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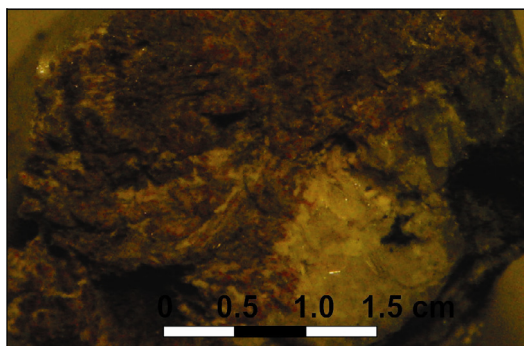
Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saaA vibrational spectroscopic study of the silicate mineral normandite – $\text{NaCa}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{Ti}, \text{Nb}, \text{Zr})\text{Si}_2\text{O}_7(\text{O}, \text{F})_2$ Ray L. Frost^{a,*}, Andrés López^a, Frederick L. Theiss^a, Ricardo Scholz^b, Antônio Wilson Romano^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, School of Mines, Federal University of Ouro Preto, Campus Morro do Cruzeiro, Ouro Preto, MG 35400-00, Brazil^c Geology Department, Federal University of Minas Gerais, Belo Horizonte, MG 31270-901, Brazil

HIGHLIGHTS

- We have studied the mineral normandite $\text{NaCa}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{Ti}, \text{Nb}, \text{Zr})\text{Si}_2\text{O}_7(\text{O}, \text{F})_2$.
- Using a combination of scanning electron microscopy with energy dispersive spectroscopy and vibrational spectroscopy.
- Normandite is a crystalline sodium calcium silicate which contains rare earth elements.

GRAPHICAL ABSTRACT



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ABSTRACT

We have studied the mineral normandite using a combination of scanning electron microscopy with energy dispersive spectroscopy and vibrational spectroscopy.

The mineral normandite $\text{NaCa}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{Ti}, \text{Nb}, \text{Zr})\text{Si}_2\text{O}_7(\text{O}, \text{F})_2$ is a crystalline sodium calcium silicate which contains rare earth elements. Chemical analysis shows the mineral contains a range of elements including Na, Mn^{2+} , Ca, Fe^{2+} and the rare earth element niobium. No Raman bands are observed above 1100 cm^{-1} . The mineral is characterised by Raman bands observed at 724, 748, 782 and 813 cm^{-1} . Infrared bands are broad; nevertheless bands may be resolved at 723, 860, 910, 958, 933, 1057 and 1073 cm^{-1} . Intense Raman bands at 454, 477 and 513 cm^{-1} are attributed to OSiO bending modes. No Raman bands are observed in the hydroxyl stretching region, but low intensity infrared bands are observed at 3191 and 3450 cm^{-1} . This observation brings into question the true formula of the mineral.

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Introduction

Normandite is a yellow to yellowish brown to orange mineral [1], of formula $\text{NaCa}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{Ti}, \text{Nb}, \text{Zr})\text{Si}_2\text{O}_7(\text{O}, \text{F})_2$ and may be described as a sodium–calcium silicate which includes Ti, Nb, Zr

in the structure [2,3]. The mineral is pleochroic and the color of the mineral depends on the axis of viewing. Normandite is the titanium analog of lavenite and is a member of the wöhlerite group, that also includes baghdadite, cuspidine, niocalite, among others. The mineral is found in miarolitic cavities in nepheline syenite [3]. The mineral occurs as needle like crystals.

The mineral is monoclinic-prismatic with space group: $P 2_1/a$ [4]. The cell dimensions are $a = 10.828\text{ Å}$, $b = 9.79\text{ Å}$, $c = 7.054\text{ Å}$,

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$Z = 4$; $\beta = 108.2^\circ$ [4]. No Raman spectroscopic studies of normandite and related minerals have been forthcoming [5]. Some infrared studies of selected calcium silicates have been undertaken [6,7]. Studies of hydrogen bonding in silicates relate the position of the hydroxyl stretching vibration to the hydrogen bond distances [8]. Some Raman spectra of calcium silicates have been collected and a number of the spectra were shown to be dependent upon the number of condensed silica tetrahedra [9]. Such detailed assignment of infrared and Raman bands for a wide range of silicate structures was made by Dowty [10–13]. The thermal decomposition of calcium silicates has also been measured [14–16].

There is an apparent lack of information on the vibrational spectra of normandite. 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. The objective of this research is to report the Raman and infrared spectra of normandite and to relate the spectra to the mineral structure.

Experimental

Samples description and preparation

The normandite 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-012. The mineral sample originated from Partomchorr Deposit, located in the northwestern portion of the Khibiny Massif, Kola Peninsula, Murmanskaya Oblast', Northern Region, Russia [2].

The Kola Peninsula is the northeastern segment of the Precambrian Baltic Shield. During the Devonian, numerous ultramafic, alkaline and carbonatitic intrusions were emplaced over an area of more than 100,000 km² which extends from eastern Finland to the eastern Kola Peninsula, and comprise the Kola Alkaline Province (KAP) [17]. The Khibiny massif was emplaced simultaneously with the subsidence of the NE-SW trending Khibiny-Kontozero-Graben and is the largest agpaitic, nepheline syenite body in the Kola Alkaline Province [18]. In general, Khibiny consists of a variety of nepheline syenites (khibinite, rischorrite, lujavrite and foyaite), foidalites (ijolite and urtite) and minor alkali syenite plus a small carbonatite stock [19].

The sample was gently crushed and the associated minerals were removed under a stereomicroscope Leica MZ4. The normandite 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>). Normandite 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 was applied to support the mineral characterization.

Raman microprobe spectroscopy

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

with 10 \times , 20 \times , and 50 \times 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 \times) were accumulated to improve the signal to noise ratio of the spectra. Raman Spectra were calibrated using the 520.5 cm⁻¹ line of a silicon wafer.

Infrared spectroscopy

Infrared spectra of normandite 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.

Spectral manipulation such as baseline correction/adjustment and smoothing were performed using the Spectralcalc 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 normandite sample studied in this work is shown in the [supplementary information as Fig. S1](#). The image shows a cleavage fragment up to 2 mm. Qualitative chemical analysis shows a homogeneous phase, composed by Ca, Al, Ti, Mn, Fe, Nb, F 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. 1).

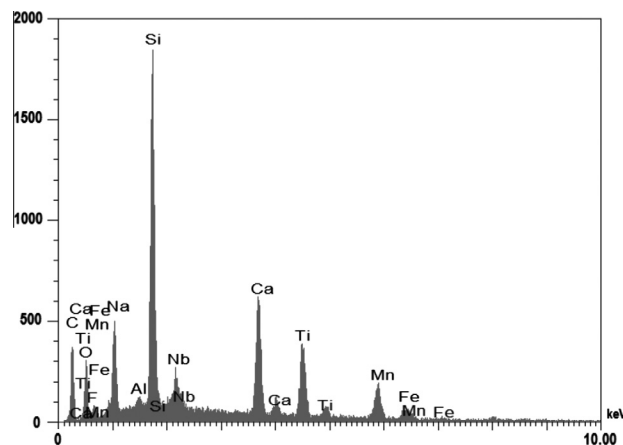


Fig. 1. EDS analysis of normandite.

Vibrational spectroscopy

The Raman spectrum of normandite over the 100 to 1100 cm^{-1} spectral range is shown in Fig. 2a. This figure shows the position and relative intensity of the Raman bands. It is noted there are large parts of the spectrum where little or no intensity is observed. The Raman spectrum is therefore subdivided into sections based upon the types of vibration being studied. It is noted that there is no intensity in the hydroxyl stretching region (2500 to 3800 cm^{-1} spectral range). The infrared spectrum of normandite over the 500 to 4000 cm^{-1} spectral range is displayed in Fig. 2b. This figure shows the position and relative intensities of the infrared bands. There is minimal intensity observed beyond 1500 cm^{-1} . The infrared spectrum is subdivided into sections based upon the type of vibration being analysed.

The Raman spectrum of normandite over the 600 to 900 cm^{-1} spectral range is shown in Fig. 3a. The structure of normandite consists of three dimensional silicates with multiple linked silica tetrahedra [20]. Raman bands are observed at 724, 748, 782, 803 and 813 cm^{-1} and are assigned to the SiO stretching vibrations. A set of Raman bands are found at 641, 649, 656 and 667 cm^{-1} . Dowty calculated the band positions for the different ideal silicate units. Dowty showed that the $-\text{SiO}_3$ units had a unique band position of 1025 cm^{-1} [13] (see Figs. 2 and 4 of this reference). Dowty calculated the Raman spectrum for these type of silicate networks and predicted two bands at around 1040 and 1070 cm^{-1} with an additional band at around 600 cm^{-1} . The infrared spectrum over the 650 to 1250 cm^{-1} spectral range is reported in Fig. 3b. The infrared spectrum is quite broad and may be resolved into

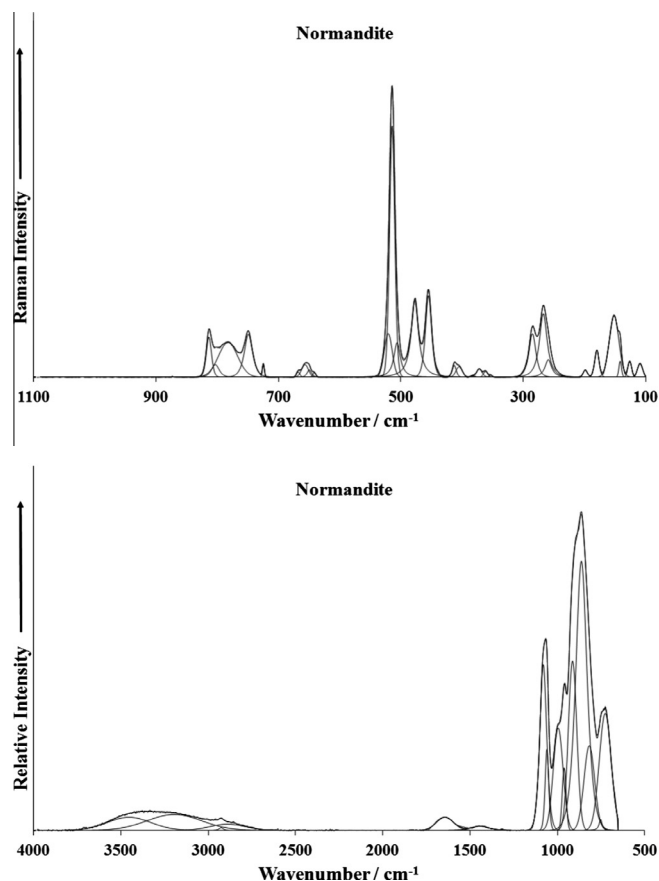


Fig. 2. (a) Raman spectrum of normandite over the 100 to 1100 cm^{-1} spectral range and (b) Infrared spectrum of normandite over the 500 to 4000 cm^{-1} spectral range.

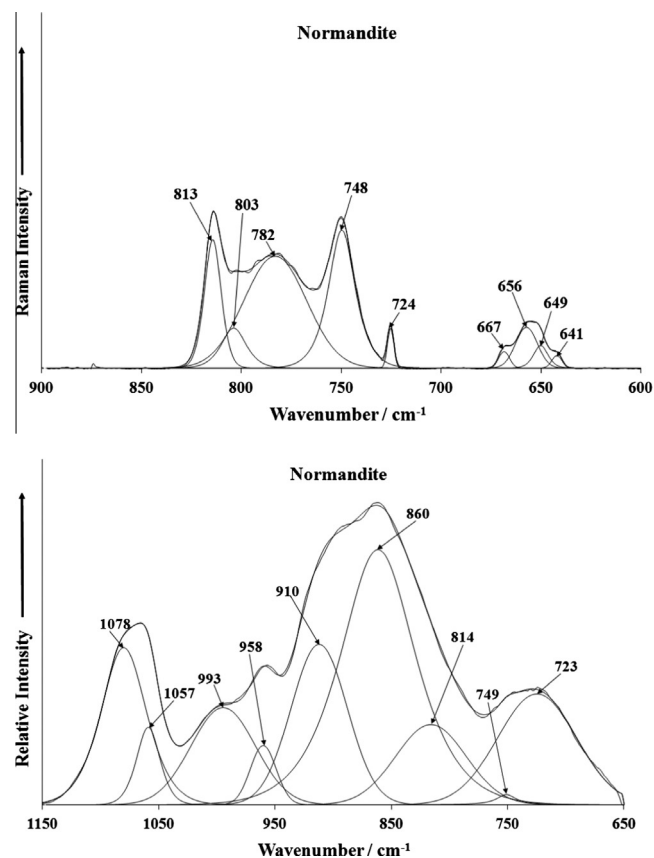


Fig. 3. (a) Raman spectrum of normandite over the 600 to 900 cm^{-1} spectral range and (b) Infrared spectrum of normandite over the 650 to 1150 cm^{-1} spectral range.

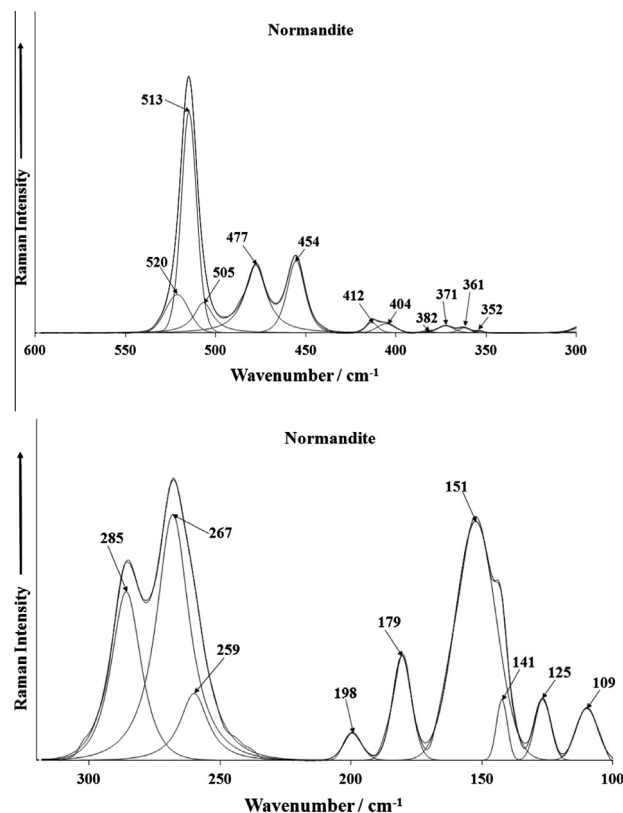


Fig. 4. (a) Raman spectrum of normandite over the 300 to 600 cm^{-1} spectral range and (b) Raman spectrum of normandite over the 100 to 350 cm^{-1} spectral range.

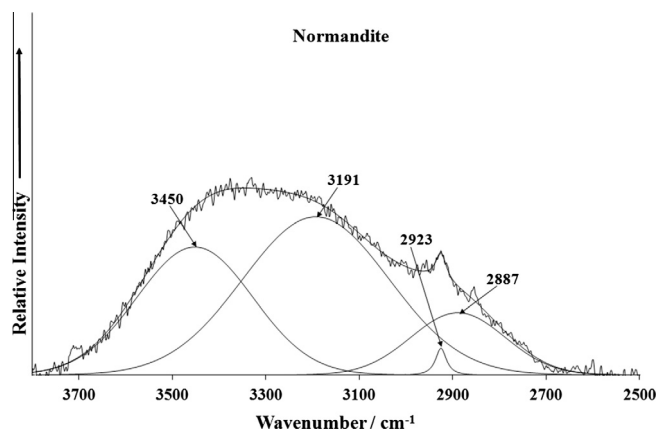


Fig. 5. Infrared spectrum of normandite over the 2500 to 3800 cm^{-1} spectral range.

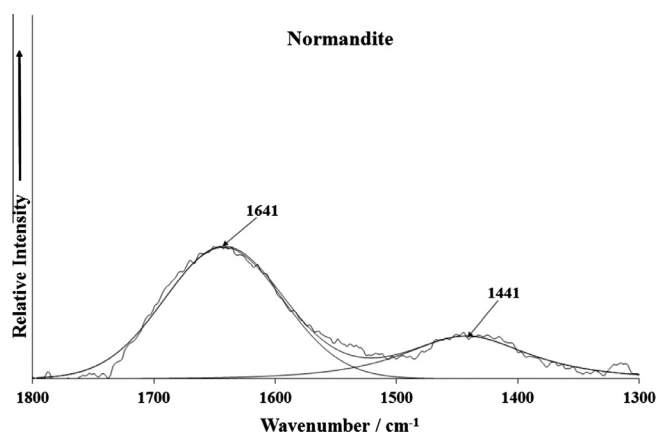


Fig. 6. Infrared spectrum of normandite over the 1300 to 1800 cm^{-1} spectral range.

component bands at 723, 749, 814, 860, 910, 958, 993, 1057 and 1078 cm^{-1} . These bands are assigned to SiO stretching vibrations.

The Raman spectrum of normandite over the 300 to 600 cm^{-1} spectral range is shown in Fig. 4a. Intense Raman bands are observed at 454, 477 and 513 cm^{-1} and are assigned to OSiO bending vibrations. Bands of lesser intensity are observed at 352, 361, 371, 382, 404 and 412 cm^{-1} . These bands may also be attributed to this vibrational mode. These bands are attributed to metal oxygen stretching vibrations (MO) (Fig. 4b). The Raman spectrum of normandite over the 100 to 350 cm^{-1} spectral range is shown in Fig. 5b. Intense Raman bands are observed at 151, 267 and 285 cm^{-1} with bands of lesser intensity noted at 109, 125, 141, 179, 198 and 259 cm^{-1} . These bands are simply described as lattice vibrations.

The Raman spectrum of normandite shows no intensity in the hydroxyl stretching region. The infrared spectrum of normandite over the 2500 to 3800 cm^{-1} spectral region is shown in Fig. 5. The infrared spectrum is quite broad. The spectral profile may be resolved into component bands at 2887, 2923, 3191 and 3450 cm^{-1} . The first two bands are due to organic compounds adsorbed on the mineral surface. The latter two bands are due to water. The water may be in the structure of normandite or may be simply adsorbed on the surface of the mineral. The position of the bands suggests the former is correct. The infrared spectrum of normandite over the 1300 to 1800 cm^{-1} spectral range is shown in Fig. 6.

Conclusions

We have studied the mineral normandite using a combination of scanning electron microscopy with energy dispersive spectroscopy and vibrational spectroscopy.

Normandite is the titanium analog of lavenite and is a member of the wöhlerite group, that also includes baghdadite, cuspidine, niocalite, among others.

The mineral normandite $\text{NaCa}(\text{Mn}^{2+}, \text{Fe}^{2+})(\text{Ti}, \text{Nb}, \text{Zr})\text{Si}_2\text{O}_7(\text{O}, \text{F})_2$ is a crystalline sodium calcium silicate which contains rare earth elements. Chemical analysis shows the mineral contains a range of elements including Na, Mn^{2+} , Ca, Fe^{2+} and the rare earth element niobium.

No Raman bands are observed in the hydroxyl stretching region, but low intensity infrared bands are observed at 3191 and 3450 cm^{-1} . This observation brings into question the true formula of the mineral. Are there OH units involved in the structure of normandite? Vibrational spectroscopy would suggest that water units are involved in the structure of normandite. As part of this research, we have undertaken a vibrational spectroscopic study of normandite to determine the characteristic bands of this mineral.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.saa.2014.07.035>.

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