances of Fe1 and Fe2 sites, and such a difference in average bond distance can be attributed to the partial Fe3 site occupation also by Al atoms. So, the crystal structure of coquimbite could be described as a  $[\text{Fe}_4(\text{H}_2\text{O})_{12}(\text{SO}_4)_6]^{10}$  framework consisting of  $[\text{Fe}1\text{Fe}2_2(\text{H}_2\text{O})_6(\text{SO}_4)_6]^{3-}$  clusters and isolated  $[\text{Fe}3(\text{H}_2\text{O})_6]^{3+}$  octahedra connected to each other only by hydrogen bonds. Ow1 and Ow3 atoms are engaged in the further interconnection of the  $[\text{Fe}_3\text{Ow}_3(\text{SO}_4)_6]$  clusters and  $[\text{FeOw}_1]_6$  octahedra. And Ow2 atoms which build hydrogen-network-bonded  $\text{H}_2\text{O}$  molecules ( $\text{H}_2\text{Ow}_2$ ) which are placed in channels running parallel to the *a* axis (in cages made by channel's intersection) occupy positions which can be compared to the corners of a flattened octahedron and there can be distinguished two bonding-scheme types for this Ow2 atoms, i.e. two hydrogen-bonded network variants around the  $\text{H}_2\text{Ow}_2$  molecules [13].

Rietveld refinement of the coquimbite structure [14] on a sample from the Richmond mine, Redding, California, proved that there is, together with the Al-for-Fe substitution on Fe3 site, also a minor Al-for-Fe substitution on the Fe1 site. Although there is a possibility of a wide range of continuous replacement of the  $\text{Fe}^{3+}$  by other ions of similar radius, such as especially aluminium, without modifying the structural type, on increasing the Al content beyond a certain limit, a structural rearrangement of the phase occurs, leading to the new mineral species aluminocoquimbite  $\text{AlFe}^{3+}(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  [15–17]. Mineral coquimbite is polytypic with paracoquimbite, a rhombohedral mineral (space group  $R\bar{3}$ ) [18]. These two minerals, i.e. two layer-like crystal structures differ in layer stacking sequences, with a repeat distance of 8.5 Å between structurally identical but spatially transposed layers.

Approximately 370 sulphate-mineral species are known to exist in nature and they are found in a variety of geological settings, including volcanic, hydrothermal, evaporitic, and chemical-weathering environments [19]. A problem in identification of such minerals with techniques like an X-ray diffraction arises when closely related minerals are found in paragenetic relationship [20]. So, vibrational spectroscopic techniques are applicable in identification of such paragenetically related minerals.

## 2. Experimental procedure

### 2.1. Samples description and preparation

The mineral coquimbite studied in this work was obtained from the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAB-101. The sample is from the Javier Ortega mine, Lucanas Province, Peru.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The coquimbite sample was phase analysed by X-ray diffraction. Scanning electron microscopy (SEM) was applied to support the mineralogical chemical.

### 2.2. Scanning electron microscopy (SEM)

Coquimbite cleavage fragments were coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron

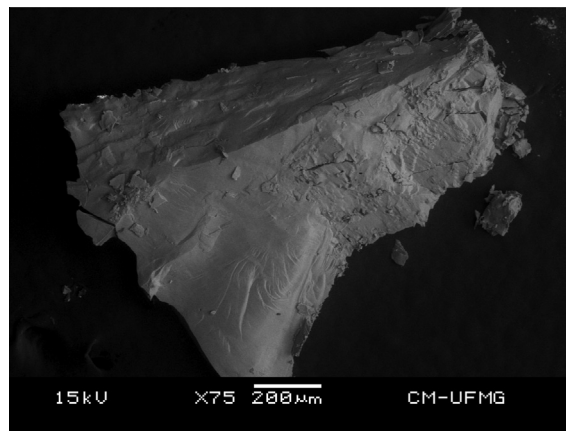


Fig. 1. Backscattered electron image (BSI) of a coquimbite crystal aggregate up to 0.5 mm in length.

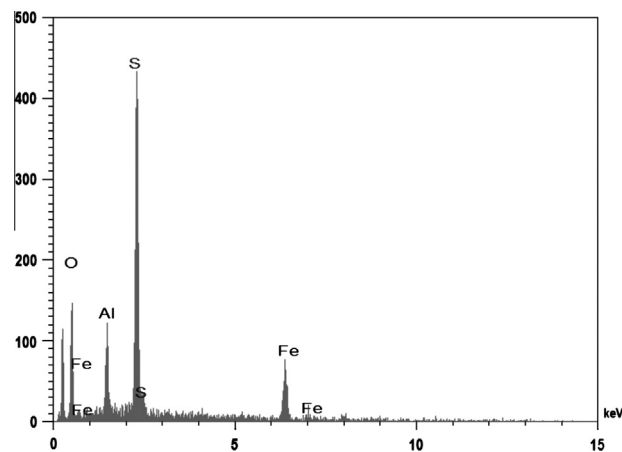


Fig. 2. EDS analysis of coquimbite.

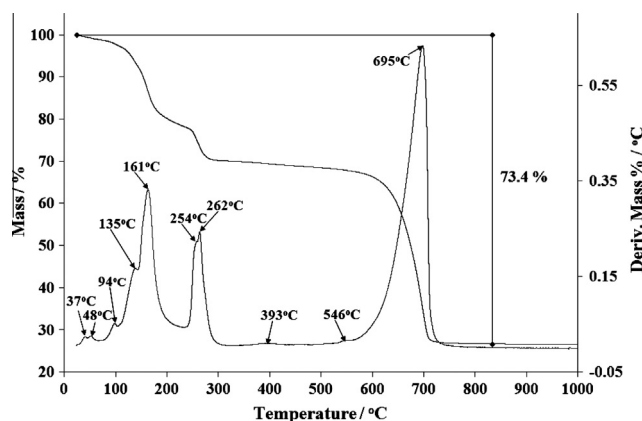


Fig. 3. Thermal analysis of coquimbite.

Download English Version:

<https://daneshyari.com/en/article/1402648>

Download Persian Version:

<https://daneshyari.com/article/1402648>

[Daneshyari.com](https://daneshyari.com)