ELSEVIER

Cronstedt's zeolite

Carmine Colella [a], Alessandro F. Gualtieri [b],*

[a] *Dipartimento di Ingegneria dei Materiali e della Produzione, Università Federico II, Piazzale V. Tecchio 80, I-80125 Napoli, Italy*
[b] *Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Via S. Eufemia 19, I-41100, Modena, Italy*

Abstract

Axel F. Cronstedt (1722–1765), famous Swedish mineralogist, was the first scientist to describe, 250 years ago, the distinctive property of zeolites, i.e., the unique frothing characteristics when heated in a blow-pipe flame. Cronstedt examined two specimens: one from Svappavaara in Northern Sweden and one that was said to come generically from Iceland. From Cronstedt's indications, the occurrence of the first specimen was near the mining area of Kiruna. The morphological characteristics of the specimen suggested that the zeolite species is stilbite which would make it the first discovered zeolite mineral.

This paper is devoted to the description of the structure and microstructure of that first discovered natural zeolite from Svappavaara (Northern Sweden). The SEM investigation of all the sample rock cavities filled with the zeolite crystals and the optical observation of the separated zeolite crystals revealed that the sample is mainly composed of stellerite with subordinate stilbite crystals which are present only in a few cavities together with stellerite. The chemical formula of the stellerite crystals derived from the EPMA and TG analyses is $(Ca_{4.03}Mg_{0.01}Na_{0.03}K_{0.11})$ $[Si_{27.81}Al_{8.19}O_{72}]\cdot 28.6H_2O$. The results of the structure refinement confirm that the investigated specimen is actually stellerite and evidenced no ordering in the tetrahedral sites. The structure refinement evidenced no ordering in the tetrahedral sites. The extraframework cation Ca is located in the centre of the main channel parallel to the a axis, on the mirror plane and is surrounded by water molecules with no contact with framework oxygen atoms. The coordination of Ca is 6-fold. A number of short water–water distances are possible by considering the different possible schemes around the Ca atom. Considering the short water–water distances and the partial occupancy of water sites, a number of octahedral coordinations around Ca are possible.
© 2007 Elsevier Inc. All rights reserved.

Keywords: Cronstedt; Zeolite; Stilbite; Stellerite; Powder diffraction; Rietveld refinement

1. Introduction

1.1. Historical background

In 1756 (250 years ago), a paper titled in Swedish "RÖN och BESKRIFNING *Om en oberkant barg art, som kallas Zeolites*", i.e., "Observation and description of an unknown mineral species, called zeolite", appeared in the Journal of the Swedish Royal Academy of Sciences [1]. In that paper, a new type of hydrated mineral showing unique frothing features when heated in a blow-pipe flame was described and a novel name recalling this property,

zeolite, was accordingly coined for it. The author was a reputed Swedish mineralogist, Axel Fredrik Cronstedt (1722–1765), credited with the title of "Reformer of Mineralogy" for his significant contributions to the advancement of this discipline. He had, in fact, made substantial improvements in chemical analysis procedures, and pointed out for the first time the difference between minerals, as single species, and rocks, as arrangements of different minerals. Moreover, he had been the author of a revolutionary mineral classification (1758), based on chemical similarity, instead of the empirical distinction between earth and rock ores.

In 1758, Cronstedt published his views on mineralogy in an anonymous handbook, titled "An attempt to systematize mineralogy and the realm of minerals", in which he

---

* Corresponding author. Tel.: +390592055810; fax: +390592055887.
E-mail address: alex@unimore.it (A.F. Gualtieri).

included and described in detail, as a new class of mineral species, zeolites [2]. In particular, three zeolite types (and some sub-types) were reported therewith, named in Latin (1) zeolites *particulis impalpabilibus* (constituted by fine particles), (2) zeolites *spatosus* (spar-like), and (3) zeolites *crystallisatus* (crystalline) [2].

The interesting book was translated into the main scientific languages of the time. On the contrary, the original article, published by the Swedish Academy of Sciences, had a published English translation only recently [3,4].

1.2. Cronstedt's zeolite

In his historical paper, Cronstedt studied two different zeolite specimens, one coming from the Svappavari (now Svappavaara) copper mine in the Kiruna area (Northern Sweden) and another coming from an unidentified locality of Iceland. The crystal morphology of the two specimens appeared somewhat different and also some physical-chemical properties were distinct, nevertheless their similar property to intumesce when heated in a blow-pipe flame suggested that they might belong to the same family. Cronstedt achieved certainty of this when, a few months later, other similar evidences were brought to his attention (see below), giving him the chance to propose the first zeolite classification. The more significant information obtained from the original paper are [4]

 (a) the Swedish specimen was light yellow, the Iceland specimen was white;
 (b) the former material was composed of spherulites and wavy fragments consisting of radiating pyramids whose apices apparently terminate in a center, the latter was a mixture of a massive opaque chalk-like material and tangled concentric wedges;

 (c) the hardness of both samples corresponded to that of normal spar or massive limestone earth;
 (d) in the blow-pipe flame both samples emitted gas and puffed up almost like borax; in the Swedish specimen, in particular, the pyramids were initially transformed into a white spongy mass which subsequently fused with a phosphorescent glow to a white glass;
 (e) when placed on charcoal the Swedish specimen, but not the Icelandic specimen, could be melted into a pure glass. Because it came from a copper mine, traces of copper impurity colored the glass in opaque reddish-brown; the green color of the flame also indicated copper.

1.3. The re-discovery of Cronstedt's zeolite

Although nobody knows the nature of the original zeolite samples studied by Cronstedt, it has been reported that it was *stilbite* [5].

On the occasion of the 250th anniversary of zeolite discovery, it has been considered of interest to identify the originally studied zeolite and to recover a sample of it for a thorough characterization. Given the information taken from the original paper, search was limited to the Swedish sample, for the lack of specific details for the Icelandic sample [1]. Iceland is very rich in zeolites of hydrothermal origin [6], so that any hypothesis on the nature of the specific zeolite specimen, studied by Cronstedt, would have been completely unfounded.

A field search in the area of Kiruna, very close to the site, where the Svappavaara zeolite likely occurs, was conducted by a local mineral collector, Mr. Dennis Holmberg (Holmberg, pers. comm.). The old Torneå copper mine, mentioned by Cronstedt, was presumably found and information on his history were collected. The mine was active in
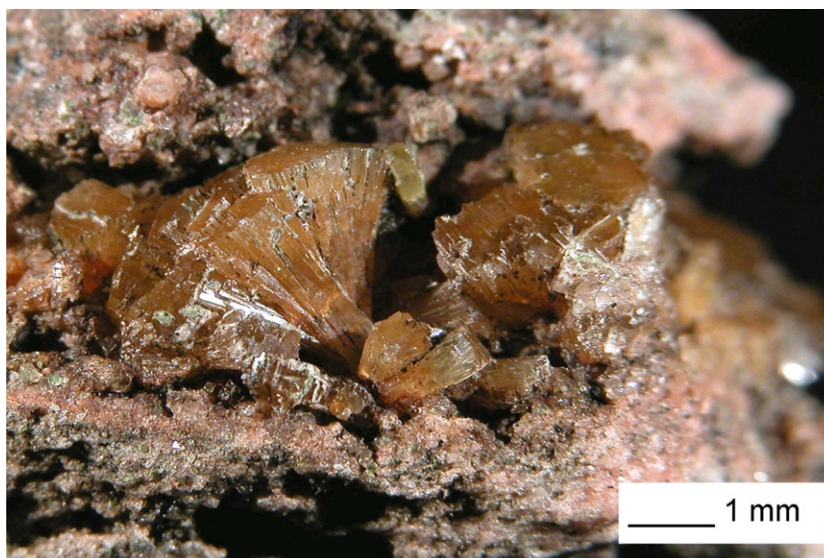

Fig. 1. A cavity showing the Cronstedt's zeolite crystals (×20).

the late 1600s and during the following two centuries. At present, the mine is abandoned and the site is under the patronage of the Swedish National Heritage Board. Many minerals of hydrothermal origin are found at the site [7]. Only two zeolites occur, one classified as *stilbite* and *chabazite*, the former being definitely much more abundant. That occurrence (Fig. 1) fits well the main indications coming from Cronstedt's historical paper, so it is highly probable that the unknown Cronstedt zeolite, or at least that coming from Sweden, was the zeolite identified as stilbite. Stilbite is a common natural zeolite with an ideal mean chemical formula $(Na_2Ca_8)[Al_{18}Si_{54}O_{144}] \cdot 60H_2O$, framework type [STI] and orthorhombic topological symmetry of the framework *Fmmm*. The real symmetry is *C2/m* with no Si/Al-order in the framework [8,9]. The symmetry of stilbite is often referred as *F2/m* to facilitate its comparison with other related structures [10]. The framework is composed of ten- and eight-member rings with the zeolite cavities occupied by Ca and Na and coordinated water molecules (Slaughter 1970). Stilbite shares the same framework type [STI] with stellerite, $Ca_8[Al_{16}Si_{56}O_{144}] \cdot 56H_2O$, and barrerite, $Na_{16}[Al_{16}Si_{56}O_{144}] \cdot 52H_2O$. Stellerite [11] has no tetrahedral Si/Al-order, and a higher symmetry *Fmmm* ($Z = 2$), which coincides with the topological symmetry of the framework. The symmetry of barrerite is orthorhombic *Amma* ($Z = 2$) [12] with a shift of one extraframework position, which triggers off framework to rotate around a screw diad parallel to a. Even for this zeolite species, no tetrahedral Si/Al-order is observed.

2. Experimental section

2.1. Specimen occurrence

The zeolite specimen was collected near a copper mine next to the Leveäniemi mine, 3 km west of Svappavaara,

active from 1654 to 1741. The Cu-mines occur close to the Gruvberget apatite iron ore, which is 1300 m long and up to 65 m thick. It is calculated to contain 64.1 M ton with 56.9 wt% Fe to a depth of about 300 m. The bedrock consists of strongly altered intermediate to mafic volcanic rocks containing scapolite and K-feldspar. Several dikes of metadiabase with a NE direction cuts the ore and its wallrocks. The Svappavaara area (Fig. 2 after [7]) is situated 42 km ESE of Kiruna in the Norrbotten county (Northern Sweden). The main rock types in that area belong to the supracrustal and intrusive rocks of Archean age. The Svappavaara group is one of the two major supracrustal petrographic units and consists of tuffites, graphite-bearing schist, biotite-rich quartzite, scapolitefels, amphibole schist, limestone, and skarn. These rocks are partly banded and may host minerals of hydrothermal origin such as zeolites. Besides stilbite, the Svappavaara minefields contain minerals like apophyllite, diopside, epidote, gypsum, hematite, calcite, chrysocolla, quartz, microcline, natrolite, and others [7]. The Cu-deposits which contain zeolite mineralizations occur mainly within volcaniclastic parts of the greenstones, andesites belonging to the Porphyrite Group and basalts from the lower part of Kiruna Porphyries. Most of them are related to shear zones, or in some cases intrusions of intermediate to felsic composition. Two clusters of mineralization can tentatively be identified. One occurs close to Svappavaara along the major tectonic zone (KADZ) running from Karesuando in a SSW-direction towards Arjeplog and the other extends from the Pahtohavare area and further westwards to Laukijärvi. Both clusters comprise mineralizations of different characters and different host rocks. Vein type mineralizations are common within the Kiruna greenstones and the Kovo group north of Kiruna. Some of the larger deposits occur rather isolated, which might be a result of limited exploration in their surroundings (e.g. Tjårrojåkka-Cu,
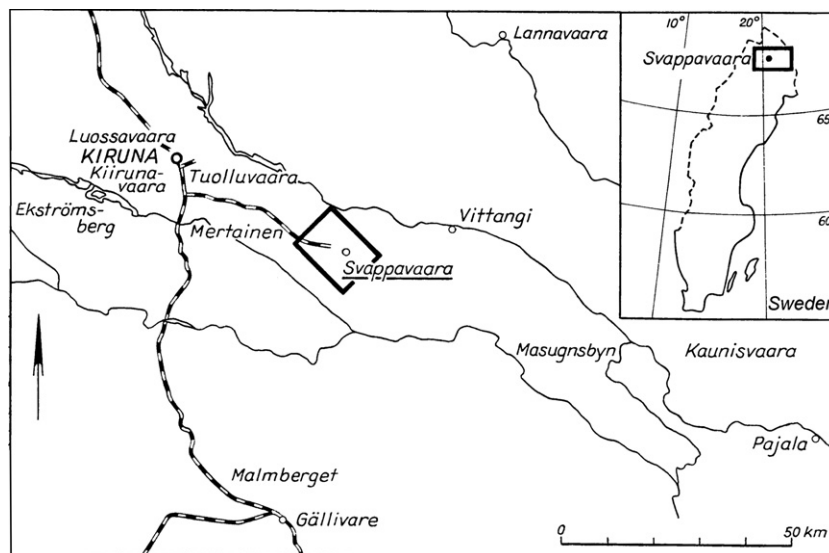

Fig. 2. Map of the occurrence area of the investigated sample (modified after [7]).

Pikkujärvi). Cu-sulphides are scattered through the Gruvberget area, with richer mineralizations mainly developed in the footwall to the iron ore. Chalcopyrite and some bornite are the main ore minerals, occurring disseminated together with magnetite in altered rocks, or as rich ore shoots at the contact to the iron ore. Druses with epidote, magnetite, pyrite, Cu-sulphides and stilbite are common within the sulphide mineralizations. Several of the mines are found close to metadiabases and Cu-mineralizations seem to be controlled by the same structures as the dikes [7].

The collected zeolite specimens are aggregates of prismatic crystals, often as leaf formed crystals of radiating aggregates, translucent, with a yellow colour vitreous-pearly lustre. The zeolite phase is associated with quartz, microcline and muscovite.

2.2. Specimen characterization

Because at a first appearance the specimens seemed morphologically heterogeneous with stellerite-like and stilbite-like crystals, all the rock specimens with vugs containing the zeolite crystals were mounted on Al stubs for SEM analysis. The samples were gold-coated (5 nm thick film) and micrographs were collected using a Philips XL 40/604 equipped with an EDS detector.

Optical observation was also performed. Zeolite crystals were dispersed in a liquid of known refraction index using cross polarization optical microscopy on a universal stage.

The chemical composition was obtained by the average of several microprobe point-analyses performed on the rim and core of two stellerite-like crystals. It was not possible to select pure stilbite-like crystals for the analysis. Electron probe micro-analysis (EPMA) was performed using an ARL-SEMQ instrument operating in wavelength-dispersive mode with 15 kV and 20 nA beam current and a defocused beam of 30 μm in diameter. Natural and synthetic silicates were used as standards, and on-line data processing was conducted using the PROBE program [13]. Microprobe data were normalized to 100 wt% using the weight loss measured by the thermogravimetric (TG) analysis and assuming that all the loss was due to evolution of water. For the TG analysis, a small number of selected stellerite-like crystals were hand ground in an agate mortar, and the powder was mounted in a platinum crucible. The analysis was performed in air using a Seiko SSC 5200 TGA equipped with their 320U Module. The weight measurement was performed through a horizontal differential balance on samples up to 200 mg using a heating rate of 10 °C/min. The total weight loss was 18.17 wt%.

For the IR measurements, some stellerite-like crystals were equilibrated at 30 °C and relative humidity of ca. 35%. Pellets were prepared using the KBr wafer technique (3 mg of sample powder and 97 mg of KBr) and data were collected at room temperature between 600 and 3800 cm^{-1} using a Bruker IFS 113 V spectrometer with a resolution of 1 cm^{-1}.

As discussed below, the specimens resulted to be non-homogeneous as they are composed of stellerite with a minor fraction of stilbite crystals. For the Rietveld structure refinement, crystals of the major zeolite phase stellerite were selected and checked using both reflected and transmitted light microscopies and separated by reflected optical microscopy. The crystals were hand ground in an agate mortar. The powder with average particle size of about 5 μm, measured with laser granulometry, was used for the XRPD measurements. Powder diffraction data were collected at the Italian beamline BM08 (GILDA) at the European Synchrotron Radiation Facility (ESRF), Grenoble (France). The beamline configuration is described in detail elsewhere [14]. The sample powder was mounted in a 0.5 mm diameter quartz capillary and kept spun during the measurement. Data were collected in parallel beam Debye geometry using a wavelength of 0.888498 Å calibrated with FIT2D [15] against the NBS 660 LaB6 standard at 298 K. A full diffraction shot was collected with an exposure time of 30 min, using an image plate (IP) detector, mounted perpendicular to the incoming beam at a distance of 275.39 mm. The images stored in the IP were recovered using a scanner with a dynamical range of 16 bit/pixel with a minimum pixel size of 50×50 μm^2. The data were extracted using FIT2D [15].

The refinements were performed using the GSAS package [16] and the EXPGUI graphical interface [17]. Stellerite starting atomic coordinates for the structural model were taken from [11] and refined in space group *Fmmm*. A tentative structure refinement using the stilbite structure model was also attempted. Stilbite starting atomic coordinates for the structural model were taken from [10] and refined in space group *F2/m*. The background profile was fitted with a Chebyshev polynomial function with 24 coefficients. The profile of the diffraction peaks was modelled using a pseudo-Voigt function with one Gaussian and two Lorentzian coefficients. The refinement of atomic coordinates, site occupancies for extraframework positions, and isotropic atomic displacement parameters (adp's) were performed with the aid of soft constraints (with an initial weight of 2500) on the tetrahedral bond lengths which were used as additional observations in the earlier stages of the refinement and the weights were progressively reduced to 1.

3. Results and discussion

SEM pictures were taken on the rock specimens containing vugs filled with zeolite crystals. Most of the crystal aggregates display the typical stellerite crystal habit with lamellar crystals terminated with the {100}, {001}, and {111} faces (see some examples in Fig. 3a and b). Only a few cavities contained twinned stilbite crystals together with the stellerite crystals (Fig. 3c). In fact, stilbite twins are pseudomerohedral because of the pseudo-orthorhombicity of the structure and commonly, stilbite twins appear as fourlings or eightlings (see the picture in the inlet box of Fig. 3c). Thus, the SEM observations indicated that
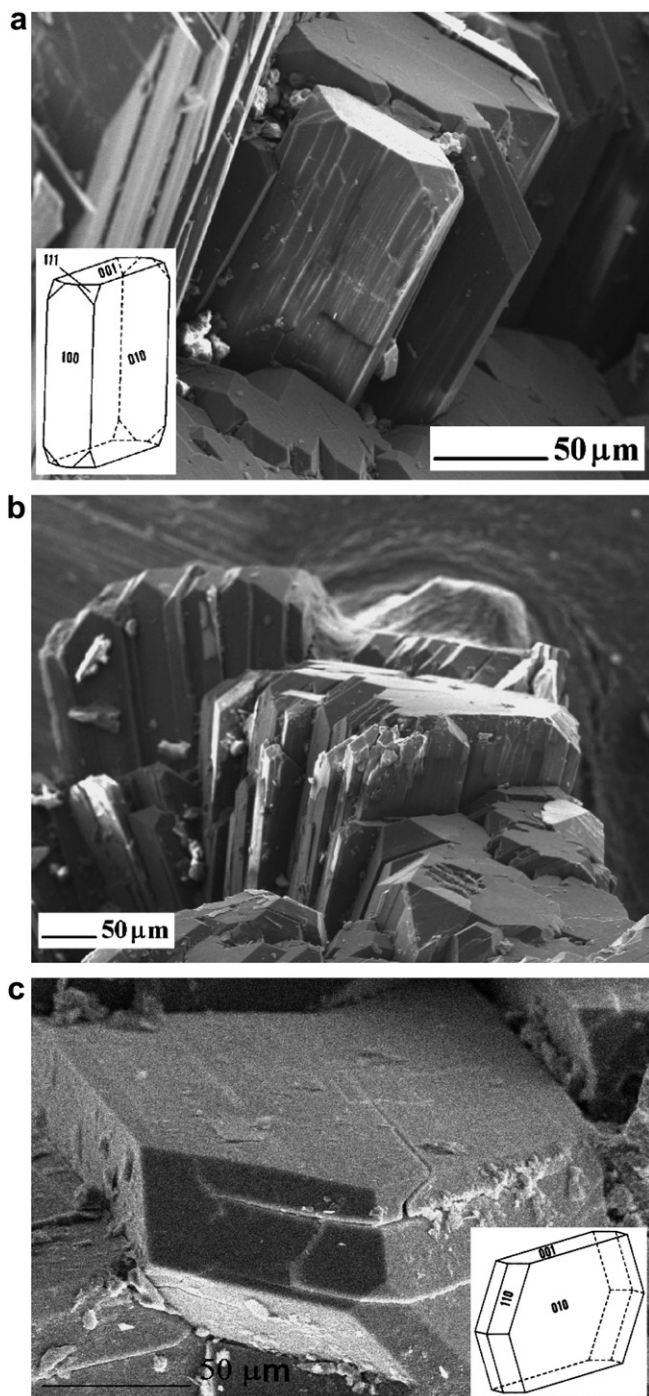
Fig. 3. SEM micrographs of some investigated specimen: (a) a cavity with stellerite crystals; (b) an aggregate with stellerite crystals; (c) one of the stilbite crystals which accompany stellerite in some zeolitized cavities.

the Cronstedt zeolite is actually stellerite with minor stilbite (estimated to be less than about 10% in volume).

The optical observations confirmed the outcome of the SEM investigation. Most of the crystals revealed to be stellerite because of the straight extinction and absence of twinning. Although experimentally difficult, a number of twinned crystals similar to those observed in [18] for monoclinic stilbite have also been observed under cross polarized

microscopy. Moreover, their extinction angle appeared to be slightly different from 90°.

The chemical formula on selected stellerite-like crystals derived from the EPMA and TG analyses with $(Si + Al) = 36$ was

$$(Ca_{4.03}Mg_{0.01}Na_{0.03}K_{0.11})[Si_{27.81}Al_{8.19}O_{72}] \cdot 28.6H_2O.$$
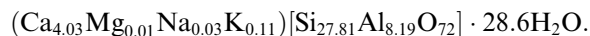
The H_2O content corresponds to the weight loss of the sample (see the TG analysis in Fig. 4). The reliability of the chemical formula is supported by the very low (-0.4%) charge balance error (E). The chemical composition is a clear indication that the crystal is actually stellerite and not stilbite although the literature reports other stilbite samples with chemical formula very similar to that of stellerite (see sample Nos. 17 and 54 in [19]).

The TG-DTG curves (Fig. 4) are typical dehydration curves of zeolite stilbite with two major loss peaks at 161 and 238 °C.

In the FTIR pattern (Fig. 5), the mode at about 1650 cm^{-1} is due to water bending, and the corresponding stretching modes are observed at about 3260, 3426, and
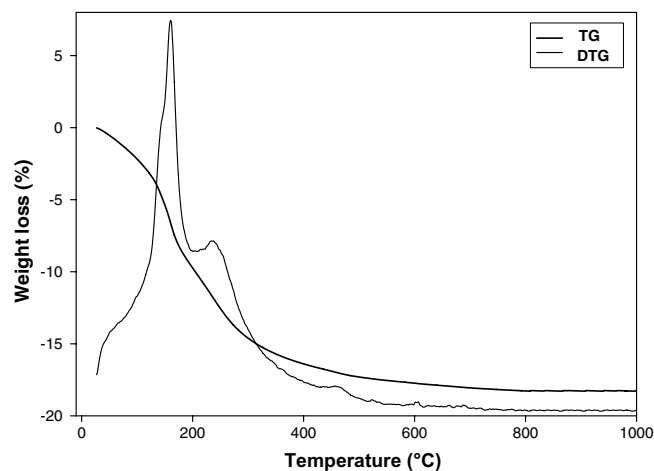

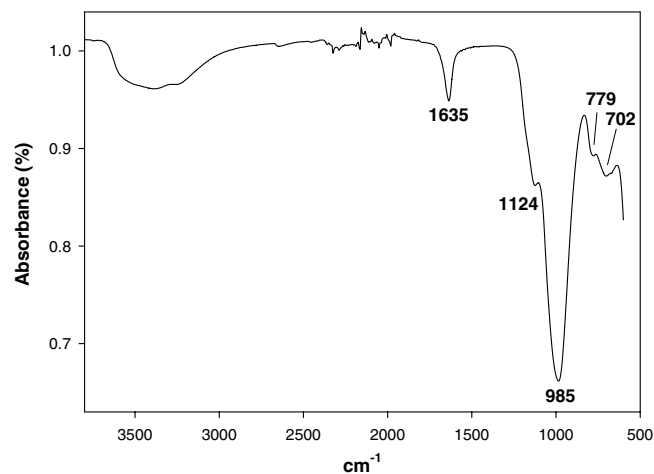Fig. 4. Results of the TG and DTG analysis of the investigated sample.

Fig. 5. Results of the FTIR analysis of the investigated stilbite sample.

Table 1
The agreement indices for the final least squares cycles of the refinements, the cell constants and volume

Total number of data points	3073
Total number of reflections	514
$R(F^2)$	0.1383
χ^2	1.538
R_{wp}	0.0278
R_p	0.0201
R_{wp} (background subtracted)	0.0488
R_p (background subtracted)	0.0318
a (Å)	13.5591(4)
b (Å)	18.1401(5)
c (Å)	17.7762(6)
V (Å^3)	4372.3(2)

3587 cm^{-1}. The pattern resembles that reported for stilbite at room temperature in [20–22]. The asymmetric stretching modes of the TO$_4$ framework are around 1030 cm^{-1} with a shoulder extending to 1145 cm^{-1}. The symmetric stretching and bending modes for TO$_4$ are observed at about 540 and 440 cm^{-1}.

Concerning the X-ray diffraction data and the structure refinement, the agreement indices for the final least squares cycles of the Rietveld refinement are reported in Table 1 together with the unit-cell parameters. Fig. 6 shows the observed (crosses) and calculated (continuous line) patterns, and difference curve (bottom line) of the refinement in the selected region 5–26°θ. Table 2 reports the refined structural data of the framework and extraframework
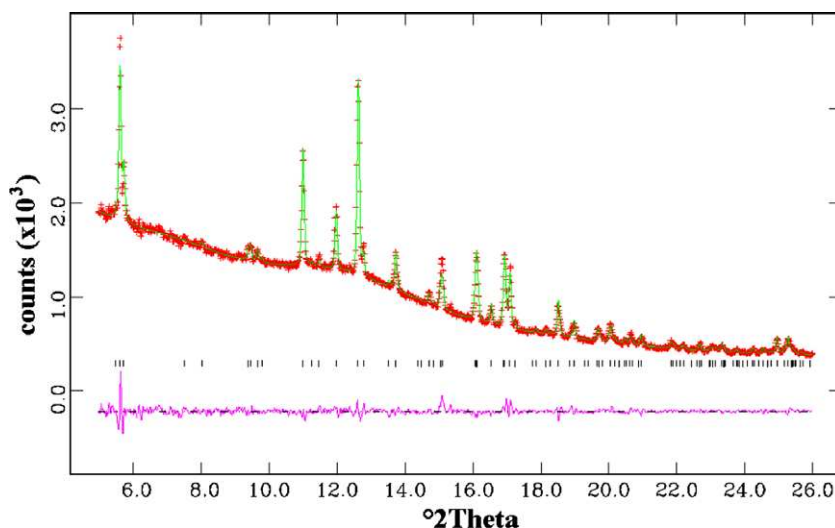

Fig. 6. The observed (crosses) and calculated (continuous line) patterns, and difference curve (bottom line) of the refinement of the stellerite sample in the selected region 5–26°2θ.

Table 2
Calculated atomic parameters of the investigated stellerite (SG: *Fmmm*)

Site	x/a	y/b	z/c	Atom type	Site symmetry	Site multiplicity	Site occupancy	U_{iso}
T1	0.3854(4)	0.3078(3)	0.3753(3)	Si	1	32	1	0.025(3)
T2	0.3036(6)	0.4118(4)	0.5	Si	m(001)	16	1	0.039(3)
T3	0.3889(5)	0.1818(4)	0.5	Si	m(001)	16	1	0.014(3)
T4	0.25	0.25	0.25	Si	222	8	1	0.034(3)
O1	0.3189(6)	0.3065(5)	0.2980(4)	O	1	32	1	0.049(3)
O2	0.3746(8)	0.2360(5)	0.4279(4)	O	1	32	1	0.028(4)
O3	0.3505(8)	0.3773(5)	0.4229(4)	O	1	32	1	0.018(4)
O4	0.5	0.3157(9)	0.3554(8)	O	m(100)	16	1	0.028(5)
O5	0.3145(7)	0.1111(6)	0.5	O	m(001)	16	1	0.012(6)
O6	0.327(2)	0.5	0.5	O	mm2(100)	8	1	0.052(6)
O7	0.5	0.1486(1)	0.5	O	mm2(010)	8	1	0.026(7)
Ca	0.5	0	0.2900(5)	Ca	mm2(001)	8	1	0.023(3)
W1	0.385(2)	0.0856(1)	0.3260(2)	O	1	32	0.21(1)	0.033(4)
W2	0.5	0.1250(9)	0.3068(1)	O	m(100)	16	0.80(2)	0.040(6)
W3	0.452(2)	0	0.4164(1)	O	m(010)	16	0.56(1)	0.035(6)
W4	0.370(8)	0	0.3651(7)	O	m(010)	16	0.24(1)	0.071(13)
W5	0.460(4)	0.5	0.3319(3)	O	m(010)	16	0.46(1)	0.072(3)
W6	0.389(2)	0.5	0.3162(2)	O	m(010)	16	0.51(1)	0.029(5)
W7	0.301(2)	0.057(2)	0.2759(2)	O	1	32	0.307(8)	0.046(2)

Table 3
Calculated atomic distances involving the framework and extraframework atoms (Å) and angles (°) involving the framework atoms of the investigated stellerite

T1–O1	1.643(9)
T1–O2	1.611(10)
T1–O3	1.590(10)
T1–O4	1.599(7)
Average	1.611
T2–O3	1.635(9)
T2–O3	1.635(9)
T2–O5	1.654(12)
T2–O6	1.632(9)
Average	1.639
T3–O2	1.627(9)
T3–O2	1.627(9)
T3–O5	1.631(12)
T3–O7	1.622(10)
Average	1.627
T4–O1	1.629(8)
T4–O1	1.629(8)
T4–O1	1.629(8)
T4–O1	1.629(8)
Average	1.629
T1–O1–T4	139.6(6)
T1–O2–T3	159.3(7)
T1–O3–T2	149.9(7)
T1–O4–T1	152.5(11)
T2–O5–T3	142.8(8)
T2–O6–T2	157.1(19)
T3–O7–T3	136.5(13)
Average	148.2
O1–T1–O2	115.0(6)
O1–T1–O3	107.0(6)
O1–T1–O4	110.5(7)
O2–T1–O3	107.8(5)
O2–T1–O4	106.8(8)
O3–T1–O4	109.6(8)
Average	109.45
O3–T2–O3	113.9(8)
O3–T2–O5	106.3(5)
O3–T2–O6	107.3(6)
O3–T2–O5	106.3(5)
O3–T2–O6	107.3(6)
O5–T2–O6	116.0(11)
Average	109.52
O2–T3–O2	104.0(7)
O2–T3–O5	113.6(5)
O2–T3–O7	109.6(6)
O2–T3–O5	113.6(5)
O2–T3–O7	109.6(6)
O5–T3–O7	106.5(8)
Average	109.48
O1–T4–O1	110.0(6)
O1–T4–O1	101.9(6)
O1–T4–O1	116.8(6)
O1–T4–O1	116.8(6)
O1–T4–O1	101.9(6)
O1–T4–O1	110.0(6)
Average	109.56
Ca–W1	2.289(26)
Ca–W1	2.289(26)
Ca–W1	2.289(26)

Table 3 (continued)

Ca–W1	2.289(26)
Ca–W2	2.287(16)
Ca–W2	2.287(16)
Ca–W3	2.337(24)
Ca–W3	2.337(24)
Ca–W4	2.21(12)
Ca–W4	2.21(12)
Ca–W5	2.24(5)
Ca–W5	2.24(5)
Ca–W6	2.417(32)
Ca–W6	2.417(32)
Ca–W7	2.907(29)
Ca–W7	2.907(29)
Ca–W7	2.907(29)
Ca–W7	2.907(29)
Average	2.431
W1–W2	1.745(29)*
W1–W4	1.71(6)*
W1–W7	1.54(4)*
W3–W3	1.29(6)*
W3–W4	1.44(12)*
W4–W7	2.12(12) × 2*
W5–W5	1.09(10)*
W5–W6	1.01(6)*
W5–W6	2.07(6)*
W7–W7	2.07(6)*
W7–W7	1.65(7)*

* Too close to be simultaneously occupied.

content of the sample. Table 3 reports the calculated atomic distances involving the framework and extraframework atoms and angles involving the framework atoms.

As anticipated, a tentative refinement using the structure of stilbite was also attempted. The structure refinements with the stilbite and stellerite models have been performed comparatively in a rigorous way using the same data set for both. The scale factor, the unit cell parameters, and the structure parameters were independently refined whereas the background, peak profile parameters were kept identical in the two refinements to rule out any possible correlation. Although the agreement factors of the refinement using the stilbite structure were close to those obtained with the stellerite structure ($R(F^2) = 0.1352$; $\chi^2 = 1.4647$; $R_{wp} = 0.0255$; $R_p = 0.019$), the preference goes to the stellerite structure because (i) the refinement of the key position of the K + Na extraframework site and/or its population invariably diverged and left severe doubts on its existence; (ii) the refined β angle is 90.137(5)°: this would be the first stilbite specimen with such a low deviation from 90° [19]. As a matter of fact, the specimens described in the literature with $\beta < 90.20°$ are all invariably classified as stellerite [19].

In Fig. 1 of Passaglia et al. [19], these authors have shown that orthorhombic stellerite generates just a minor peak (the 240 reflection) and a sharp major peak (the 204 reflection) in the 23–24.5°2θ region using copper radiation (the 13–14.5°2θ region using 0.888498 Å: Fig. 7) and classified that peak group of type "a". On the other hand, stilbite generates a minor peak (the 240 reflection) and a
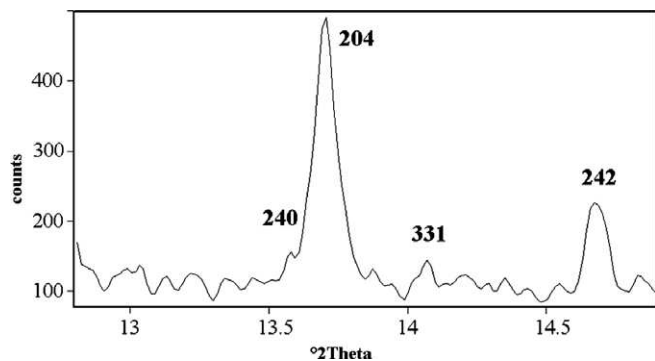
Fig. 7. The 13–14.5°2θ region of the synchrotron powder diffraction pattern (using 0.888498 Å) which is critical to assess whether the sample is stellerite and/or stilbite (see the text for details).

broadened peak (the convolution of the 204 and 20$\bar{4}$ reflections) in that region when the β angle is close to 90.30° (peak group of type ''b''). The pattern of our sample collected with a good peak resolution permitted by the synchrotron XRPD experiment (Fig. 7) in that region is very similar to the peak group of type ''a'' produced by stellerite specimens. This is another indication that the investigated sample is actually stellerite and not stilbite.

Fig. 8 displays the refined structure of stellerite, showing that it is composed of large intersecting relatively open channels of 10- and 8-member rings. The 10-member rings channels are parallel to the a axis. The two types of 8-membered rings are parallel to the ab-plane and alternate in the a direction.

Although no evidence of ordering in the tetrahedral sites was found, the larger average T–O distance may indicate that Al has a slight preference for the T2 site (see Table 3). On the other hand, Galli and Alberti [11] speculated that Al could be located in tetrahedron Si(5) (T4 in this work) because of the presence of Ca near to that site. With this assumption, in our refinement, the cation closest connection to the tetrahedral cation (Ca–T1 = 4.81 Å) should

indicate that Al is located in T1. Unfortunately, this seems to be unlikely because T1–O average distance is only 1.611 Å, the shortest average T–O distance.

Ca is located in the centre of the main channel parallel to the a axis, on the mirror plane and is totally surrounded by water molecules with no contact with framework oxygen atoms (extraframework cation site of type IV [23]). The number of calculated water molecules from the structure refinement well matches that from the TG analysis: 28.88 vs. 28.6. With respect to monoclinic stilbite, in stellerite there are no Na atoms either over or under T4 and the Ca atoms remain on the mirror planes with no deviation from the orthorhombic symmetry. In agreement with [11], the Ca coordination should be 6-fold (a distorted octahedron). A number of short water–water distances are explained by considering the different possible schemes around the Ca atom. Considering that W7 with a low site population is rather distant (Ca–W7 = 2.907(29) Å), the short water–water distances, and the partial occupancy of water sites, many different octahedral coordinations around Ca are possible. For example, if we consider the two W2 to be occupied and W1 vacant, the following octahedral coordinations are found: (i) W2 × 2, W3, W4, W5, and W6; (ii) W2 × 2, W4 × 2, W5, W6; (iii) W2 × 2, W3, W4, W6 × 2; (iv) W2 × 2, W4 × 2, W6 × 2. When W6 is empty, 5-fold coordination is also possible.

The Ca coordination number observed in stellerite is smaller than that observed for stilbite [10] where Ca has a 9-fold coordination with water molecules. For three stilbites samples, Quartieri and Vezzalini also found nine water sites at the coordination distance from the Ca site (five water sites on the mirror plane with Ca, the others lie almost on a plane normal to the mirror plane and parallel to the large channel axis) [24]. For the other two stilbite samples, they found eleven water molecule sites (five water sites on the mirror plane with Ca and six almost on a plane normal to the mirror plane). On the other hand, Slaughter and Galli found a smaller coordination number:
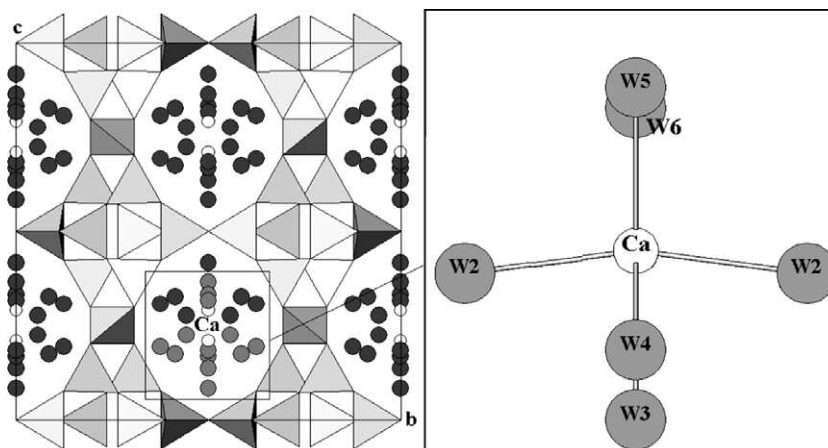

Fig. 8. The refined structure of Cronstedt's stellerite along the a-axis and the most statistically represented coordination environment of the Ca extraframework cation.

8-fold coordination with a mean cation-anion distance of about 2.47 Å [8,9].

4. Conclusions

This paper is devoted to the identification and structural characterization of the first zeolite studied by Cronstedt. It provides evidence that the first zeolite studied by Cronstedt was actually a mixture of stellerite with minor (less than 10% volume) stilbite from the Kiruna area, Northern Sweden. The re-discovery of the Cronstedt zeolite has an undoubted valence of historical character, as this event is the first step of a long and exciting story involving the discovery and study of natural zeolites that still continues today.

Especially the SEM pictures taken on all the available rock specimens containing cavities filled with zeolite crystals showed that most of the crystal aggregates display the typical stellerite crystal habit with lamellar crystals terminated with the {100}, {001}, and {111} faces. Only a few cavities also contained twinned stilbite crystals. These observations supported by the optical microscopy investigation indicated that the Cronstedt zeolite crystals are actually stellerite with minor stilbite. The results of the structure refinement confirm that the investigated specimen is stellerite. No clear evidence of ordering in the tetrahedral sites was found. The only extraframework cation (Ca) is located in the center of the main channel parallel to the a axis, on the mirror plane and is surrounded by water molecules only with no contact with framework oxygen atoms.

References

[1] A.F. Cronstedt, Kongl Vetenskaps Academiens Handlingar Stockholm, 17, 1756, p. 120.
[2] A.F. Cronstedt, Försök till Mineralogie eller Mineral-Rikets Upställning, Wildiska, Stockholm, 1758, p. 99.
[3] G. Sumelius, in: M.L. Occelli, H.E. Robson (Eds.), Synthesis of Microporous Materials, vol. 1, Molecular Sieves, van Norstrand Reinhold, New York, 1992, p. 1.
[4] L. Schlenker, G.H. Kühl, in: R. von Ballmoos, J.B. Higgins, M.M.J. Treacy (Eds.), Proceedings 9th International Zeolite Conference, Butterworth-Heinemann, Boston, 1993, p. 3.
[5] D.W. Breck, Zeolite Molecular Sieves: Structure, Chemistry, and Use, John Wiley & Sons, New York, 1974, p. 10.
[6] H. Kristmanndóttir, J. Tómasson, in: L.B. Sand, F.A. Mumpton (Eds.), Natural Zeolites. Occurrence, Properties, Use, Pergamon Press, Elmsford, U.S.A., 1978, p. 277.
[7] R. Frietsch, Berggrund och Malmer I Svappavaarafältet, Norra Sverige, Sveriges Geologiska Undersökning (1966) 282.
[8] E. Galli, Acta Crystallogr. B 27 (1971) 833.
[9] M. Slaughter, Am. Mineral. 55 (1970) 387.
[10] G. Cruciani, G. Artioli, A.F. Gualtieri, K. Ståhl, J.C. Hanson, Am. Mineral. 82 (1997) 729.
[11] E. Galli, A. Alberti, Bull. Soc. Fr. Mineral. Cr. 98 (1975) 11.
[12] E. Galli, A. Alberti, Bull. Soc. Fr. Mineral. Cr. 98 (1975) 331.
[13] J.J. Donovan, Advanced Microbeam, 4217C Kings Graves Road, Vienna, Ohio, 44473, 1995.
[14] C. Meneghini, G. Artioli, A. Balerna, A.F. Gualtieri, P. Norby, S. Mobilio, J. Synchrotron Rad. 8 (2001) 1162.
[15] A.P. Hammersley, S.O. Svensson, M. Hanfland, A.N. Fitch, D. Häusermann, High Pressure Res. 14 (1996) 235.
[16] A.C. Larson, R.B. Von Dreele, Generalized Structure Analysis System, Los Alamos, New Mexico, LA-UR-86-748, 2000, p. 179.
[17] B.H. Toby, J. Appl. Cryst. 34 (2001) 210.
[18] M. Akizuki, H. Konno, Am. Mineral 70 (1985) 814.
[19] E. Passaglia, E. Galli, L. Leoni, G. Rossi, Bull. Minéral. 101 (1978) 368.
[20] P.S.R. Prasad, K. Shiva Prasad, S. Ramana Murthy, Am. Mineral. 90 (2005) 1636.
[21] V. Crupi, D. Majolino, R. Migliardo, V. Venuti, U. Wanderlingh, Eur. Phys. J. 12E (2003) 55.
[22] J. Li, J. Qiu, Y. Sun, Y. Long, Micropor. Mesopor. Mater. 37 (2000) 365.
[23] G. Gottardi, E. Galli, Natural Zeolites, Springer, Verlag, 1985, p. 409.
[24] S. Quartieri, G. Vezzalini, Zeolites 7 (1987) 163.