



# Infrared and Raman spectroscopic characterization of the carbonate bearing silicate mineral aerinite – Implications for the molecular structure



Ray L. Frost<sup>a,\*</sup>, Ricardo Scholz<sup>b</sup>, Andrés López<sup>a</sup>

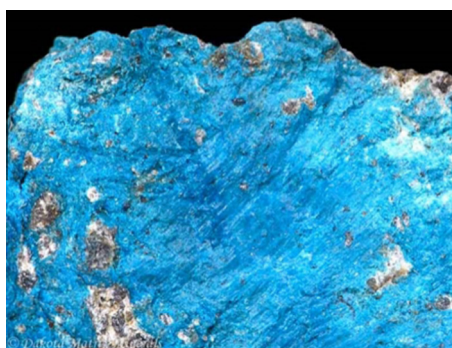
<sup>a</sup> School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia

<sup>b</sup> Geology Department, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35,400-00, Brazil

## HIGHLIGHTS

- The mineral aerinite contains both silicate and carbonate units which is unusual.
- It is a highly colored mineral being bright blue/purple.
- We have analyzed aerinite using EDX and SEM techniques.
- Raman bands attributable to silicate and carbonate units are observed.
- Multiple hydroxyl vibrations support the concept that water is in different molecular environments.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The mineral aerinite is an interesting mineral because it contains both silicate and carbonate units which is unusual. It is also a highly colored mineral being bright blue/purple. We have studied aerinite using a combination of techniques which included scanning electron microscopy, energy dispersive X-ray analysis, Raman and infrared spectroscopy. Raman bands at 1049 and 1072  $\text{cm}^{-1}$  are assigned to the carbonate symmetric stretching mode. This observation supports the concept of the non-equivalence of the carbonate units in the structure of aerinite. Multiple infrared bands at 1354, 1390 and 1450  $\text{cm}^{-1}$  supports this concept. Raman bands at 933 and 974  $\text{cm}^{-1}$  are assigned to silicon–oxygen stretching vibrations. Multiple hydroxyl stretching and bending vibrations show that water is in different molecular environments in the aerinite structure.

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## Introduction

The mineral aerinite has been known for a long period of time [1,2] and was described in many archeological artifacts [3,4] and is known as an important pigment in Romanesque paintings [5–8]. The word “Aerinite” come from the Greek word “aiernos”

which means sky or atmosphere. Aerinite chemical formula can be written as  $\text{Ca}_4(\text{Al,Fe,Mg})_{10}\text{Si}_{12}\text{O}_{35}(\text{OH})_{12}\text{CO}_3 \cdot 12\text{H}_2\text{O}$ . The mineral is a bluish-purple inosilicate and crystallizes with monoclinic symmetry [9–11]. It is interesting that the color of the mineral is so intense blue. Normally, one might expect such intense colors from copper bearing minerals, yet aerinite contains no copper. The unit cell parameters refined by synchrotron powder diffraction are:  $a = b = 16.9161(1) \text{ \AA}$ ,  $c = 5.2289(1) \text{ \AA}$ ,  $V = 1296 \text{ \AA}^3$ , space group  $P3c1$ . Aerinite shows a complex crystal structure. It is crystal

\* Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804.

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

structure can be best understood by introducing cylindrical basic building units consisting on three pyroxene chains pointing inwards to accommodate tri- and divalent metal cations at the centers of the resulting face-sharing octahedra. Out of the three symmetry-independent three-fold rotation axes in the unit cell, two are occupied by such cylindrical units and the third by  $\text{CO}_3$  groups. Consequently, each unit is surrounded by three similar ones [9–11].

In nature, aerinite occurs as fibrous masses and coatings. It has a dark blue color and vitreous luster. It is a low-temperature hydrothermal phase occurring in zeolite facies alteration of mafic rocks. Associated minerals include prehnite, scolecite and mesolite.

Due to the similar macroscopic aspects of the mineral in comparison with a number of Cu silicates, such as ajoite [11], apachite, chrysocolla [12], plancheite [13], gilalite, shattuckite [14] and several others. A complete vibrational spectroscopic study can be an important non-destructive tool in the determination of such minerals. In order to distinguish these minerals from aerinite, it is important to show the presence of carbonate. This work is the first systematic spectroscopy study of the mineral aerinite, indeed studies have been undertaken to study the effect of temperature on aerinite [9,11].

The aim of this paper is to present the Raman and infrared spectra of aerinite and to relate the spectra to the structure of the mineral, the structure of which remains uncertain. This research reported here, is part of systematic studies on the

vibrational spectra of minerals of secondary origin in the oxide supergene zone and their synthetic analogs.

## Experimental

### Samples description and preparation

The aerinite sample studied in this work was collected from the Estopiñán dam, Estopiñán del Castillo, Huesca, Aragón, Spain. The sample was incorporated to the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAC-132. The sample was gently crushed and the associated minerals were removed under a stereomicroscope Zeiss Stemi DV4 from the Museu de Ciência e Técnica of the Federal University of Ouro Preto. Scanning electron microscopy (SEM) was applied to support the mineral characterization. A picture of the mineral aerinite is given in the graphical abstract.

### Scanning electron microscopy (SEM)

Experiments and analyses involving electron microscopy were performed in the Center of Microscopy of the Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil. Aerinite crystal aggregate was coated with a 5 nm layer of evaporated Au. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment.

### Raman spectroscopy

Crystals of aerinite were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with

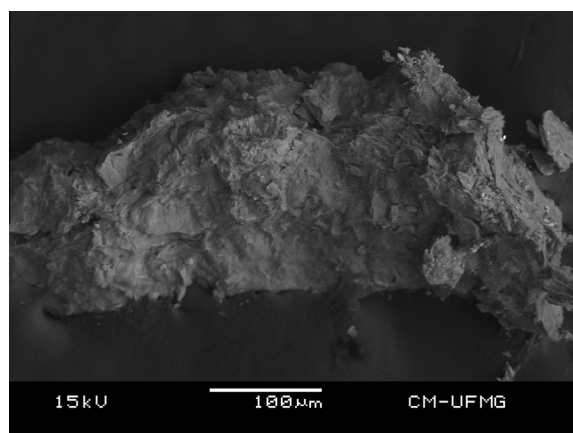


Fig. 1. Backscattered electron image (BSI) of an aerinite crystal up to 1.0 mm in length.

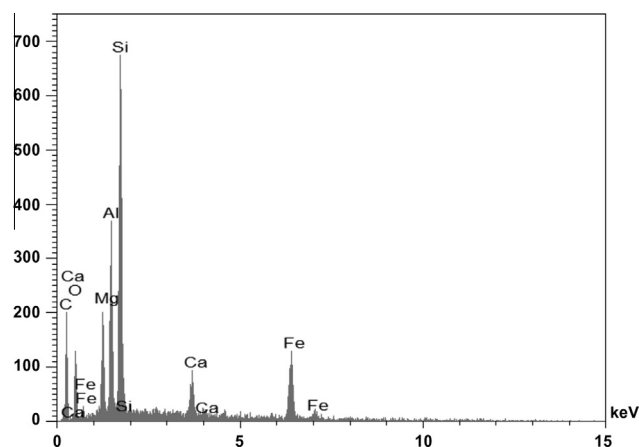


Fig. 2. EDS analysis of aerinite.

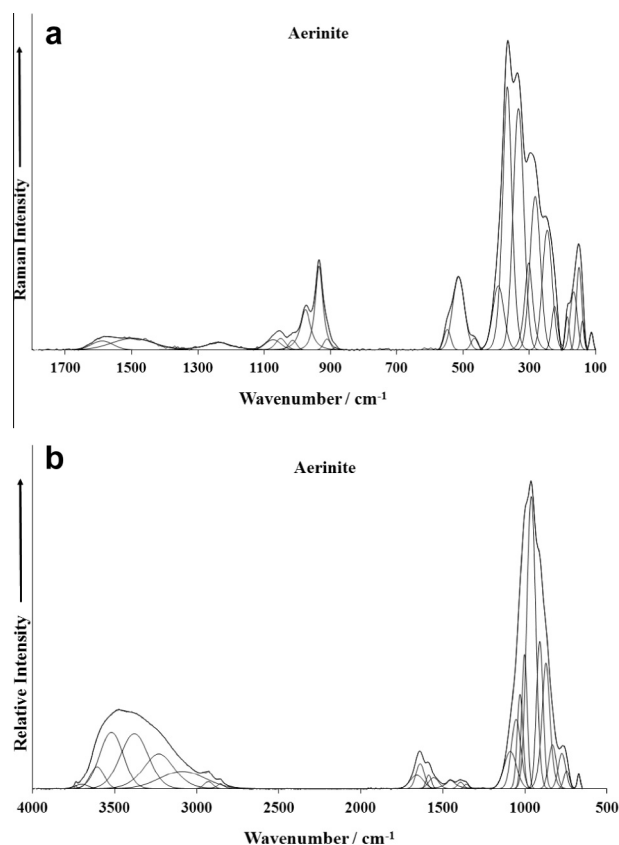


Fig. 3. (a) Raman spectrum of aerinite (upper spectrum) over the 100–1800  $\text{cm}^{-1}$  spectral region and (b) infrared spectrum of aerinite (lower spectrum) over the 500–4000  $\text{cm}^{-1}$  spectral region.

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