Mitt. Abt. Miner. Landesmuseum Joanneum | Heft 59 | Graz 1991

The laser Raman spectrum of nordstrandite from Stradner Kogel, south of Bad Gleichenberg, Styria, Austria

K. A. RODGERS

Summary

Small, 1–2 mm, nodules of nordstrandite, $Al(OH)_3$, from Stradner Kogel, south of Bad Gleichenberg (Styria, Austria), consist of very thin (< 0.1 μ) laminae ranging from 0.5 to 3 μ across, and stacked in lamellar packets 5 to 10 μ high. The laser Raman spectrum shows strong scattering bands at 3487, 3563 and 3618 cm^{-1} in the ν (OH)-stretching region, and at 1018 (w), 588 (mw), 541 (s), 441 (mw), 386 (m), 377 (m), 303 (vs), 282 (m), 252 (m), 237 (mw), and 116 (m) cm^{-1} probably arising mainly from Al-O and lattice vibrations. A similar result was obtained for nordstrandite from Gunong Kapor, Sarawak. The nordstrandite spectrum is distinctive from those of bayerite and gibbsite and laser Raman microscopy offers a simple, non-destructive means of identifying such minerals, particularly where they are fine-grained.

Zusammenfassung

Kleine, 1 bis 2 mm messende Halbkugeln von Nordstrandit, $Al(OH)_3$, vom Stradner Kogel, südlich Bad Gleichenberg (Steiermark, Österreich), bestehen aus sehr dünnen (< 0.1 μ) Blättchen von 0.5 bis 3 μ Durchmesser, die zu 5 bis 10 μ hohen Schichtpaketen gestapelt sind. Das Laser-Raman-Spektrum zeigt im ν (OH)-Streckschwingungsbereich starke Banden bei 3487, 3563 und 3618 cm^{-1}, und bei 1018 (s), 588 (ms), 541 (st), 441 (ms), 386 (m), 377 (m), 303 (sst), 282 (m), 252 (m), 237 (ms), und 116 (m) cm^{-1} Banden, die wahrscheinlich hauptsächlich durch Al-O- und Gitterschwingungen hervorgerufen werden. Ein ähnliches Ergebnis wurde bei Nordstrandit von Gunong Kapor, Sarawak, beobachtet. Das Spektrum von Nordstrandit unterscheidet sich von denen von Bayerit und Gibbsit. Weiters bietet die Laser-Raman-Mikroskopie eine einfache, zerstörungsfreie Bestimmungsmöglichkeit derartiger Minerale, insbesondere wenn diese feinkristallin sind.

Introduction

Laser Raman spectroscopy may be used to distinguish the polymorphs of aluminium hydroxide, gibbsite and bayerite (HUNEKE et al., 1980), and the Raman microprobe provides a non-destructive method of analyzing small quantities of such minerals, particularly where the habit or fine grain size preclude use of other techniques (e. g. CRESTIN-DESJOBERT et al., 1987; RODGERS et al., 1989; COONEY et al., 1989; RODGERS et al., 1991). The Raman spectra of other modifications of aluminium hydroxide are not known, and that of the rare triclinic form, nordstrandite, has been obtained using a relatively pure, microcrystalline sample from Stradner Kogel, Austria – Australian Museum sample no. D49262.

Occurrence

ALKER et al. (1981) described nordstrandite, coexisting with hydrotalcite and motukoreaite, in cavities of a hauyne-nephelinite from Stradner Kogel, a quarry near Wilhelmsdorf about 10 km south of Bad Gleichenberg. The mineral occurs in the Stradner quarry as white to pale grey, flinty, hemispherical nodules, 1–2 mm in diameter, nested on fine-grained, translucent, phillipsite that lines the cavities (Fig. 1). The surfaces of the hemispheres are studded with elongate rhombohedra of hydrotalcite, terminated by (0001) pinacoids, and consist of very thin (< 0.1 μ) laminae of nordstrandite ranging from 0.5 to 3 μ across, stacked in offset lamellar packets 5 to 10 μ high (Fig. 2). The nodules break with an uneven fracture.

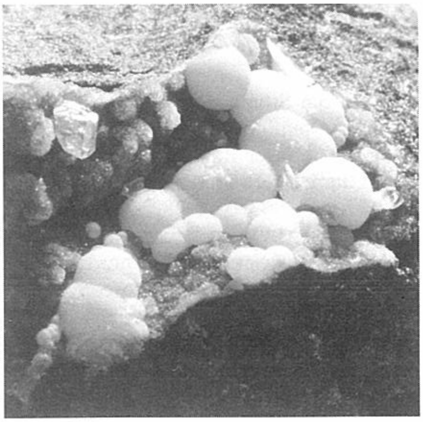
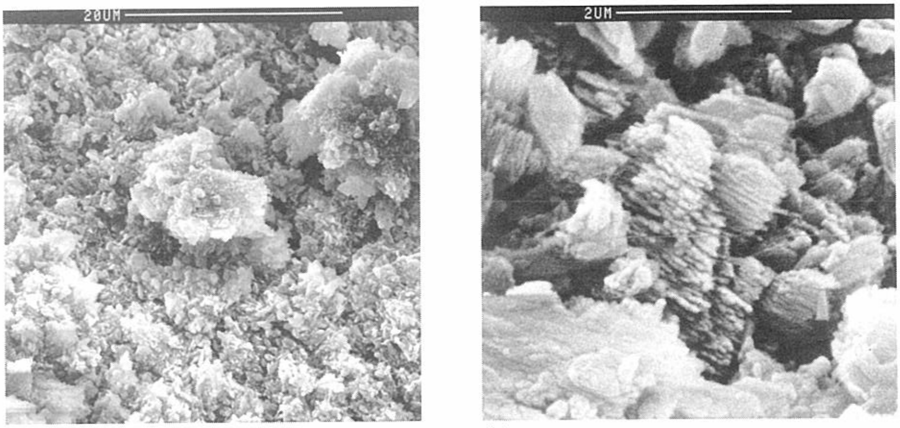


Fig. 1:
Nordstrandite nodules on phillipsite in nephelinite cavity, Stradner Kogel; Australian Museum specimen no D49262. Base of photograph is 12 mm long.



(a) (b)

Fig. 2:
Scanning electron microscope photographs of surface texture of nordstrandite nodule from Stradner Kogel: (a) subparallel aggregate of imperfectly crystallised nordstrandite microlites forming greater part of nodule surface – scale bar is 20 μ long; (b) packets of thin nordstrandite laminae – scale bar is 2 μ long.

Experimental

Small splinters of nordstrandite were pried from the edge of broken nodules and crushed on a glass microscope slide by firm but gentle pressure with a second slide. Grinding was minimised to reduce the possibility of straining and deforming crystal structures or inducing any change of state.

As in X-ray powder diffraction, glass slides offer an ease of application. Nonetheless, as particle mounts, they suffer from several disadvantages. The technique is prone to a high level of preferred orientation particularly with minerals possessing a dominant cleavage such as nordstrandite, although, in samples whose grain size is less than the focused beam (< 10 µ), as at Stradner Kogel (Fig. 2), a quantity of fine particles can be irradiated, and preferred orientation may not present a significant problem. However, where a sampled particle is slight, the Raman spectrum of glass mounted grains may contain appreciable noise, particularly in the region 700–1100 cm^{-1} associated with Si-O and Al-O spectra excited from the glass. This proved to be the case with the Stradner Kogel nordstrandite and the derived spectrum was arithmetically corrected by subtracting that of glass.

The Raman spectra of the crushed fragments were recorded by microsampling using a Jobin-Yvon U 1000 instrument with 514.5 nm Ar^+ as the exciting line. Power loss throughout the system was marked and with laser power of 1000 mW only 100 mW was recorded at the sampling lens: an uncoated x40 objective of a Nikkon microscope. Monochannel Ga-As photomultiplier detectors were employed. Spectra were recorded from 3000–3700 cm^{-1} and 100–1200 cm^{-1}.

Results

In the O-H stretching region nordstrandite displays three prominent scattering bands at 3487, 3563 and 3618 cm^{-1} (Fig. 3). In contrast gibbsite exhibits four pronounced bands at 3363, 3434, 3524 and 3618 cm^{-1} and bayerite three at 3425, 3544 and 3653 cm^{-1} (HUNEKE et al., 1980; COONEY et al., 1989).

All polymorphs possess a common structural element consisting of a layer of Al ions sandwiched between two sheets of hexagonally close-packed (hcp) hydroxyl ions; the Al ions occupying two-thirds of the octahedral interstices within the layers. The structure of gibbsite, bayerite and nordstrandite differ in the stacking order of the double layer (e. g. WEFERS & MISRA, 1987) and differences in the vibrational spectra of the aluminium hydroxide polymorphs in the ν (OH)-stretching region may be related to differences in the position and strength of hydrogen bonds within and between layers (e. g. RUSSEL et al., 1974; KULIKOVA et al., 1974).

RUSSEL et al. (1974) assigned an absorption band at 3460 cm^{-1}, in the infrared spectrum of gibbsite, to vibrations of (OH) groups involved in hydrogen bonds existing between hydroxyl layers. Bands at 3529 and 3622 cm^{-1} were associated with longer hydrogen bonds lying within the hcp plane. A similar interpretation is possible for bayerite, taking into account differences in symmetry and the arrangement of hydrogen bonds determined by ZIGAN et al. (1978). Although HAUSCHILD (1963) concluded that the infrared spectrum of nordstrandite indicated the presence of hydrogen bonds in the structure, neither the position of hydrogen atoms nor the direction and influence of any hydrogen bonds has been determined.

The structure of nordstrandite is considered by SAALFELD & JARCHOW (1968) to be intermediate between gibbsite and bayerite. The frequency of the Raman OH-stretching bands of nordstrandite suggests that any effect of hydrogen bonding on the stretching vibrations of nordstrandite's hydroxyl groups is akin to that observed from the longer intralayer hydrogen bonds in gibbsite and bayerite. For example, the nordstrandite band at 3618 cm^{-1} has the same frequency as that in gibbsite correlated with hydrogen bonds within the hcp hydroxyl layer.

The absence of lower frequency (OH) Raman bands in the nordstrandite spectrum, such as arise in gibbsite and bayerite from the relatively shorter interlayer hydrogen bonds, may indicate that what interlayer bonding exists in nordstrandite is relatively weaker than in gibbsite, or that interlayer hydrogen bonding in nordstrandite is reduced in the modified structure.

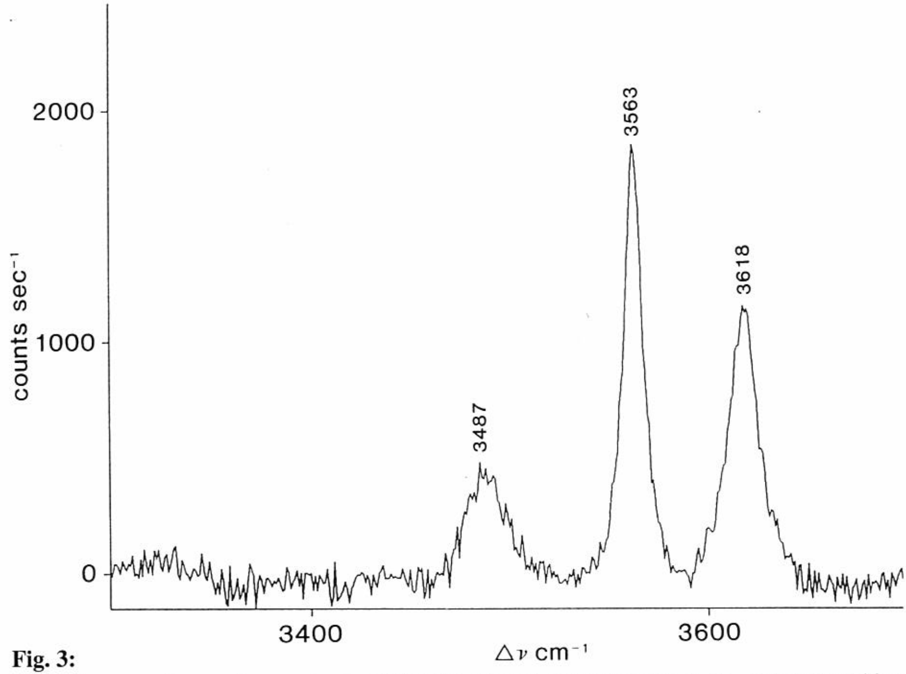


Fig. 3:
Laser Raman microprobe spectrum of Stradner Kogel nordstrandite in the ν-OH stretching region from 3300 to 3700 Δ cm^{-1}.

Vivien et al. (1973) reported that group factor analysis of nordstrandite, based on published crystallographic data, failed to give satisfactory agreement between calculated and observed vibration bands; a circumstance compounded by the lack of information on the position of hydrogen atoms within the structure. However, these authors also noted that their data indicated triclinic (C_i^1) nordstrandite exhibited more infrared-active vibrations than either the more symmetrical bayerite (C_{2h}^5) or gibbsite (C_{2h}^5). This difference is not apparent from the Raman spectra, particularly in the region 100–1200 cm^{-1} as compared in Fig. 4. Vivien et al. (1973) assigned absorption bands in this region to Al-O vibrations. Those below about 200 cm^{-1} might also arise from lattice vibrations. Whatever the eventual assignments, it is clear that sufficient differences exist between the spectra of the three polymorphs for laser Raman microscopy to offer a ready and efficient means of non-destructive identification.

Sand-sized grains of nordstrandite described by Wall et al. (1962) from soils of Gunong Kapor, Bau mining district, West Sarawak (Natural History Museum, London, specimen BM-1962, 229), gave a similar spectrum to that of the Stradner Kogel sample. Although the scattering bands occupied similar positions and were of the same relative intensity, the Sarawak material proved highly fluorescent with adverse signal to noise ratios. This fluorescence could arise from either humic acids or transition metal ions, possibly present in the red-stained Sarawak grains as a result of their mode of occurrence. These interferences are absent from the Stradner Kogel nodules.

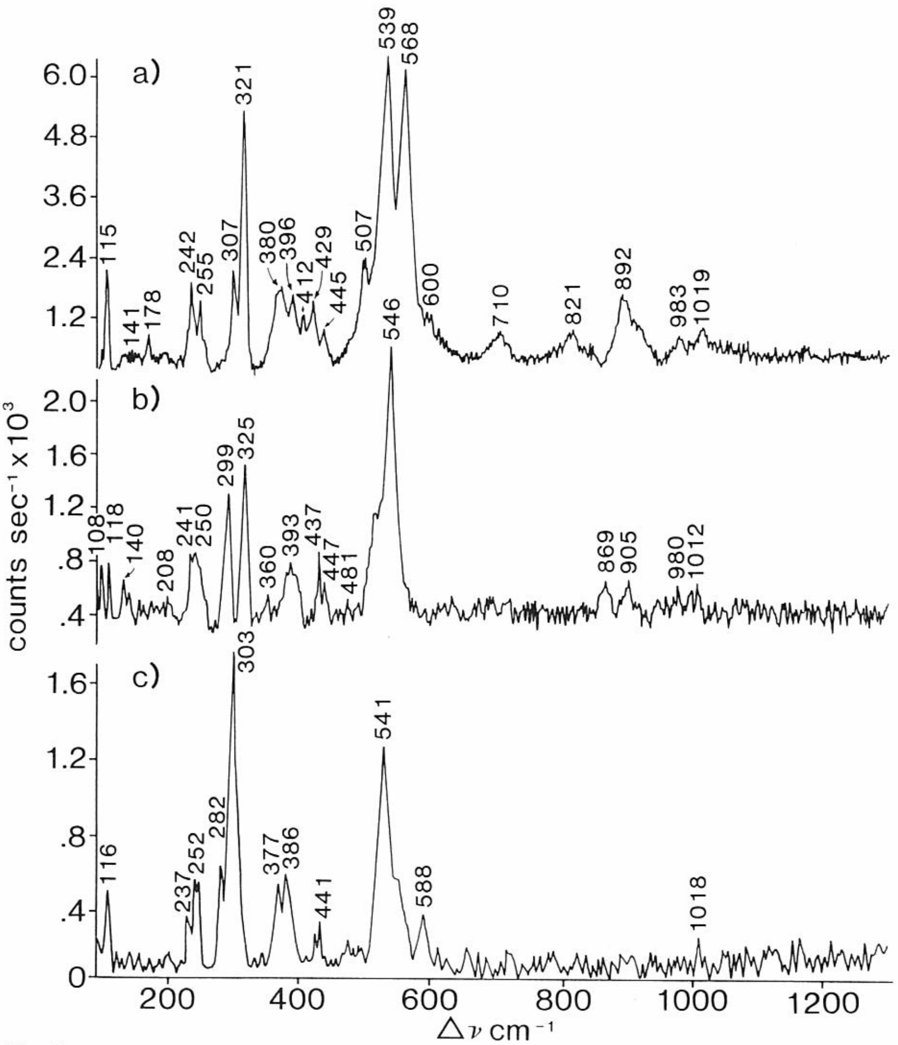


Fig. 4:
Laser Raman microprobe spectra of aluminium hydroxide polymorphs from 100 to 1300 Δ cm^{-1}. (a) microcrystalline gibbsite, Dundas, Tasmania, Australian Museum specimen D42734; (b) freshly precipitated synthetic bayerite; (c) nordstrandite, Stradner Kogel.

This study was supported by a Visiting Fellowship awarded by the Australian Museum. Thanks are due to Professor R. COONEY, Drs. J. SEAKINS and F. L. SUTHERLAND and Mr. G. AVERN, Mr. C. BENTO, Mrs. C. CANTRELL, Mrs. M. KUMVAJ, Mr. R. RATAJCZAK and Mr. T. TRNSKI for assistance. Equipment funding was provided by the University of Auckland Research Committee, the University Grants Committee and the New Zealand Lottery Grants Board (Scientific). Dr. W. POSTL (Steiermärkisches Landesmuseum Joanneum, Abteilung für Mineralogie, Graz, Austria) provided the nordstrandite-probe from Stradner Kogel, Austria.

Literature

ALKER, A., GOLOB, P., POSTL, W., & WALTINGER, H., 1981: Hydrotalkit, Nordstrandit und Motukoreait vom Stradner Kogel, südlich Gleichenberg, Steiermark. – Mitt.-Bl. Abt. Miner. Landesmuseum Joanneum, 49, 1–13.

COONEY, R. P., RODGERS, K. A., & GREGORY, M. R., 1989: Laser Raman spectrum of bayerite from Raoul Island, Kermadec Group, South Pacific. – Vulkanologiya i Seismologiya, No. 5, 97–99. [In Russian].

CRESTIN-DESJOBERT, S., CRUEGE, F., & GOUT, R., 1987: The use of the Raman microprobe for studying bauxites. Terra Cognita, 7, 14.

HAUSCHILD, U., 1963: Über Nordstrandit, γ-$Al(OH)_3$. – Zeit. anorgan. allgem. Chemie, 324, 15–30.

HUNEKE, J. T., CRAMER, R. E., ALVAREZ, R., & EL-SWAIFY, S. A., 1980: The identification of gibbsite and bayerite by laser Raman spectroscopy. – Soil Sci. Soc. America, Journ. 44, 131–134.

KULIKOVA, G. V., TSEKHOVOL'SKAYA, D. I., & SHITOV, V. A., 1974: First find of nordstrandite in the USSR. – Dokl. Akad. Nauk. SSSR, 217, 106–109.

RODGERS, K. A., GREGORY, M. R., & COONEY, R. P., 1989: Bayerite, $Al(OH)_3$, from Raoul Island, Kermadec Group, South Pacific. – Clay Mins, 24, 531–538.

RODGERS, K. A., GREGORY, M. R., & BARTON, R., 1991: Bayerite, nordstrandite, gibbsite, brucite and pseudoboehmite in discharged caustic waste from Campbell Island, Southwest Pacific. – Clays, Clay Mins, 39, 103–107.

RUSSELL, J. D., PARFITT, R. L., FRASER, A. R., & FARMER, V. C., 1974: Surface structures of gibbsite, goethite and phosphated goethite. – Nature, 248, 220–221.

VIVIEN, D., STEGMANN, M. C., & MAZIÈRES, C., 1973: Contribution a l'étude par spectroscopie infrarouge et RMN large band des hydroxides d'aluminium: gibbsite, bayerite, nordstrandite. – Journ. Chim. Phys., 70, 1502–1508.

WALL, J. R. D., WOLFENDEN, E. B., BEARD, E. H., & DEANS, T., 1962: Nordstrandite in soil from West Sarawak, Borneo. – Nature, 196, 264–265.

WEFERS, K., & MISRA, C., 1987: Oxides and hydroxides of aluminium. – Aloca Technical Paper 19 (revised).

ZIGAN, F., JOSWIG, W., & BURGER, N., 1978: Die Wasserstoffpositionen im Bayerit, $Al(OH)_3$. – Z. Krist. 148, 255–273.

Address of author:
Prof. Dr. K. A. RODGERS
Department of Geology, University of Auckland
Private Bag Auckland
New Zealand

Zeitschrift/Journal: Mitteilungen der Abteilung für Mineralogie am Landesmuseum Joanneum

Jahr/Year: 1991

Band/Volume: 59

Autor(en)/Author(s): Rodgers K. A.

Artikel/Article: The laser Raman spectrum of nordstrandite from Stradner Kogel, south of Bad Gleichenberg, Styria, Austria 19-24