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A vibrational spectroscopic study of the silicate mineral analcime – $Na_2(Al_4SiO_4O_{12})\cdot 2H_2O$ – A natural zeolite

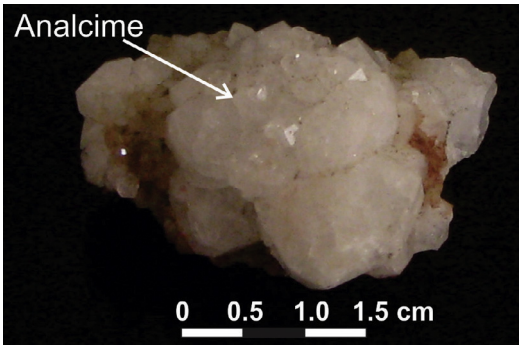
Ray L. Frost [a,*], Andrés López [a], Frederick L. Theiss [a], Antônio Wilson Romano [b], Ricardo Scholz [c]

[a] School of Chemistry, Physics and Mechanical Engineering, Science and Engineering Faculty, Queensland University of Technology, GPO Box 2434, Brisbane, Queensland 4001, Australia
[b] Geology Department, Federal University of Minas Gerais, Belo Horizonte, MG 31270-901, Brazil
[c] Geology 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 analcime using SEM with EDX and vibrational spectroscopy.
- Analcime $Na_2(Al_4SiO_4O_{12})\cdot 2H_2O$ is a crystalline sodium silicate.
- Chemical analysis shows the mineral contains Na, Al, Fe^{2+} and Si.
- Multiple water bands indicate that water is involved with differing hydrogen bond strengths.

GRAPHICAL ABSTRACT



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ABSTRACT

We have studied the mineral analcime using a combination of scanning electron microscopy with energy dispersive spectroscopy and vibrational spectroscopy. The mineral analcime $Na_2(Al_4SiO_4O_{12})\cdot 2H_2O$ is a crystalline sodium silicate. Chemical analysis shows the mineral contains a range of elements including Na, Al, Fe^{2+} and Si. The mineral is characterized by intense Raman bands observed at 1052, 1096 and 1125 cm^{-1}. The infrared bands are broad; nevertheless bands may be resolved at 1006 and 1119 cm^{-1}. These bands are assigned to SiO stretching vibrational modes. Intense Raman band at 484 cm^{-1} is attributed to OSiO bending modes. Raman bands observed at 2501, 3542, 3558 and 3600 cm^{-1} are assigned to the stretching vibrations of water. Low intensity infrared bands are noted at 3373, 3529 and 3608 cm^{-1}. The observation of multiple water bands indicate that water is involved in the structure of analcime with differing hydrogen bond strengths. This concept is supported by the number of bands in the water bending region. Vibrational spectroscopy assists with the characterization of the mineral analcime.

Introduction

The zeolite minerals form a complex group of aluminosilicates that often occur as accessory minerals in intermediate and basic rocks. Zeolites are microporous crystalline compounds with extremely narrow pore size distributions, which have found several applications being used as ion exchangers, catalysts, among others. Analcime – $Na_2(Al_2Si_4O_{12})\cdot 2H_2O$, is one of the most common minerals with the zeolite type structure. The mineral shows different symmetry of crystallization. The crystal structure was first determined by Taylor [1] with cubic symmetry and later refined by Pechar [2,3] and refined by neutron diffraction by Ferraris et al. [4] with triclinic symmetry. Analcime is usually classified as a zeo-

* Corresponding author. Tel.: +61 7 3138 2407; fax: +61 7 3138 1804.
E-mail address: r.frost@qut.edu.au (R.L. Frost).

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lite mineral, but structurally and chemically it is more similar to the feldspathoids. Analcime occurs as a primary mineral in analcime basalt and other alkaline igneous rocks. It also occurs as cavity and vesicle fillings associated with prehnite, calcite and zeolites.

The genesis of analcime may be related to the crystallization from a trachytic melt as a primary magmatic mineral, as proposed by Peterson et al. [5] and Roux and Hamilton [6]; or it may have been produced by ion exchange from preexisting leucite [7]. The mineral analcime as well as its similar synthetic analogs are of interest due to their application in different industries, such as the removal of nuclear wastes [8], the removal of heavy metals [9,10] and in ceramics [11].

Some Raman spectra of sodium aluminum silicates have been collected and a number of the spectra were shown to be dependent upon the number of condensed silica tetrahedra [12]. Such detailed assignment of infrared and Raman bands for a wide range of silicate structures was made by Dowty [13–16]. The thermal decomposition of sodium silicates has also been measured [17–19]. There is an apparent lack of information on the vibrational spectra of analcime. The reason for such a lack of information is not known; yet the mineral contains siloxane units. Such units lend themselves to vibrational spectroscopy. Raman spectroscopy has proven most useful for the study of mineral structure [20–25]. The objective of this research is to report the Raman and infrared spectra of analcime and to relate the spectra to the mineral structure.

Experimental

Samples description and preparation

The analcime sample studied in this work occurs as single crystals with tabular habitus up to 5 cm. The sample is part of the collection of the Geology Department of the Federal University of Ouro Preto, Minas Gerais, Brazil, with sample code SAD-014. The mineral sample originated from Moonen Bay, Dunvegan, Duirinish, Isle of Skye, North West Highlands (Inverness-shire), Scotland, UK.

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The analcime sample studied in this work was analyzed by scanning electron microscopy (SEM) in the EDS mode to support the mineral characterization.

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 (http://www.microscopia.ufmg.br). Analcime crystals were coated with a 5 nm layer of evaporated carbon. Secondary Electron and Backscattering Electron images were obtained using a JEOL JSM-6360LV equipment. Qualitative and semi-quantitative chemical analyses in the EDS mode were performed with a ThermoNORAN spectrometer model Quest and were applied to support the mineral characterization.

Raman microprobe spectroscopy

Crystals of analcime were placed on a polished metal surface on the stage of an Olympus BHSM microscope, which is equipped with 10×, 20×, and 50× objectives. The microscope is part of a Renishaw 1000 Raman microscope system, which also includes a monochromator, a filter system and a CCD detector (1024 pixels). The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm^{-1} and a precision of ±1 cm^{-1} in the range between 200 and 4000 cm^{-1}. Repeated acquisitions on the crystals using the highest magnification (50×) were accumulated to improve the signal to noise ratio of the Raman spectra. Raman spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

Infrared spectroscopy

Infrared spectra of analcime were obtained using a Nicolet Nexus 870 FTIR spectrometer with a smart endurance single bounce diamond ATR cell. Spectra over the 4000–525 cm^{-1} range were obtained by the co-addition of 128 scans with a resolution of 4 cm^{-1} and a mirror velocity of 0.6329 cm/s. Spectra were co-added to improve the signal to noise ratio. The infrared spectra are given in Supplementary information.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectracalc software package GRAMS (Galactic Industries Corporation, NH, USA). Band component analysis was undertaken using the Jandel 'Peakfit' software package that enabled the type of fitting function to be selected and allows specific parameters to be fixed or varied accordingly. Band fitting was done using a Lorentzian–Gaussian cross-product function with the minimum number of component bands used for the fitting process. The Gaussian–Lorentzian ratio was maintained at values greater than 0.7 and fitting was undertaken until reproducible results were obtained with squared correlations of r^2 greater than 0.995.

Results and discussion

Mineral characterization

The SEM image of analcime sample studied in this work is shown in Fig. 1. The image shows a cleavage fragment up to 2 mm. Qualitative chemical analysis shows a homogeneous phase, composed by Na, Al, O and Si. The chemical data is in agreement with the chemical formula for the mineral. No other contaminant elements were observed and the sample can be considered as a pure single phase (Fig. 2).

Vibrational spectroscopy

The Raman spectrum of analcime over the 100–4000 cm^{-1} spectral range is shown in Fig. 3a. This figure shows the position and relative intensity of the Raman bands. It is noted there are

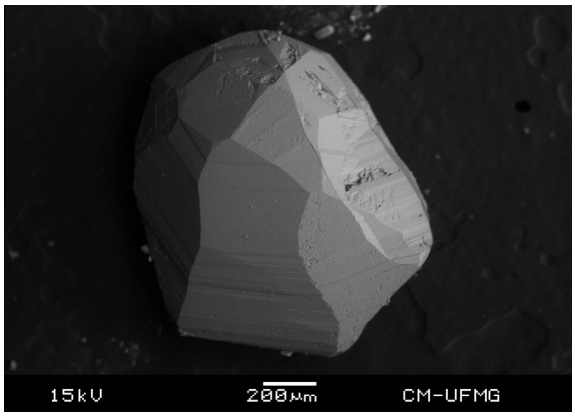

Fig. 1. Backscattered electron image (BSI) of an analcime single crystal up to 1.0 mm in length.