

## NIVEOLANITE, THE FIRST NATURAL BERYLLIUM CARBONATE, A NEW MINERAL SPECIES FROM MONT SAINT-HILAIRE, QUEBEC, CANADA

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### ABSTRACT

A new mineral species, niveolanite, the first natural carbonate of beryllium, was found in the Poudrette pegmatite, Poudrette quarry, Mont Saint-Hilaire, Quebec, Canada. It is associated with albite, aegirine, natrolite, gonnardite, siderite, petersenite-(Ce), franconite, dawsonite, analcime, quartz, eudidymite, catapleite, gaidonnayite, monazite-(Ce), calcite, adamsite-(Y), shomiokite-(Y), galena, sphalerite and rutile in cavities; earlier minerals are microcline, nepheline, annite, sodalite and zircon. Niveolanite occurs as soft fibrous (random, matted, radiating, subparallel, sheaf- or spray-like) aggregates up to 2 cm consisting of fibers up to 1.4 cm long and 0.01 mm thick. Rarely, aggregates of acicular crystals up to 1 cm long and 0.03 mm thick, elongate along [001], with a tetragonal or octagonal cross-section, and fibrous pseudomorphs after eudidymite are observed. Individual crystals of niveolanite are colorless and transparent. Aggregates are snow-white to pearl-white, with a silky luster. The density calculated for the empirical formula with 1.66 H<sub>2</sub>O *pfu* is 2.06, whereas that for the less hydrous variety (1 H<sub>2</sub>O *pfu*) is 1.82 g/cm<sup>3</sup>. Niveolanite is optically uniaxial positive,  $\omega$  1.469(1),  $\varepsilon$  1.502(1). The IR spectrum is unique. The averaged chemical composition (Na, K and Ca were determined by electron microprobe, Be by ICP-OES, [CO<sub>2</sub> + H<sub>2</sub>O] from loss on ignition, CO<sub>2</sub> by selective absorption) is: Na<sub>2</sub>O 19.81, K<sub>2</sub>O 0.07, CaO 3.88, BeO 16.65, CO<sub>2</sub> 29.81, H<sub>2</sub>O 26.93, total 97.15 wt.%. The empirical formula calculated for 1 C *apfu* is: (Na<sub>0.94</sub>Ca<sub>0.10</sub>) $\Sigma$ <sub>1.04</sub>Be<sub>0.98</sub>(CO<sub>3</sub>)<sub>1.00</sub>(OH)<sub>1.10</sub>•1.66H<sub>2</sub>O. In moist air, niveolanite strongly absorbs molecular water; the process of its hydration–dehydration is easily reversible. Niveolanite is tetragonal, *P4/mcc*, *a* 13.1304(19), *c* 5.4189(11) Å, *V* 934.3(3) Å<sup>3</sup>, *Z* = 8. The strongest ten lines of the X-ray powder diagram [*d* in Å (*I*)(*hkl*)] are: 13.01(100) (100), 9.20(62)(110), 4.343(27)(300), 3.611(34)(320), 3.269(22)(311), 3.256(95)(400), 2.693(44)(002), 2.605(37)(430,500),

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2.489(60)(202), and 2.076(32)(620). The crystal structure was solved using a single crystal and synchrotron radiation,  $R = 0.0358$ . Niveolanite represents a new structure-type. Its structure includes isolated, infinite chains of  $\text{BeO}_2(\text{OH})_2$  tetrahedra linked via common OH groups; two other vertices of each Be tetrahedron are shared with  $(\text{CO}_3)$  groups, and Na cations occupy seven-fold polyhedra  $[\text{NaO}_6(\text{H}_2\text{O})]$  forming columns. Chains of Be tetrahedra and columns of Na polyhedra are aligned along the  $c$  axis, just as broad channels in which  $\text{H}_2\text{O}$  molecules are located. The structural formula is:  $\{(\text{Na}_{0.9}\text{Ca}_{0.1})(\text{H}_2\text{O})_{0.9}(\text{OH})_{0.1}\}\{\text{Be}(\text{OH})\}(\text{CO}_3)\bullet 0\text{--}1\text{H}_2\text{O}$ . The idealized formula is:  $\text{NaBe}(\text{CO}_3)(\text{OH})\bullet 1\text{--}2\text{H}_2\text{O}$ . The mineral was named from *Latin niveus*, snow-white, and *lana*, wool, alluding to the visual similarity of its aggregates to snow-white, fluffy flocks of wool. The cotype specimens are deposited in the Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, and the Canadian Museum of Nature, Ottawa.

**Keywords:** niveolanite, new mineral species, beryllium carbonate, crystal structure, synchrotron radiation, infrared spectrum, peralkaline pegmatite, Mont Saint-Hilaire, Quebec, Canada.

## SOMMAIRE

Nous décrivons la nivéolanite, nouvelle espèce minérale, le premier exemple d'un carbonate de béryllium à être découvert dans la nature, dans la pegmatite Poudrette à la carrière Poudrette, mont Saint-Hilaire, Québec, Canada. Lui sont associés albite, aegyrine, natrolite, gonnardite, sidérite, petersenite-(Ce), franconite, dawsonite, analcime, quartz, eudidymite, catapléite, gaidonayite, monazite-(Ce), calcite, adamsite-(Y), shomiokite-(Y), galène, sphalérite et rutile dans les cavités; parmi les minéraux précoces sont microcline, néphéline, annite, sodalite et zircon. La nivéolanite se présente en fibres molles (agencées aléatoirement ou en amas feutrés, fibroradiés, subparallèles, ou en essais divergents) atteignant 2 cm; les fibres atteignent une longueur de 1.4 cm et une épaisseur de 0.01 mm. Il est rare de voir des agrégats de cristaux aciculaires jusqu'à 1 cm de long et d'une épaisseur de 0.03 mm, allongées selon [001], montrant une section tétragonale ou octagonale, et des amas fibreux en pseudomorphose de la eudidymite. Les cristaux individuels de nivéolanite sont incolores et transparents. Les agrégats sont blanc-neige ou blanc perlé, avec un éclat soyeux. La densité calculée pour la formule empirique ayant  $1.66 \text{ H}_2\text{O}$  *pfu* est 2.06, tandis que pour la variété moins riche en  $\text{H}_2\text{O}$  ( $1 \text{ H}_2\text{O}$  *pfu*), elle est  $1.82 \text{ g/cm}^3$ . La nivéolanite est uniaxe positive,  $\omega$  1.469(1),  $\varepsilon$  1.502(1). Le spectre infra-rouge est unique. La composition chimique moyenne (Na, K et Ca déterminés avec une microsonde électronique, Be par ICP-OES,  $[\text{CO}_2 + \text{H}_2\text{O}]$  par perte au feu, et  $\text{CO}_2$  par absorption sélective) est:  $\text{Na}_2\text{O}$  19.81,  $\text{K}_2\text{O}$  0.07,  $\text{CaO}$  3.88,  $\text{BeO}$  16.65,  $\text{CO}_2$  29.81,  $\text{H}_2\text{O}$  26.93, pour un total de 97.15% (poids). La formule empirique calculée pour un atome de C par formule unitaire serait  $(\text{Na}_{0.94}\text{Ca}_{0.10})_{\Sigma 1.04}\text{Be}_{0.98}(\text{CO}_3)_{1.00}(\text{OH})_{1.10}\bullet 1.66\text{H}_2\text{O}$ . Dans l'air humide, la nivéolanite absorbe fortement l'eau moléculaire; le processus de l'hydratation-déshydratation est facilement réversible. La nivéolanite est tétragonale,  $P4/mcc$ ,  $a$  13.1304(19),  $c$  5.4189(11) Å,  $V$  934.3(3) Å<sup>3</sup>,  $Z = 8$ . Les dix raies les plus intenses du spectre de diffraction [ $d$  en Å ( $I$ )( $hkl$ )] sont: 13.01(100)(100), 9.20(62)(110), 4.343(27)(300), 3.611(34)(320), 3.269(22)(311), 3.256(95)(400), 2.693(44)(002), 2.605(37)(430,500), 2.489(60)(202), et 2.076(32)(620). Nous avons résolu la structure cristalline sur monocristal en utilisant un rayonnement synchrotron jusqu'à un résidu  $R$  de 0.0358. La nivéolanite représente un nouveau type de structure contenant des chaînes infinies isolées de tétraèdres  $\text{BeO}_2(\text{OH})_2$  liés par leurs groupes OH partagés; deux des autres sommets de chaque tétraèdre Be sont partagés avec des groupes  $(\text{CO}_3)$ , et les atomes de Na se trouvent dans des polyèdres à sept coins  $[\text{NaO}_6(\text{H}_2\text{O})]$  disposés en colonnes. Les chaînes de tétraèdres Be et les colonnes de polyèdres Na sont alignées le long de l'axe  $c$ , formant de larges canaux dans lesquels logent les molécules de  $\text{H}_2\text{O}$ . La formule structurale est:  $\{(\text{Na}_{0.9}\text{Ca}_{0.1})(\text{H}_2\text{O})_{0.9}(\text{OH})_{0.1}\}\{\text{Be}(\text{OH})\}(\text{CO}_3)\bullet 0\text{--}1\text{H}_2\text{O}$ . La formule idéalisée est  $\text{NaBe}(\text{CO}_3)(\text{OH})\bullet 1\text{--}2\text{H}_2\text{O}$ . Le nom du minéral est dérivé du latin pour blanc-neige (*niveus*) et laine (*lana*), allusion à la ressemblance des agrégats à des amas de laine blanche. Les échantillons cotypes ont été déposés au Musée minéralogique Fersman de l'Académie des Sciences de Russie à Moscou et au Musée canadien de la Nature à Ottawa.

(Traduit par la Rédaction)

**Mots-clés:** nivéolanite, nouvelle espèce minérale, carbonate de béryllium, structure cristalline, rayonnement synchrotron, spectre infra-rouge, pegmatite hyperalkaline, mont Saint-Hilaire, Québec, Canada.

## INTRODUCTION

Ninety-nine valid mineral species with essential beryllium were known until now. Eight of them are represented by oxides and hydroxides, four by borates, twenty-four by phosphates, two by arsenates, and sixty-one by silicates (including one arsenite-silicate). We report here the hundredth beryllium mineral, the first natural carbonate of this element. It was found in late assemblages in a peralkaline pegmatite of the mineralogically famous Mont Saint-Hilaire pluton, Quebec, Canada. The new species is named *niveolanite* from

the Latin *niveus*, snow-white, and *lana*, wool, alluding to the visual similarity of typical aggregates of the mineral to snow-white, fluffy flocks of wool (Cyrillic: нивеола́нит). The purpose of this paper is to document the physical and chemical attributes of this new species, and to report details of its crystal structure. Both the new mineral and its name have been approved by the IMA CNMNC (IMA no. 2007-032). The cotype specimens are deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow (registration no. 3631/1), and the Canadian Museum of Nature, Ottawa (catalog no. CNMNC 86052).

## BACKGROUND INFORMATION

The discovery and study of this mineral took ten years. It was first collected in June 1998 by László and Elsa Horváth and was first considered to be the visually nearly identical, partially studied, REE-bearing carbonate phase designated as UK91, which was found earlier in a different part of the same pegmatite. After confirming that the mineral contains no REE, it was submitted to the Canadian Museum of Nature (CMN) for identification in 1999. It was quickly confirmed as a potentially new species, a hydrous Na,Ca carbonate, by X-ray diffraction (XRD) and electron-microprobe (EDS mode) methods and designated by R.A. Gault as an undetermined phase, UK113. An analysis of the structure was attempted, but was unsuccessful owing to unsuitable single crystals, which are very thin fibers. Consequently, further investigation of this phase at the CMN ceased in 2000.

The same mineral was independently collected by I.V. Pekov and D.I. Belakovskiy at the same locality in August 1998 during an excursion with L. Horváth. In Moscow, this material was checked by XRD, EDS and IR spectroscopy with the same result: it was found that the mineral is an unknown hydrous Na,Ca carbonate potentially interesting for study. In 2006, it was confirmed (R.A. Gault, pers. commun., *via* L. Horváth) that no further work will be attempted at CMN, and the UK113 investigation was transferred to the Moscow team, namely I.V. Pekov and coauthors. N.V. Chukanov directed his colleagues' attention to the very unusual character of the IR spectrum, for carbonates with only large cations and presumably the presence of a high-field-strength cation (for details, see below). It was obvious that such a cation could be only light, *i.e.*, non-detectable by routine electron-microprobe analysis. We thought that it could be lithium, as the existence of a natural beryllium carbonate seemed hardly probable, especially as even synthetic Be carbonates are considered as exotic compounds, with very few data relevant published data. The mineral was analyzed by A.A. Agakhanov for light cations, using inductively coupled plasma – optical emission spectroscopy (ICP–OES). The analysis gave an unexpected result: there is no lithium, but much beryllium is present. At this point, additional UK113 study material, which consisted of distinct batches (with varied mineral assemblages, morphology and different collection dates) was supplied by the Horváths for the investigation. A crystal suitable for single-crystal X-ray study was selected, and its investigation was carried out using conventional radiation. The structure model was found, but the crystal was extremely thin and twinned, yielding an unacceptably high *R* value. The structure refinement was successfully performed on the same crystal using synchrotron radiation, accounting for twinning, and the model was completely confirmed.

## OCCURRENCE AND GENERAL APPEARANCE

The type locality of niveolanite is the Poudrette pegmatite, Poudrette quarry, Mont Saint-Hilaire, Rouville County, Quebec, Canada (Long. 45°33'36.9" N, Lat. 73°08'31.4" W).

General geological and petrological data for the Mont Saint-Hilaire alkaline pluton, which belongs to the Monteregian alkaline province, were published by Currie *et al.* (1983), and mineralogical information was summarized by Horváth & Gault (1990). To date, more than 370 species have been confirmed from the pluton, including the 52 mineral species first described from there.

The Poudrette pegmatite is the largest of the pegmatites exposed to date in the Mont Saint-Hilaire complex, in the extreme southern corner of the current Poudrette quarry, which combines the former Demix quarry on the northwest and the original Poudrette quarry on the southeast into a single excavation. The pegmatite has yielded the greatest number of mineral species at Mont Saint-Hilaire, *viz.*, approximately 150, including six new ones: lukechangite-(Ce), horváthite-(Y), adamsite-(Y), reederite-(Y), thomasclarkite-(Y) and niveolanite. The entire zone surrounding the pegmatite is remarkably prolific in mineral species, in large part owing to the close proximity of a zone of hyperagpaitic xenoliths and the contacts between various rock units (nepheline syenite, sodalite syenite and others) and a giant hornfels xenolith. The new species abenakiite-(Ce), gaultite, griceite, martinite, nalipoite, rouvilleite and silinaite were described from these hyperagpaitic xenoliths, and many of the rare and unusual species for which Mont Saint-Hilaire is renowned were found only in these xenoliths.

The Poudrette pegmatite is a dyke 2–4 m thick, at least 70 m long, which has been exposed ~35–40 m vertically. The dyke cuts a huge xenolith of hornfels (~200 m long, ~120 m wide and unknown vertical dimension) and continues to an unknown depth. The main pegmatite dyke is nearly vertical, oriented in W–NW to E–SE direction and is associated with numerous veins 2–15 cm wide that radiate outward from the main dyke. These veins contain many of the same minerals, including niveolanite, as found in the main pegmatite dyke. One of these veins yielded the first specimen of this mineral used in the initial XRD identification (CMN) and the thickest crystals, used for structural study.

The pegmatite dyke is characterized by rhythmically banded contact zone with alternating bands of hornfels and aplite, grading into a lining of mainly microcline, nepheline, aegirine and commonly some eudialyte-group minerals. The core zones of the dyke are hydrothermally altered. Albite and zeolites are major constituents, and a great variety of late-stage carbonate minerals, including many carbonates of lanthanides and

Y, have been documented. There are significant spatial variations in mineralogy within the dyke, with concentration of specific minerals in a given zone and their total absence in others. For instance, in one large zone, the core consists of columnar pseudomorphs of mainly analcime after natrolite, associated with smoky quartz and also intermixed with albite and siderite with minor amounts of chabazite-Na, phillipsite-Na, rhodochrosite and others. In other zones, pseudomorphs of a mixture of albite, calcite and siderite after aegirine are abundant. Some zones are very rich in partial or complete pseudomorphs of alkali-free REE-bearing carbonates [ancylite-(Ce), calcioancylite-(Ce), bastnäsite-(Ce), synchysite-(Ce) or their mixtures] after petersenite-(Ce) and remondite-(Ce). In some of these pseudomorph-rich zones, there are significant amounts of powdery dawsonite filling the interstices as well as local concentrations of cryolite, horváthite-(Y), donnayite-(Y), franconite, sabinaitite and others. Other zones are devoid of such pseudomorphs but have a great diversity of Na-bearing carbonate minerals, namely petersenite-(Ce), remondite-(Ce), adamsite-(Y), shomiokite-(Y), horváthite-(Y), donnayite-(Y), thomasclarkite-(Y), sabinaitite, dawsonite and others.

In total, 25 carbonates, including three insufficiently studied (UK = unknown) phases, have been identified in the Poudrette pegmatite (in the dyke and satellite veins). It is remarkable that sabinaitite,  $\text{Na}_4\text{Zr}_2\text{TiO}_4(\text{CO}_3)_4$ , a mineral with such unusual cations as Zr and Ti for a natural carbonate, occurs as rich aggregations in some zones of the pegmatite. Niveolanite, a mineral with another exotic cation for natural carbonates, beryllium, is also present in more than minute quantities; other beryllium minerals are represented here by leifite and its K-analogue (IMA 2007–017), eudidymite, epididymite, beryllonite, genthelvite, leucophanite and, in the dyke contacts, beryl.

The first samples of niveolanite were collected on working level 8 of the quarry. Probably the richest zone was in the temporarily exposed level 9, trench excavation, in the main dyke and some of the “offshoot” veins found in 2000 and 2002. It is likely that more niveolanite remains in the unexposed parts of the pegmatite.

Niveolanite occurs in cavities, typically in the interstices of microcline and aegirine crystals. It forms two morphological varieties: fibrous and the very rare acicular type. Fibrous (random, matted, radiating, subparallel, sheaf- or spray-like) aggregates are up to 2 cm across. Aggregates are usually soft, flexible and “fluffy”, like wool flocks (Fig. 1). Individual fibers, typically curved and divergent, are usually up to 2–3 mm long and <1  $\mu\text{m}$  thick, rarely up to 1.4 cm long and up to 0.01 mm thick. In some cavities, aggregates of acicular crystals (up to 1 cm long and 0.03 mm thick) were found, with tetragonal or octagonal cross-sections (Fig. 2). The crystals are elongate along  $\{001\}$ ;  $\{100\}$  and  $\{110\}$  probably are the major crystal forms,

but well-developed terminations were not observed. Some of the crystals are in fact parallel intergrowths of extremely thin acicular subindividuals. Fibrous niveolanite also forms partial to almost complete pseudomorphs after lamellar crystals of eudidymite of up to  $0.1 \times 0.5 \times 1$  cm. In this case, eudidymite was undoubtedly the source of beryllium for the niveolanite.

The minerals closely associated with niveolanite in cavities include albite (commonly epitactic on microcline), aegirine, natrolite, gonnardite (invariably epitactic on natrolite), siderite, petersenite-(Ce), franconite and fine, powdery dawsonite. Less common associated minerals are analcime, quartz, eudidymite, catapleiite, gaidonnayite, monazite-(Ce), calcite, adamsite-(Y), shomiokite-(Y), galena, sphalerite and rutile. Brown films of a solid bituminous substance were observed in some cavities with niveolanite. Microcline, aegirine, nepheline, albite, annite, sodalite and zircon form a massive pegmatite matrix in these areas.

#### PHYSICAL AND OPTICAL PROPERTIES

Niveolanite is snow-white to pearl-white in aggregates. Separate individuals are colorless and transparent. The streak is white, and the luster, silky. The mineral is non-fluorescent under ultraviolet radiation. Cleavage and parting were not observed, either megascopically or under the microscope; the fracture is splintery (observed under the electron microscope). Acicular crystals are brittle, fibrous individuals are flexible. It was impossible to measure hardness and density because of the character of aggregates, which are wool-like or consist of extremely thin needles. The density calculated for the empirical formula obtained from the chemical data (hydrous variety with 1.66  $\text{H}_2\text{O}$  *pfu*) is 2.06, whereas the density of the variety of the mineral poorer in  $\text{H}_2\text{O}$  (1  $\text{H}_2\text{O}$  *pfu*) calculated from structural data is 1.82  $\text{g}/\text{cm}^3$ ; for an explanation of this discrepancy, see below.

Niveolanite is optically uniaxial positive. Its indices of refraction measured in dry room-temperature conditions (*i.e.*, for the poorly hydrous variety) are:  $\omega$  1.469(1),  $\epsilon$  1.502(1). Under the microscope, the niveolanite crystals are colorless, nonpleochroic, with a positive elongation.

#### INFRARED SPECTROSCOPY

Niveolanite was mixed with anhydrous KBr, pelletized, and analyzed using a Specord 75 IR spectrophotometer. The IR spectrum of the KBr disk was subtracted from the overall spectrum. Polystyrene and gaseous  $\text{NH}_3$  were used as frequency standards; the precision of the frequency measurement is  $\pm 1$   $\text{cm}^{-1}$ ; the mean resolution for the region of 400–1600  $\text{cm}^{-1}$  is 0.8  $\text{cm}^{-1}$ .

The infrared-absorption spectrum of niveolanite (Fig. 3a) is unique and can be used to identify it. It shows that the mineral is obviously a hydrous carbonate. Some individual features of the spectrum are caused by the presence of beryllium, a small high-field-strength cation; the metal–ligand force constant for Be–O is about 2 mdyne/Å (Young & Koppel 1964, Huckaby *et al.* 1975).

According to the IR spectrum, the CO<sub>3</sub> groups in niveolanite are strongly polarized. Indeed, the non-degenerate mode of C–O stretching vibrations (in the range of 1030–1080 cm<sup>-1</sup>), which should be inactive in case of symmetric non-polarized carbonate group, is present in the IR spectrum. It means that simultaneous elongation of all three C–O bonds of the CO<sub>3</sub><sup>2-</sup> anion is accompanied by strong changes of electric dipole moment. Moreover, the corresponding band at 1059 cm<sup>-1</sup> is very intense, and it shows a very strong polarization of CO<sub>3</sub> groups (note that the intensity of an absorption band is proportional to the square of the normal coordinate derivative of the electric dipole moment). Another indication of this polarization is the unusually strong splitting of the band of asymmetric C–O stretching vibrations in the range 1392–1567 cm<sup>-1</sup>. In case of symmetric CO<sub>3</sub> groups (with a three-fold axis), only a single band would be present in this range.

The origin of the band at 1117 cm<sup>-1</sup> remains unclear. Most likely, this band corresponds to complex modes involving hydrogen atoms. The bands in the frequency region of 692–905 cm<sup>-1</sup> presumably can be assigned to resonance modes involving bending vibrations of the groups CO<sub>3</sub> and Be–OH, combined with Be–O stretching vibrations.

Most hydrogen bonds in a niveolanite sample kept for a long time in dry atmosphere have medium strengths and correspond to the band of O–H stretching vibrations at 3380 cm<sup>-1</sup>. The presence of H<sub>2</sub>O molecules is confirmed by the existence of H–O–H bending mode corresponding to the shoulder at 1640 cm<sup>-1</sup>. A minor portion of the OH groups forms weaker hydrogen bonds (the shoulder at 3550 cm<sup>-1</sup>). The position of the latter shoulder is the same as that of the strongest band of O–H stretching vibrations in the IR spectrum of clinobehouite, Be(OH)<sub>2</sub>.

In air oversaturated with water vapor, niveolanite strongly absorbs molecules of water, and after exposure for 15 seconds, it gives an IR spectrum significantly different from that of a dry sample (Fig. 3b). The “wetting” of the mineral results in the complication of its IR spectrum in the frequency range of O–H stretching vibrations (in particular, the splitting of corresponding band into five poorly resolved components located at 3320, 3390, 3445, 3500 and 3610 cm<sup>-1</sup>) and in the development of total absorption in this range. After the exposure of a KBr pellet with “wet” niveolanite to dry air for one hour, the pellet becomes opaque and strongly dispersive (a typical sign that KBr extracts

the redundant water from “wet” niveolanite), whereas total extinction of O–H stretching bands decreases. This experiment demonstrates that hydration–dehydration of niveolanite is reversible.

The only plausible assignment of the band at 560 cm<sup>-1</sup> is to a Be–O–C bending vibration.

#### CHEMICAL DATA

The chemical composition of the new mineral species was studied using a combination of methods. The levels of Na, K and Ca were determined with a Camebax SX 100 electron microprobe in wavelength-dispersion (WDS) mode, using an operating voltage of 30 kV and an estimated beam-current of 15 nA. The electron beam was rastered over an area of 5 × 5 μm<sup>2</sup> to minimize damage to the sample. As standards, we used jadeite (Na), orthoclase (K) and augite (Ca). Eight point-analyses were obtained for three “thick” (>0.01 mm) crystals.

The content of Be was determined using the ICP–OES method. The 10 mg sample was dissolved in 34 vol.% HNO<sub>3</sub> using a polypropylene vessel. After evaporation, a dry residuum was dissolved in 2% HNO<sub>3</sub> and analyzed using a Varian VISTA Pro instrument.

The content of the volatile constituents, CO<sub>2</sub> + H<sub>2</sub>O was determined from loss on ignition (LOI). The sample of fibrous niveolanite was heated to 1000°C in an oxygen stream. In this experiment, CO<sub>2</sub> was selectively absorbed in pipes filled with “ascarite”, an asbestiform material saturated with NaOH. The H<sub>2</sub>O content was calculated as LOI minus the value for CO<sub>2</sub>.

The averaged chemical composition of niveolanite (ranges of eight point-analyses for Na, K and Ca are in parentheses) is: Na<sub>2</sub>O 19.81 (18.9–20.8), K<sub>2</sub>O 0.07 (0.00–0.15), CaO 3.88 (3.6–4.5), BeO 16.65, CO<sub>2</sub> 29.81, H<sub>2</sub>O 26.93, for a total of 97.15 wt.%.

The Na<sub>2</sub>O and CaO contents in a fibrous aggregate of niveolanite, independently determined using ICP–OES (for the same sample as was used for Be determination), are 18.9 and 4.3 wt.%, respectively, which are in agreement with the electron-probe data. We checked using the electron microprobe (WDS mode for F and energy-dispersive spectroscopic mode for elements with Z > 11) that the contents of other elements with Z > 8 are below detection limits. The absence of Li and B was confirmed by ICP–OES. The IR spectrum and crystal-structure data gave no evidence of nitrogen-bearing and organic groups in niveolanite.

The empirical formula calculated for 1 C *apfu* is: (Na<sub>0.94</sub>Ca<sub>0.10</sub>)<sub>Σ1.04</sub>Be<sub>0.98</sub>(CO<sub>3</sub>)<sub>1.00</sub>(OH)<sub>1.10</sub>•1.66H<sub>2</sub>O. The OH:H<sub>2</sub>O ratio was calculated from charge balance (for a detailed explanation, see below).

The low value of the analytical total (97.15 wt.%) is probably caused by the zeolitic character of the mineral: part of the H<sub>2</sub>O is very weakly bonded (in the broad channel: see below) and could have been mobilized





FIG. 1. Typical wool-like aggregate of fibrous niveolanite on albite (dark particles are fragments of bituminous films). Photo: I.V. Pekov & A.V. Kasatkin.

easily during analysis. Consequently, the H<sub>2</sub>O content could vary from crystal to crystal, and the content obtained on the bulk sample could have differed from the contents in crystals studied with other methods.

The Gladstone–Dale compatibility index (Mandarino 1981) calculated for the variety with 1.76 H<sub>2</sub>O *pfu* using its  $D_{\text{calc}} = 2.06 \text{ g/cm}^3$  is 0.058, good.

Niveolanite dissolves slowly in both concentrated and dilute HCl under room-temperature conditions, with weak effervescence. Such instability, typical for carbonates, makes niveolanite a toxic mineral, a potential source of mobile Be<sup>2+</sup> ions.

#### X-RAY CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

A crystal of niveolanite measuring  $\sim 20 \times 20 \times 500 \mu\text{m}$  was used for determination of the structure at room temperature with an Xcalibur S diffractometer equipped with a CCD detector. A total of 9663 reflections were obtained in the  $\theta$  range from 4.40 to 32.53°. A tetragonal

unit-cell with  $a$  13.077(5),  $c$  5.404(3) Å ( $Z = 8$ ) was revealed. The space group,  $P4/mcc$ , was determined on the basis of the systematic absences. The crystal structure of niveolanite was solved through direct methods and refined with the use of SHELX software package (Sheldrick 1997a, b). Unfortunately, the acicular shape of the crystal and unaccounted twinning did not lead to good agreement between observed and calculated  $F$  values. At the same time, all atoms except H were located, and the intensity calculations (Yvon *et al.* 1977) for the model structure demonstrated a good agreement with X-ray powder-diffraction data collected in the computer-controlled STOE STADI MP diffractometer (CuK $\alpha_1$  radiation,  $\lambda = 1.54056$  Å; Table 1). Therefore, it was decided to carry out a structural study of niveolanite using synchrotron radiation for data collection.

The same crystal was studied at the Swiss–Norwegian Beam Lines (SNBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. Diffraction data were collected at 296 K using the MAR345 Image Plate detector, at a wavelength of 0.71468 Å and

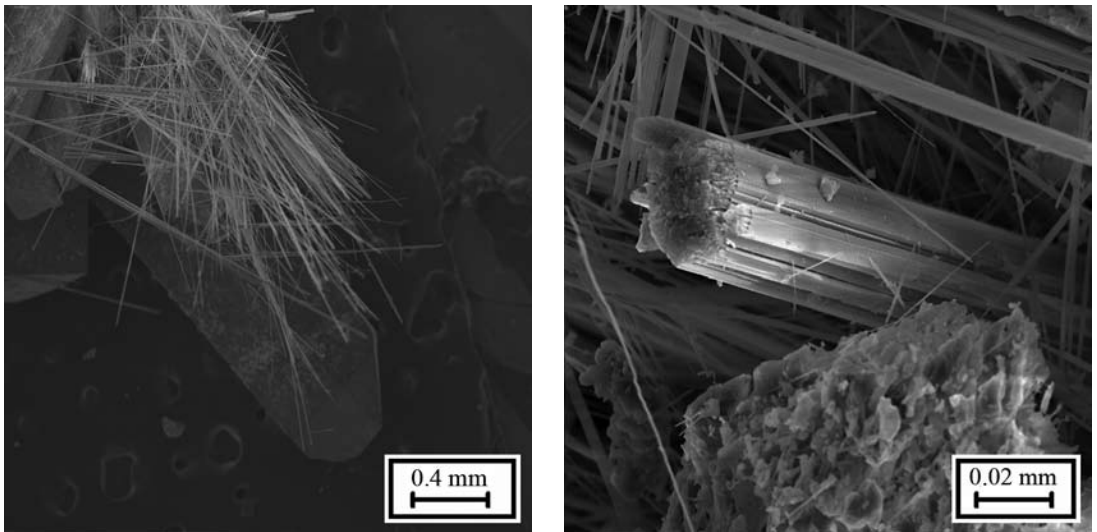


FIG. 2. Acicular niveolanite (SEM image). (a) Sprays on quartz and albite, (b) Naturally broken and regenerated “thick” crystal among typical very thin acicular crystals.

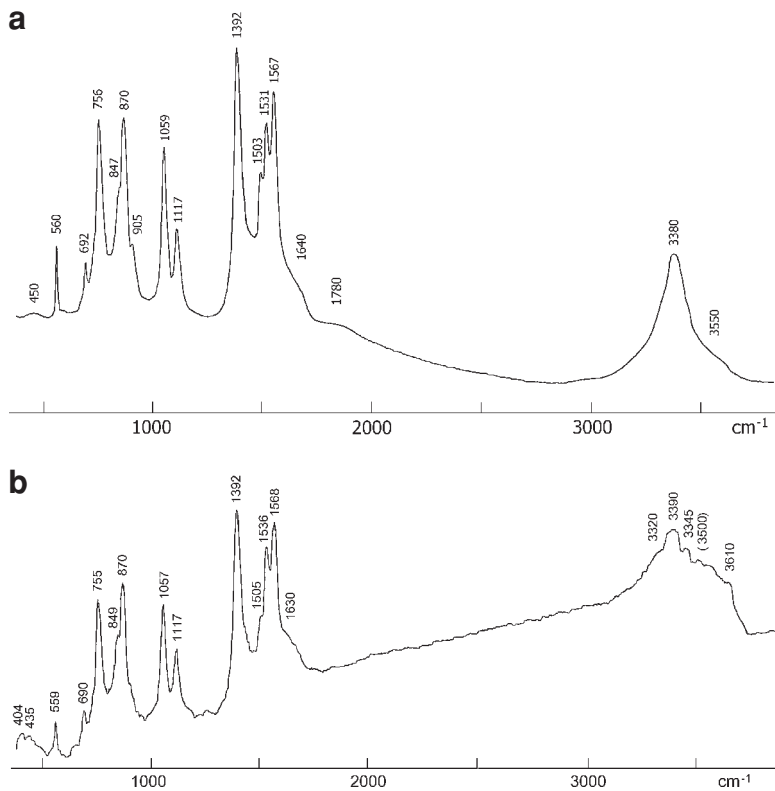


FIG. 3. IR spectra of niveolanite. (a) Spectrum of sample kept in dry air; (b) spectrum of sample exposed to moist air.

the crystal-to-detector distance of 150 mm. A total of 343 frames with exposure time 60 seconds have been collected. All diffraction intensities could be indexed by assuming two intergrown domains, each possessing a primitive tetragonal lattice. The two domains are related by 180° rotation around the [0.49 0.87 0] direction, both in direct and reciprocal space. Both domains were accounted for during the intensity integration. In all, 8946 diffraction peaks were integrated using CRYSTALIS software (Oxford Diffraction 2006). Although overlapping intensities were omitted (less than 1% of reflections were rejected owing to overlaps between the two domains before merging), a highly redundant dataset (~98% complete) was obtained for the first domain. The data were corrected for Lorentz factor and polarization effects. Absorption correction and scaling of frames for the decaying intensity of the synchrotron beam were performed using SADABS (Sheldrick 1997c).

The tetragonal unit-cell, with  $a$  13.1304(19),  $c$  5.4189(11) Å and space group  $P4/mcc$ , was determined on the basis of the systematic absences, which confirmed the data obtained as the result of the first solution of the structure. The structure was solved and refined anisotropically using SHELX (Sheldrick 1997a, b) to  $R = 0.0358$  for 411 unique reflections with  $I > 2\sigma(I)$ . Further details of the single-crystal X-ray data

collection and structure refinement of niveolanite are given in Table 2.

The structure model of niveolanite also confirmed the data obtained using conventional radiation.

The H atom of the hydroxyl group was located from difference-Fourier maps and refined isotropically. With PLATON (Spek 2003), we did not detect higher metric or crystallographic symmetry.

The atom coordinates, displacement parameters, selected interatomic distances and bond-valence sums for niveolanite (Bresé & O'Keeffe 1991) are reported in Tables 3, 4, and 5, respectively. A set of structure factors is available from the Depository of Unpublished Data on the MAC website [document Niveolanite cm46\_1343].

Niveolanite is the first naturally occurring beryllium carbonate, representative of a new structure-type. The crystal structure of niveolanite (Figs. 4a, b) includes single infinite chains  $[-(\text{OH})-(\text{BeO}_2)]_\infty$  formed by  $\text{BeO}_2(\text{OH})_2$  tetrahedra with two distances of Be–O equal to 1.640(2) Å and two distances Be–OH equal to 1.623(2) Å. Adjacent Be tetrahedra are linked *via* common OH groups; two other vertices of each Be tetrahedron are shared with  $(\text{CO}_3)$  groups; C–O distances in them vary from 1.272(4) to 1.291(2) Å. The configuration of Be chains with adjacent  $\text{CO}_3$  groups is shown on Figure 5a. The Na cations occupy seven-fold polyhedra  $[\text{NaO}_6(\text{H}_2\text{O})]$  and are linked to each other by edges, forming isolated columns. Each  $(\text{CO}_3)$  group shares two vertices with two adjacent Be tetrahedra, whereas its third vertex is shared with three Na polyhedra (each  $\text{CO}_3$  group is connected by two edges with two Na polyhedra). Chains of Be tetrahedra and columns of Na

TABLE 1. X-RAY POWDER-DIFFRACTION DATA OF NIVEOLANITE

$l_{\text{meas}}$	$d_{\text{meas}}, \text{Å}$	$l_{\text{calc}}$	$d_{\text{calc}}, \text{Å}$	$hkl$
100	13.01	100	13.130	100
62	9.20	44	9.285	110
15	6.51	2	6.565	200
		2	5.872	210
27	4.343	5	4.377	300
18	4.138	1	4.152	310
16	4.004	2	3.982	211
34	3.611	7	3.642	320
22	3.269	11	3.300	311
95	3.256	29	3.283	400
		1	3.095	330
10	2.900	1	2.936	420
18	2.730	6	2.746	411
44	2.693	5	2.709	002
37	2.605	1, 10	2.626	430, 500
24	2.582	3, 2	2.601, 2.581	112, 421
12	2.561	3	2.575	510
60	2.489	10	2.504	202
19	2.444	3	2.460	212
		2	2.363	431
20	2.173	5	2.188	600
18	2.139	2, 1	2.174, 2.159	322, 610
12	2.091	8	2.090	402
32	2.076	1	2.076	620
		2	2.064	412
10	2.036	2	2.050	540
18	1.978	4	1.991	422
10	1.875	1, 4	1.886, 1.876	432, 700
12	1.863	4	1.867	512
16	1.853	2	1.857	710
		2	1.841	631
10	1.810	3	1.821	640
11	1.805	1	1.812	522
16	1.751	5	1.763	442
14	1.716	1, 2	1.726, 1.726	213, 641
15	1.690	4	1.702	602
12	1.528	1, 1, 2	1.547, 1.531, 1.526	660, 552, 750

The values of  $d_{\text{calc}}$  and  $l_{\text{calc}}$  were calculated from single-crystal structural data obtained using synchrotron radiation; all reflections of the calculated X-ray powder diagram with  $l_{\text{calc}} \geq 1$  are included.

TABLE 2. DATA COLLECTION AND REFINEMENT DATA FOR NIVEOLANITE

Formula, from structure refinement	$(\text{Na}_{0.93}\text{Ca}_{0.09})\text{Be}(\text{CO}_3)[(\text{OH})_{0.92}\text{O}_{0.08}]\cdot\text{H}_2\text{O}$
Formula weight	128.23
Temperature	296(1) K
Radiation and wavelength	synchrotron, 0.71468 Å
Crystal system, space group	tetragonal, $P4/mcc$
Unit-cell dimensions	$a$ 13.1304(19) Å $c$ 5.4189(11) Å $V$ 934.3(3) Å <sup>3</sup>
Unit-cell volume	8
Z	1.823 g/cm <sup>3</sup>
Density (calculated)	0.344 mm <sup>-1</sup>
Absorption coefficient $\mu$	517
$F(000)$	0.50 × 0.02 × 0.02 mm
Crystal size	MAR345 Image plate
Data collection	3.49 to 24.15°
$\theta$ range for data collection	-15 ≤ $h$ ≤ 15, -15 ≤ $k$ ≤ 15, -6 ≤ $l$ ≤ 6
Index ranges	8946
Reflections collected	414 ( $R_{\text{int}} = 0.0358$ )
Independent reflections	411
Reflections with $I > 2\sigma(I)$	direct methods
Structure solution	full-matrix least-squares on $F^2$
Refinement method	0.0404, 0.9997
Weighting parameters $a, b$	50
Number of refined parameters	$R_1 = 0.0358, wR_2 = 0.0993$
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_2 = 0.0361, wR_2 = 0.0996$
$R$ indices (all data)	1.292
Goodness-of-fit on $F^2$	0.26 and -0.22 e/Å <sup>3</sup>
Largest diff. peak and hole	

Shown in parentheses are the estimated standard deviations referred to the last digits.



polyhedra are parallel to the *c* axis, as are broad channels in which H<sub>2</sub>O molecules constituting one vertex of the Na polyhedra are located. As a result, niveolanite could show a zeolite-like behavior.

Some Na is replaced by Ca, with a coupled substitution of part of H<sub>2</sub>O (OW in Tables 3–5) coordinating Na by (OH): Na<sup>+</sup> + (H<sub>2</sub>O)<sup>0</sup> → Ca<sup>2+</sup> + (OH)<sup>-</sup>. We prefer this scheme to another, Na<sup>+</sup> + (OH)<sup>-</sup> → Ca<sup>2+</sup> + O<sup>2-</sup>, which involves substitution (OH)<sup>-</sup> by O<sup>2-</sup> on the Be–(OH)–Be bridge [O(3) in Tables 3–5], comparing local charge on O(3) and OW (Table 5). Also, we take into account that OW is bonded to (Na,Ca), unlike O(3), shared only between two Be tetrahedra.

The broad channels may also contain additional molecules of H<sub>2</sub>O (Fig. 4), but they were not located reliably on Fourier maps. The highest peak on the difference-Fourier map has 0.26 e/Å<sup>3</sup>, and the coordinates *x* 0.454(4), *y* 0.402(4), *z* 0.211(13). This peak can be interpreted as the oxygen atom of a H<sub>2</sub>O molecule inside the channel, with a weak occupancy-factor, 0.0450(12), and *U*<sub>iso</sub> equal to 0.085(18) Å<sup>2</sup>. The number of these sites, grouped in two “rings”, is 16 per unit cell (Fig. 4), but adjacent sites in a “ring” cannot be occupied together because of the short distance (1.0 Å). Thus, the maximum possible number of these “zeolitic” H<sub>2</sub>O molecules in niveolanite is eight per unit cell, or one per the formula (*Z* = 8).

TABLE 3. FRACTIONAL COORDINATES OF ATOMS, ATOMIC DISPLACEMENT PARAMETERS AND OCCUPANCY COEFFICIENTS FOR NIVEOLANITE

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Na <sub>0.90(2)</sub> Ca <sub>0.09(14)</sub>	0.41084(9)	0.10533(11)	0.5	0.0283(6)
Be	0.84477(19)	0.15523(19)	0.25	0.0140(9)
C	0.6772(2)	0.1176(2)	0.5	0.0176(7)
O(1)	0.72297(11)	0.13374(13)	0.7073(3)	0.0262(5)
O(2)	0.58599(16)	0.0851(2)	0.5	0.0307(7)
O(3)	0.90044(17)	0.11618(16)	0.5	0.0134(6)
H	0.959(3)	0.124(3)	0.5	0.024(10)*
OW	0.4249(8)	0.2935(5)	0.5	0.243(6)

Shown in parentheses are the estimated standard deviations referred to the last digits. \* *U*<sub>eq</sub>.

## DISCUSSION

In its “fully hydrated” (supposedly initial) form, niveolanite contains 2 H<sub>2</sub>O *pfu*. This was predicted by structural data (presence of the position suitable for H<sub>2</sub>O in the broad channel) that was directly confirmed by the IR spectrum obtained from the sample exposed to moist air and by chemical data (the measured value is 1.66 H<sub>2</sub>O) obtained for a sample kept in air with a normal content of moisture. These weakly bonded intrachannel H<sub>2</sub>O molecules can form H-bonds (revealed in the IR spectra) with each other and with O atoms of H<sub>2</sub>O molecules, forming “pendent” vertices of Na polyhedra. However, weakly bonded intrachannel molecules of H<sub>2</sub>O can easily migrate and leave a crystal in dry air, unlike the more strongly bonded H<sub>2</sub>O coordinating Na cations. Thus, taking into account the reversible character of hydration–dehydration processes in niveolanite, we conclude that the degree of its hydration strongly depends on air moisture and varies between 1 and 2 H<sub>2</sub>O *pfu*.

Taking into account all above-mentioned substitutions and different character of H<sub>2</sub>O molecules in the structure, we can write the simplified structural formula of niveolanite as follows: {(Na<sub>0.9</sub>Ca<sub>0.1</sub>) [(H<sub>2</sub>O)<sub>0.9</sub>(OH)<sub>0.1</sub>]}{Be(OH)}(CO<sub>3</sub>)•0–1H<sub>2</sub>O. The idealized formula of the mineral, with variable general number of molecules of H<sub>2</sub>O, can be written as: NaBe(CO<sub>3</sub>)(OH)•1–2H<sub>2</sub>O (*Z* = 8).

The crystal structure of niveolanite is unique. The bonds between Be tetrahedra along [001] are re-inforced by CO<sub>3</sub> groups, located from both sides of the [BeO<sub>2</sub>(OH)]<sub>∞</sub> chains. Consequently, the *c* period of the structure is almost equal to two edges of Be tetrahedra: ~2.7 Å × 2 corresponds to 5.4 Å. This structural feature has a lot in common with chains in many structures of beryllium minerals, where the core of the chain is formed by Be tetrahedra. However, in such minerals, the bonds between the neighboring Be tetrahedra are re-inforced by Si tetrahedra [*e.g.*, euclase, AlBe(SiO<sub>4</sub>)(OH) (Mrose & Appleman 1962), and sphaerobrandite, Be<sub>3</sub>SiO<sub>4</sub>(OH)<sub>2</sub> (Pekov *et al.* 2003)] or by

TABLE 4. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE STRUCTURE OF NIVEOLANITE

Be	–O(3)	1.623(2) × 2	O(3)–Be–O(3)	114.4(2)	Na,Ca	–O(2)	2.315(2)
	–O(1)	1.640(2) × 2	O(3)–Be–O(1)	105.49(9) × 2		–O(1)	2.3962(18) × 2
<Be–O>		1.631	O(3)–Be–O(1)	110.39(9) × 2		–OW	2.478(6)
			O(1)–Be–O(1)	110.8(2)		–O(2)	2.501(3)
			<O–Be–O>	109.5		–O(2)	2.7227(6) × 2
					<Na,Ca–O>		2.505
C	–O(2)	1.272(4)	O(2)–C–O(1)	119.54(13) × 2			
	–O(1)	1.291(2) × 2	O(1)–C–O(1)	120.9(3)	O(3)–H		0.77(4)
<C–O>		1.285	<O–C–O>	120.0			
	O(2)–O(1)	2.215(2) × 2					
	O(1)–O(1)	2.247(3)					

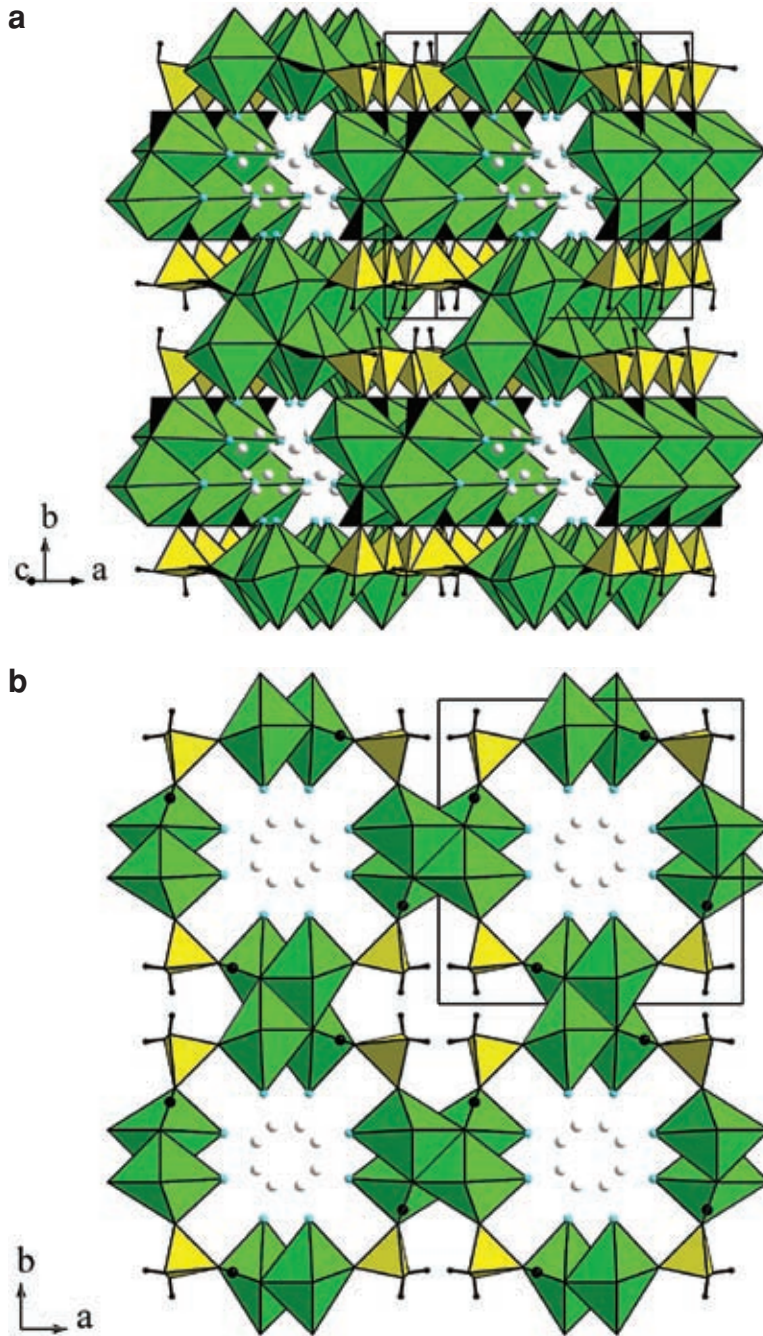


FIG. 4. Crystal structure of niveolanite. (a) general view, (b) projection on (001) plane. The Na polyhedra are gray, Be tetrahedra are light gray, C triangles are black; in (b), the C atoms are black circles. The H<sub>2</sub>O molecules involved in Na polyhedra are marked as gray circles, possible positions of H<sub>2</sub>O molecules in the channels are white circles, and the hydrogen atoms of OH groups are small black circles.

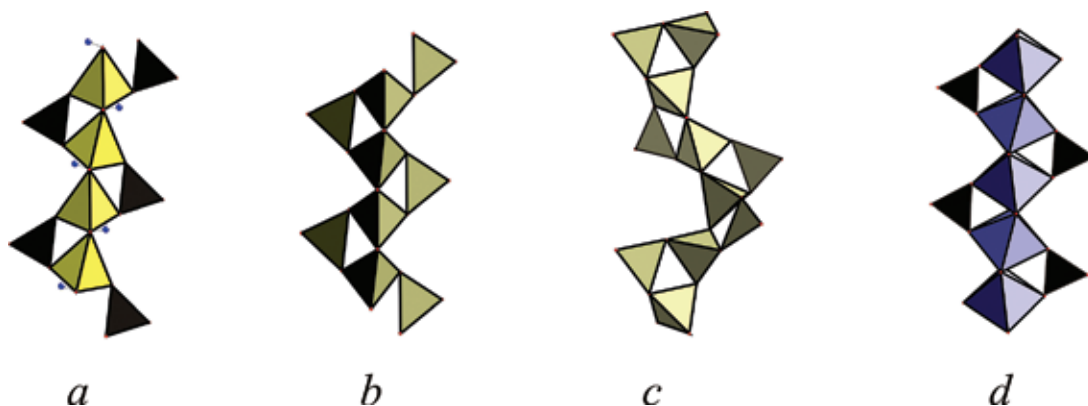


FIG. 5. Chains in the structures:  $[\text{IVBe}^{\text{III}}\text{C}]$  in niveolanite (a),  $[\text{IVB}^{\text{III}}\text{B}]$  in calciborite (b),  $[\text{IVB}^{\text{III}}\text{B}]$  in kernite (c), and  $[\text{VIAl}^{\text{III}}\text{C}]$  in dundasite (d).

TABLE 5. BOND-VALENCE SUMS CALCULATIONS FOR NIVEOLANITE

	(Na,Ca)	Be	C	$\Sigma$
O(1)	0.21 <sup>*2</sup>	0.50 <sup>*2</sup>	1.31 <sup>*2</sup>	2.02
O(2)	0.26 0.15 0.08 <sup>**</sup>		1.38	1.95
O(3) <sup>*</sup>		0.53 <sup>**</sup>		1.06
OW <sup>**</sup>	0.16			0.16
$\Sigma$	1.15	2.06	4.00	

\* O atom of (OH) group; \*\* O atom of H<sub>2</sub>O molecule coordinating (Na,Ca). The parameters are taken from Brese & O'Keeffe (1991).

P tetrahedra [v  yrynenite,  $\text{MnBe}(\text{PO}_4)(\text{OH})$  (Huminicki & Hawthorne 2000)]. Similar elements were revealed in hopeite,  $\text{Zn}_3(\text{PO}_4)_2(\text{H}_2\text{O})_4$  (Hill & Jones 1976) and phosphopyllite,  $\text{Zn}_2\text{Fe}(\text{PO}_4)_2(\text{H}_2\text{O})_4$  (Hill 1977), where Zn tetrahedra form the chain and P tetrahedra re-inforce their contacts. In clinohedrite,  $\text{CaZn}(\text{SiO}_4)(\text{H}_2\text{O})$  (Simonov *et al.* 1977), (Zn,O) chains are also fixed by Si tetrahedra.

Published crystal-structure data for three synthetic Be-bearing carbonates only were found:  $[\text{Co}(\text{NH}_3)_6]_2[\text{Be}_4\text{O}(\text{CO}_3)_6] \cdot 10\text{H}_2\text{O}$ , space group  $R3c$  (Adam & Dahm 2000);  $\text{K}_6[\text{Be}_4\text{O}(\text{CO}_3)_6] \cdot 7\text{H}_2\text{O}$ ,  $P\bar{1}$ , and  $\text{K}_6[\text{Be}_4\text{O}(\text{CO}_3)_6]$ ,  $R\bar{3}$  (Dahm & Adam 2002). The structures of all these compounds differ significantly from the structure of niveolanite.

Some borate minerals also exhibit similarity with niveolanite. For example, similar elements of the structure were found in calciborite,  $\text{Ca}_2(\text{BO}_3\text{BO})_2$  (Shashkin *et al.* 1970), where the chains formed by B tetrahedra and B triangles (Fig. 5b), with the local symmetry 4 (Belokoneva 2005), have the same configuration as the Be-C chains in niveolanite.

Some similarity in the configuration of the chains formed by Be tetrahedra and CO<sub>3</sub> groups in the structure of niveolanite can also be found with the infinite borate chains in the structure of kernite,  $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  (Cooper *et al.* 1973) (Fig. 5c). The symmetry and topology analysis of the B chain in the structure of kernite allow the consideration of this mineral as a pentaborate with a pentablock  $[2\Delta + 3T]$  as a building unit. Thus the chain in the structure of kernite has the local symmetry 2<sub>1</sub> (Belokoneva 2005).

Among carbonates, dundasite,  $\text{PbAl}_2(\text{CO}_3)_2(\text{OH})_4 \cdot \text{H}_2\text{O}$  (Cocco *et al.* 1972), for example, and related minerals show some common features in the configuration of chains built by edge-sharing Al octahedra in which two other vertices are common with CO<sub>3</sub> groups (Fig. 5d), as with the chains in the structure of niveolanite.

The Poudrette pegmatite, as was noted above, is strongly enriched in diverse late-stage carbonate minerals. In particular, such exotic phases in nature as a Zr,Ti carbonate, sabinaitite and niveolanite are found here in significant amounts. This feature undoubtedly reflects the extremely high activity of CO<sub>2</sub> in late alkaline hydrothermal solutions, which seems an agent not only destructive for the earlier-formed rare-element silicates, but also a parent medium for crystallization of carbonate minerals containing these remobilized cations.

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