

REVIEW

Cancrinite-group minerals: Crystal-chemical description and properties under non-ambient conditions—A review

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ABSTRACT



This is a review of the thermal and compressional behavior of cancrinite-group minerals with a description of the mechanisms, at the atomic scale, that govern their *P-T*-induced structure evolution. The open-framework structure of this group of feldspathoids is characterized by the [CAN] topology, which contains large parallel channels (confined by 12-membered rings of tetrahedra), surrounded by columns of cages. At least two structural “subgroups” can be identified according to the nature of the constituents filling the cages, irrespective of the channel population. The minerals of the “cancrinite subgroup” show $[\text{NaH}_2\text{O}]^+$ clusters into the cages and those of the “davynite subgroup” contains $[\text{CaCl}]^+$ clusters. Beside a similar bulk compressibility and expansivity at room conditions for all the minerals of the group, a different elastic anisotropy, coupled with different deformation mechanisms of the tetrahedral framework, were found to be mainly controlled by the nature of the population filling the cages. The role played by the channel populations appears to be secondary. These experimental findings allow us to provide a model of the structure evolution in response to the different cage content, i.e., NaH_2O^+ and CaCl^+ .

The high-temperature studies of the hydrous members of the cancrinite subgroup reveal a slow dehydration process, often irreversible at the timescale of the experiments and leading to quasi-anhydrous high-temperature forms that keep their crystallinity even up to 800–900 K (at room *P*). The experiments at high pressure on the cancrinite-group minerals show a high-*P* stability, at least up to 7–8 GPa (at room-*T*), which is quite surprising if we consider their microporous nature. The *P*-induced stability is the effect of a pronounced structural flexibility, which in turn is based mainly on tilting of rigid tetrahedra around O atoms that behave as hinges. The character and the mechanisms that govern the *P-T*-induced *P*6₃-to-*P*6₃/*m* phase transition in the compounds of davynite subgroup are also discussed.

Keywords: Feldspathoids, cancrinite, davynite, vishnevite, balliranoite, temperature, pressure, elastic behavior, host-guest interactions, framework deformation, Invited Centennial article, Review article

INTRODUCTION

Feldspathoids are a loosely defined class of minerals with a structure characterized by a three-dimensional framework of linked SiO_4 and AlO_4 (more rarely PO_4 or BeO_4) tetrahedra. This framework contains open cavities (in the form of channels and cages), usually occupied by cations (mainly Na^+ , K^+ , Ca^{2+}), anions (mainly CO_3^{2-} , SO_4^{2-} , Cl^-), and molecules (mainly H_2O). Compared with feldspars, the aluminosilicate feldspathoids are deficient in SiO_2 . They occur in a wide variety of geological environments and conditions, from sedimentary to alkali-rich SiO_2 -poor igneous rocks or metamorphic and metasomatic rocks, from crustal to upper mantle conditions. Some feldspathoids have been found in meteorites (e.g., in carbonaceous chondrites, Grossman 1980).

This class of minerals is the major host of C, S, or Cl structurally incorporated in silicates. The structural diversity of feldspathoids is reflected by their complex systematics with at least

three different principal families: analcime-leucite (e.g., Gatta et al. 2006, 2008a), nepheline-kalsilite (e.g., Gatta and Angel 2007; Gatta et al. 2010, 2011), and cancrinite-sodalite (e.g., Gatta et al. 2012a; Lotti et al. 2012; Löns and Schulz 1967). Minerals of the melilite family (i.e., melilite *sensu stricto*, gehlenite, and akermanite) are also considered as feldspathoids (Edgar 1984). A comprehensive overview on the structures of feldspathoids is reported in Merlino (1984).

When compared to other silicates, only a modest number of experiments have been devoted to cancrinite-group minerals at high pressure or high temperature. Some *in situ* experiments at high temperature on the most important member of the group (i.e., cancrinite *sensu stricto*) actually provided conflicting results (Hassan 1996a, 1996b; Sirbescu and Jenkins 1999; Hassan et al. 2006; Isupova et al. 2010; Gatta et al. 2014). A full characterization of the phase stability fields of cancrinite-group minerals and of the reactions at the field boundaries is still missing or limited to restricted experimental conditions (e.g., Sirbescu and Jenkins 1999 and references therein). To overcome this deficiency, we

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have recently conducted a series of in situ experiments on the behavior of cancrinite-group minerals at non-ambient conditions (i.e., high pressure, low and high temperature), as part of a wider research project on microporous materials at extreme conditions (e.g., Gatta et al. 2012a, 2013a, 2013b, 2014; Lotti et al. 2012, 2014a, 2014b; Lotti 2014).

The aim of this manuscript is a synthesis of previously published data on the behavior of cancrinite-group minerals at non-ambient conditions, to provide a model of their thermo-elastic behavior and of the main deformation mechanisms, at the atomic scale, in response to the applied temperature (T) and pressure (P). In particular, the role played by the different extraframework constituents is reviewed and discussed.

CRYSTAL CHEMISTRY OF CANCRINITE-GROUP MINERALS

Minerals of the cancrinite group share the tetrahedral [CAN] framework-type, built by the stacking of layers made by unconnected single six-membered rings of tetrahedra (hereafter S6Rs) occupying A or B positions, respectively, according to an $\cdots AB(A) \cdots$ sequence (Gies et al. 1999; Baerlocher et al. 2007). Each S6R is connected to three rings in adjacent layers, giving rise to the three-dimensional framework (Fig. 1, see also http://www.iza-structure.org/databases/Catalog/ABC_6.pdf). The [CAN] framework contains columns of base-sharing cages (i.e., *can* units or cancrinite cages), where the bases correspond to the single six-membered rings perpendicular to the c -axis (S6R $\perp$ [0001], Fig.

1). These columns surround parallel channels to [0001] and are confined by 12-membered rings of tetrahedra (12R) (Fig. 1). The framework can also be described as made of double *zigzag* chains of tetrahedra (*dzc* units, Smith 2000), made by edge-sharing four-membered rings (S4R), running along the c -axis, which border 6R-windows $\angle$ [0001] linking cages and channels (Fig. 1). The topological symmetry of the [CAN] framework is $P6_3/mmc$ (Baerlocher et al. 2007). Overall, materials with [CAN] framework type are considered as “microporous materials” (sensu Rouquerol et al. 1994), having cavities with free diameters shorter than 2 nm.

Twelve mineralogical species sharing the [CAN] topology have so far been reported (Bonaccorsi and Merlino 2005; Pekov et al. 2011a) (Table 1) and 11 of them show an aluminosilicate framework; the only exception is tiptopite, with a P/Be-framework (Table 1; Peacor et al. 1987). In cancrinite-group minerals, the Si/Al-distribution of the $(Al_6Si_6O_{24})^{6-}$ -framework is fully ordered, with a lowering of the symmetry from $P6_3/mmc$ to $P6_3$ (or $P6_3/m$), with only rare exceptions (Rastsvetaeva et al. 2007; Ogorodova et al. 2009). In this group of minerals, the extraframework population can be subdivided according to the structural voids, namely: (1) the *can* cages and (2) the 12R-channels. Only two mutually exclusive configurations of the cage constituents are shown by the aluminosilicate cancrinite-group minerals: the first is given by the repetition of $[Na \cdot H_2O]^+$ clusters, so that chains along the columns of *can* units arise, and, similarly, the second configuration is represented by chains of $[Ca \cdot Cl]^+$ clusters (Fig. 2). In contrast, a complex chemical variability is shown by the

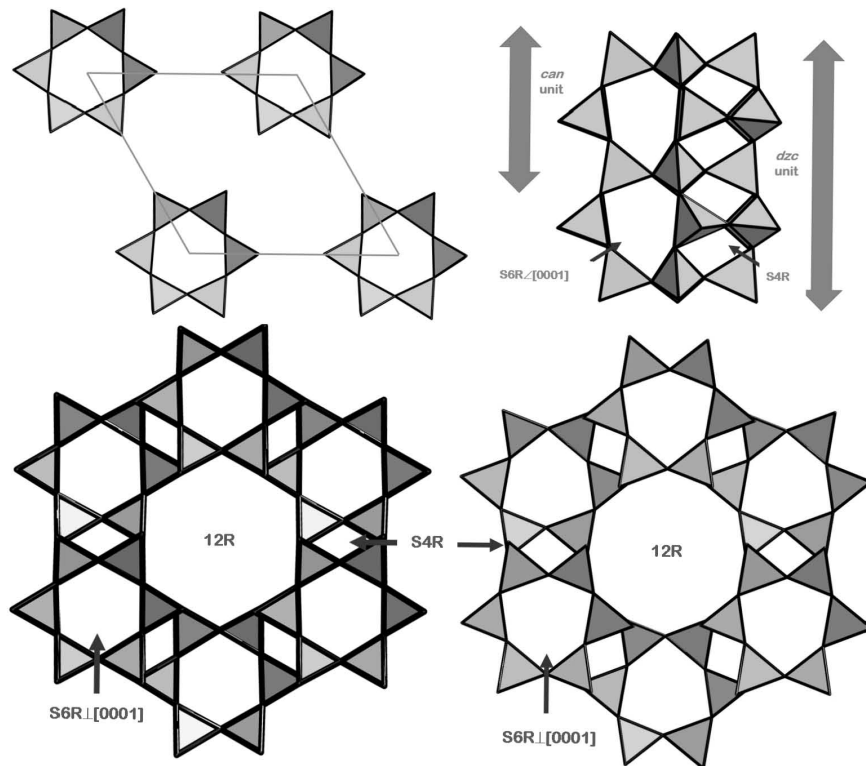


FIGURE 1. (top left) The hexagonal array of single six-membered rings of tetrahedra in the plane perpendicular to the c -axis (S6R $\perp$ [0001]). (top right) A portion of a column of *can* units. Two base-sharing cages are shown, along with a portion of a *dzc* chain. (bottom left) The [CAN] framework viewed down [0001] of davynite and (bottom right) cancrinite. The S6R $\perp$ [0001] cage-bases, the large 12R-channel and the S4R-units are shown.

12R-channel population, made by cations, anions, and molecular components, though a general scheme can be extrapolated. Na^+ is always the prevailing cation, it can be partially replaced by Ca^{2+} and K^+ in one or two crystallographic sites close to the channel walls (Fig. 3); a more complex positional disorder was also reported (e.g., Gatta et al. 2013a). Nevertheless, a similar bonding environment of cations can be described, with 4–5 bonds to the framework oxygen atoms on the wall-side and a variable coordination with the anionic groups or molecules on the other side. Anions and molecules occupy the center of the channel (Fig. 3), often in mutually exclusive split positions, so that several possible configurations can occur within the same channel. These

configurations can be ordered, leading to superstructures (see next section). The most common anionic and molecular species in cancrinite-group minerals are: CO_3^{2-} , SO_4^{2-} , Cl^- , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} , OH^- , and H_2O . The most abundant anion is conventionally used as “species-defining criterion” (Bonaccorsi and Merlino 2005; Pekov et al. 2011a).

For a comparative and comprehensive analysis of the HP-HT crystal-chemistry of this mineral group, two “subgroups” can be defined: the “cancrinite subgroup,” showing chains of $[\text{Na-H}_2\text{O}]^+$ clusters, and the “davyne subgroup,” with $[\text{Ca-Cl}]^+$ chains (Fig. 2). In the next sections we describe the crystallochemical features and the occurrences of these isotypic minerals.

TABLE 1. Cancrinite-group minerals

	Chemical formula	Z	Unit-cell constants (<i>a</i> , <i>c</i> ; Å)	Space group	Ref.
Cancrinite subgroup					
cancrinite	$[(\text{Na},\text{Ca})_6(\text{CO}_3)_{1.4-1.7}][\text{Na}_2(\text{H}_2\text{O})_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$	1	12.615, 5.127	$P6_3$	a
vishnevite	$[(\text{Na},\text{K})_6(\text{SO}_4)][\text{Na}_2(\text{H}_2\text{O})_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$	1	12.685, 5.179	$P6_3$	a, b
hydroxycancrinite	$[\text{Na}_6(\text{OH})_2][\text{Na}_2(\text{H}_2\text{O})_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$	1	12.740, 5.182	$P3$	a
cancrillite	$\text{Na}_7\text{Al}_5\text{Si}_7\text{O}_{24}(\text{CO}_3) \cdot 3\text{H}_2\text{O}$	1	12.575, 5.105	$P6_3/mc$	a
pitiglianoite	$[(\text{Na},\text{K})_6(\text{SO}_4)][\text{Na}_2(\text{H}_2\text{O})_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$	3	22.121, 5.221	$P6_3$	a
kyanoxalite	$[\text{Na}_5(\text{C}_2\text{O}_4)_{0.5-1}(\text{H}_2\text{O})_{2-3}][\text{NaH}_2\text{O}][\text{Si}_{6-7}\text{Al}_{5-6}\text{O}_{24}]$	1	12.74, 5.21	$P6_3$	c
depmeierite	$[\text{Na}_6(\text{PO}_4)_{0.67}\text{H}_2\text{O}][\text{NaH}_2\text{O}][\text{Si}_6\text{Al}_6\text{O}_{24}]$	1	12.73, 5.18	$P6_3$	c
Davyne subgroup					
davyne	$[(\text{Na},\text{K})_6(\text{SO}_4\text{Cl})][\text{Ca}_2\text{Cl}_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$	1	12.705, 5.368	$P6_3/m$ or $P6_3$	a, d
balliranoite	$[(\text{Na},\text{Ca})_6(\text{CO}_3)_{1.4-1.7}][\text{CaCl}_2][\text{Al}_6\text{Si}_6\text{O}_{24}]$	1	12.695, 5.325	$P6_3$	a, e
microsommitte	$[\text{Na}_4\text{K}_2(\text{SO}_4)][\text{Ca}_2\text{Cl}_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$	3	22.142, 5.345	$P6_3$	a
quadridavyne	$[(\text{Na},\text{K})_6\text{Cl}_2][\text{Ca}_2\text{Cl}_2][\text{Si}_6\text{Al}_6\text{O}_{24}]$	4	25.771, 5.371	$P6_3/m$	a
tiptopite	$[(\text{Li}_{2.9}\text{Na}_{1.7}\text{Ca}_{0.7})(\text{OH})_2(\text{H}_2\text{O})_{1.3}][\text{K}_2][\text{Be}_6\text{P}_6\text{O}_{24}]$	1	11.655, 4.692	$P6_3$	f

Notes: Chemical formulas based on 12 tetrahedral cations. References: a = Bonaccorsi and Merlino (2005); b = Della Ventura et al. (2007); c = Pekov et al. (2011a); d = Lotti et al. (2014a); e = Lotti et al. (2014b); f = Peacor et al. (1987).

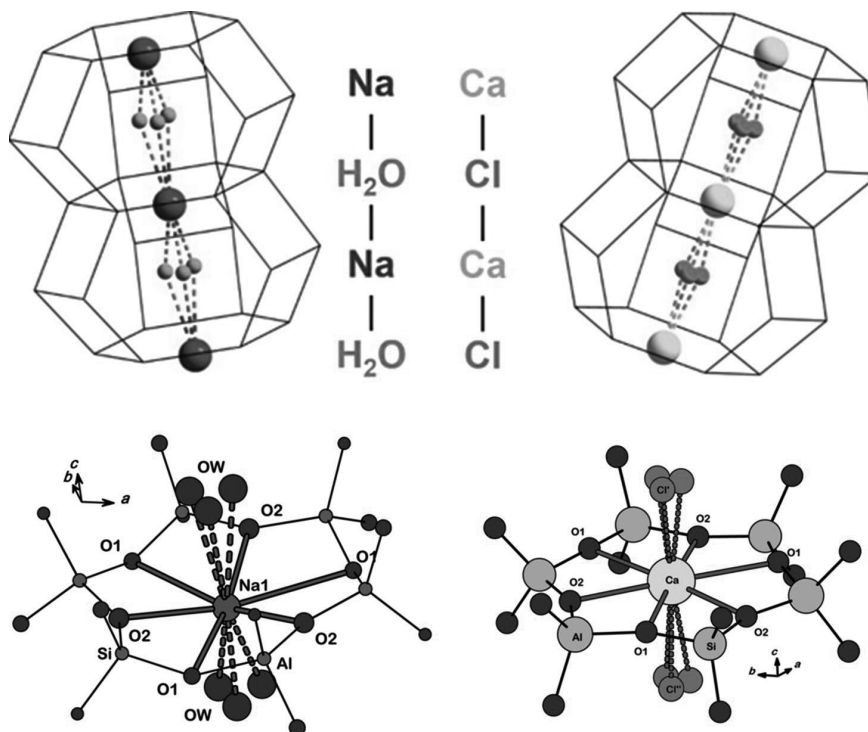


FIGURE 2. (top) Schematic view of the Na-H₂O and Ca-Cl chains in the columns of *can* units of cancrinite- and davyne-subgroup minerals, respectively. (bottom) Cage-Na⁺ (left) and cage-Ca²⁺ (right) coordination environments in cancrinite and davyne, respectively. Dashed lines represent mutually exclusive bonds.

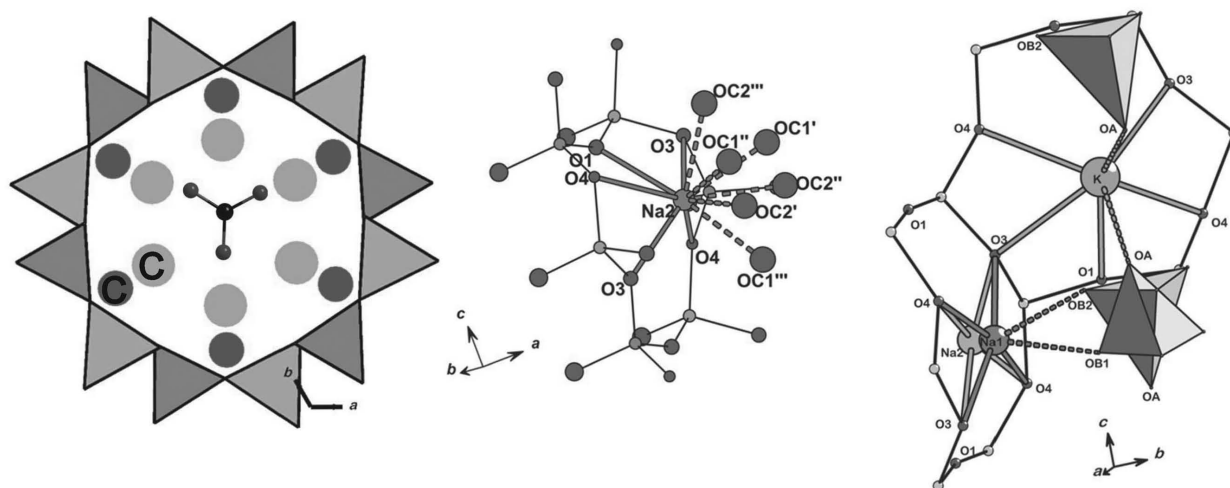


FIGURE 3. (left) Schematic view (down the *c*-axis) of the extraframework population in the channels of cancrinite-group minerals, showing the cationic sites (C), close to the channel walls, and the anions/molecules positions, at the center of the channel. (middle) Coordination shell of the (Na⁺, Ca²⁺) cations in the channels of cancrinite and balliranoite. (right) The two possible and mutually exclusive configurations of the channel population in vishnevite and davyne: the SO₄²⁻ group can coexist with an “external” Na site at the same *z* coordinate, but it is mutually exclusive with the “internal” K site. If the maximum content of one SO₄²⁻ per formula unit is reached, the channel must be internally ordered. The potential upward and downward configurations of the SO₄²⁻ tetrahedra are shown. Dashed lines represent mutually exclusive bonds.

The “cancrinite subgroup”

In the structural cages of this subgroup, the Na⁺ site is slightly displaced from the $S6R \perp [0001]$ -plane, with a stronger bond to one of the neighboring H₂O-oxygen sites, positioned out of the threefold axis approximately at the cage center (Fig. 2). Therefore, each H₂O molecule shows a shorter bond to one Na⁺ cation and a longer one to the other Na-neighbor, which, in turn, is strongly bonded to the next H₂O molecule (Fig. 2). Similarly, Na⁺ shows shorter bonds to the three O2 oxygen sites than those to the three O1 sites. As a consequence, a significant deviation from the hexagonal shape is shown by the $S6R \perp [0001]$ (Fig. 1). The Na⁺ coordination environment can, therefore, be described by a first tetrahedral shell (3·O2 + Ow') along with a second larger tetrahedral one (3·O1 + Ow''), giving rise to a distorted ditrigonal bipyramid (C.N. = 4 + 4).

Cancrinite sensu stricto [(Na,Ca)₆(CO₃)_{1.4–1.7}][NaH₂O]₂[Al₆Si₆O₂₄] (Table 1; Bonaccorsi and Merlino 2005) is, by far, the most widespread mineral of the group. Its crystal structure was first solved by Pauling (1930), and then refined by Jarchow (1965). Cancrinite contains CO₃²⁻ as main anionic component in the channel voids. The CO₃²⁻ groups occupy the center of the channel in two mutually exclusive and iso-oriented configurations, for which the neighboring cations face an edge of the triangular anionic group, giving rise to two bonds to the closer oxygen atoms (Fig. 3). Due to the resulting short C–C contacts, not all the sub-cells can be occupied by the carbonate anions, with positional order/disorder leading also to superstructures (e.g., Foit et al. 1973; Grundy and Hassan 1982; Hassan and Buseck 1992).

Vishnevite [(Na,K)₆(SO₄)] [NaH₂O]₂[Al₆Si₆O₂₄] (Table 1; Hassan and Grundy 1984; Della Ventura et al. 2007) is the (SO₄²⁻)-dominant end-member. Two distinct configurations can be defined for the channel population. The first, with

[Na₃(SO₄)⁺ clusters, is given by the Na⁺ cations and sulfate tetrahedral groups at the center of the channel, for which the triangular basis is generally found to point a vertex toward the neighboring Na⁺ atoms, so that a single Na–O_{SO4} bond occurs (Fig. 3). The second, with only Na and K sites bonded to the framework O atoms, is commonly associated to vacancies at the anionic sites (at the channel center), to avoid too short K–O bonds (Fig. 3). A channel can be internally ordered. If there is an ordered distribution of these configurations among adjacent channels, a superstructure with a new unit cell *a*-parameter, equal to $\sqrt{3}a_{\text{vish}}$, arises. This gives rise to a new mineralogical species called pitiglianoite (Table 1; Merlino et al. 1991; Della Ventura et al. 2005; Bonaccorsi et al. 2007), which shares with vishnevite a common *c*-parameter.

Hydroxycancrinite (or “basic cancrinite”) is the (OH)-dominant end-member of the cancrinite subgroup (Table 1) and is often reported as a synthetic product. In Nature, it is rare and usually represented by intermediate members of the cancrinite-hydroxycancrinite series in the peralkaline plutons of the Kola peninsula, Russia (Pekov et al. 2011a). Kyanoxalite is the C₂O₄²⁻-member (Table 1). It is very rare in Nature; minerals of the cancrinite-kyanoxalite series have, up to now, been found only at the Lovozero alkaline pluton, Kola peninsula, Russia (Chukanov et al. 2010a; Olysysh et al. 2011; Pekov et al. 2011a). Depmeierite is the PO₄³⁻-dominant member of the cancrinite subgroup (Table 1) and has been reported only from Mt. Karnasurt, Kola peninsula, Russia (Pekov et al. 2011b).

Cancrisilite is the only member of the cancrinite group of minerals showing the framework enriched in Si⁴⁺, with an ideal Si⁴⁺:Al³⁺ ratio of 7:5 (Table 1). This leads to a disordered Si/Al-distribution in the tetrahedral framework, with an increase in symmetry from *P6₃* to *P6₃mc* (Ogorodova et al. 2009).

The “davynite subgroup”

The davynite-subgroup minerals contain chains of alternating $[\text{Ca-Cl}]^+$ clusters. The Ca^{2+} site lies close to the $\text{S6R}\perp[0001]$ “plane” (i.e., the cage basis) and is bonded to the three O2 and the three O1 atoms, showing similar bond lengths (Fig. 2). Therefore, only a small deviation from the perfect hexagonal shape of the $\text{S6R}\perp[0001]$ is observed in davynite-subgroup minerals (Fig. 1). The Cl^- anion is placed approximately at the center of the cage in three mutually exclusive positions out of the threefold axis (Fig. 2). Each Ca^{2+} cation is bonded to the two neighboring Cl^- , giving rise to a slightly distorted hexagonal bipyramidal coordination shell (C.N. = 8).

Davynite $[(\text{Na},\text{K})_6(\text{SO}_4,\text{Cl})][\text{CaCl}]_2[\text{Al}_6\text{Si}_6\text{O}_{24}]$ (Table 1; Hassan and Grundy 1990; Bonaccorsi et al. 1990; Gatta et al. 2013a; Lotti et al. 2014a) and balliranoite $[(\text{Na},\text{Ca})_6(\text{CO}_3)_{1.4-1.7}][\text{CaCl}]_2[\text{Al}_6\text{Si}_6\text{O}_{24}]$ (Table 1; Chukanov et al. 2010b; Gatta et al. 2013b; Lotti et al. 2014b) are the $(\text{SO}_4^{2-},\text{Cl}^-)$ - and CO_3^{2-} -end-members, respectively, and show a channel configuration analogous to that of vishnevite (for davynite) and cancrinite (for balliranoite) (Fig. 3). In microsommite (Table 1; Bonaccorsi et al. 2001), the ordered distribution along the channel of SO_4^{2-} groups and vacancies at the anionic sites (at the channel center) leads to a superstructure similar to that shown by pitiglianoite ($\mathbf{a}_{\text{MIC}} = \sqrt{3} \cdot \mathbf{a}_{\text{DAV}}$, $\mathbf{c}_{\text{MIC}} = \mathbf{c}_{\text{DAV}}$), whereas in the pure Cl^- -end-member, quadridavynite (Table 1; Bonaccorsi et al. 1994), a different kind of superstructure occurs, with $\mathbf{a}_{\text{QUA}} = 2 \cdot \mathbf{a}_{\text{DAV}}$ and $\mathbf{c}_{\text{QUA}} = \mathbf{c}_{\text{DAV}}$.

Natural occurrence of cancrinite-group minerals

Cancrinite-group minerals are typical of silica-undersaturated rocks and rich in alkalis, particularly Na. They are commonly related to alkaline magmatism (Deer et al. 2004). Cancrinite-group minerals are widespread both in intrusive igneous rocks, such as nepheline syenites, and in extrusive rocks, such as phonolites. In addition, they can be found in metasomatic environments related to alkaline magmas and/or limestone wallrocks.

Pekov et al. (2011a) suggested the distinction between cancrinite and davynite subgroups to have also a genetic relevance, being the minerals of the first subgroup most commonly found in intrusive environments and those of the second subgroup in effusive and metasomatic settings. Cancrinite-subgroup minerals are widespread in intrusive alkaline magmatic complexes, where they can crystallize: (1) as primary phases during the late-magmatic stage, typical of vein- and dike-intrusions or pegmatites (e.g., Erd and Czamanske 1983; Deer et al. 2004), or (2) as secondary phases from hydrothermal alteration of pre-existing minerals (e.g., Bell et al. 1996; Sindern and Kramm 2000; Fall et al. 2007).

The davynite-subgroup minerals can be typically found in effusive and metasomatic environments, especially in lithic blocks within pyroclastic, tephritic, and pumice deposits. They generally occur in cavities of skarn-like rocks, likely formed as thermal metamorphic and metasomatic products, around the magmatic chamber walls (e.g., Deer et al. 2004; Fulignati et al. 2005; Sapozhnikov 2010; Harlow and Bender 2013).

DESCRIPTION OF THE COMPRESSIONAL AND EXPANSION BEHAVIOR: THE EQUATIONS OF STATE

For a comparative analysis of the elastic behavior of cancrinite-group minerals, their volume compressibility and expansivity parameters are here determined by fitting the experimental unit-cell data to P - V and T - V equations of state. The isothermal Birch-Murnaghan equation of state (BM-EoS) was adopted for the high-pressure data. The BM-EoS is based on the assumption that the strain energy in a solid can be described as a Taylor series in the Eulerian finite strain,

$$f_e = [(V_0/V)^{2/3} - 1]/2 \quad (\text{Birch 1947; Angel 2000}).$$

In the HP-studies of cancrinite-group minerals (Lotti et al. 2012, 2014a, 2014b; Lotti 2014), the polynomial truncated to third order in energy (III-BM EoS) was used, with the following form:

$$P = 3K_0 f_e (1 + 2f_e)^{5/2} [1 + 3/2(K' - 4)f_e],$$

where K_0 is the isothermal bulk modulus, i.e., the inverse of the volume compressibility:

$$K_0 = 1/\beta_V = -V \cdot (\partial P / \partial V),$$

and K' is its pressure-derivative (i.e., $K' = \partial K_0 / \partial P$). When a BM-EoS is truncated to second order in energy, $K' = 4$ is implied. “Linearized” BM-equations of state, for which the cube of a linear parameter (e.g., unit-cell edge) replaces the volume, were adopted to fit the experimental P - V data and, therefore, to describe the anisotropy of the elastic behavior. The obtained “linear- K_0 ” (Angel 2000) is one third of the inverse of the linear volume compressibility: $K_{l0} = 1/3\beta_l$.

The elastic behavior in the low- T range (ca. 110–293 K) was described by Gatta et al. (2012a, 2013a, 2013b) fitting the experimental data with an equation directly derived from the thermodynamic definition of the thermal expansion coefficient:

$$\alpha_V = V^{-1}(\partial V / \partial T), \quad V(T) = V_0 e^{[\alpha_V(T-T_0)]},$$

assuming a constant α_V value due to the low number of the experimental data. The high-temperature elastic behavior of cancrinite was described by Gatta et al. (2014) with a modified second-order polynomial equation proposed by Berman (1988) and implemented in the EOSFIT7 software (Angel et al. 2014):

$$V(T) = V_0 [1 + a_0(T - T_0) - 2(10a_0 + a_1)(T^{1/2} - T_0^{1/2})],$$

where $\alpha_V = a_0 + a_1(T - T_0)$, a_0 and a_1 are two refinable parameters.

COMPRESSIONAL BEHAVIOR OF THE CANCRINITE-GROUP MINERALS

The P -induced evolution of the unit-cell parameters of the studied cancrinite-group minerals is shown in Figure 4, and the elastic parameters, refined from BM-EoS fits, are listed in Table 2. These parameters show that all the studied minerals have similar bulk moduli at room conditions, where the refined K_0 values (~47 GPa) fall in the range so far reported for open-

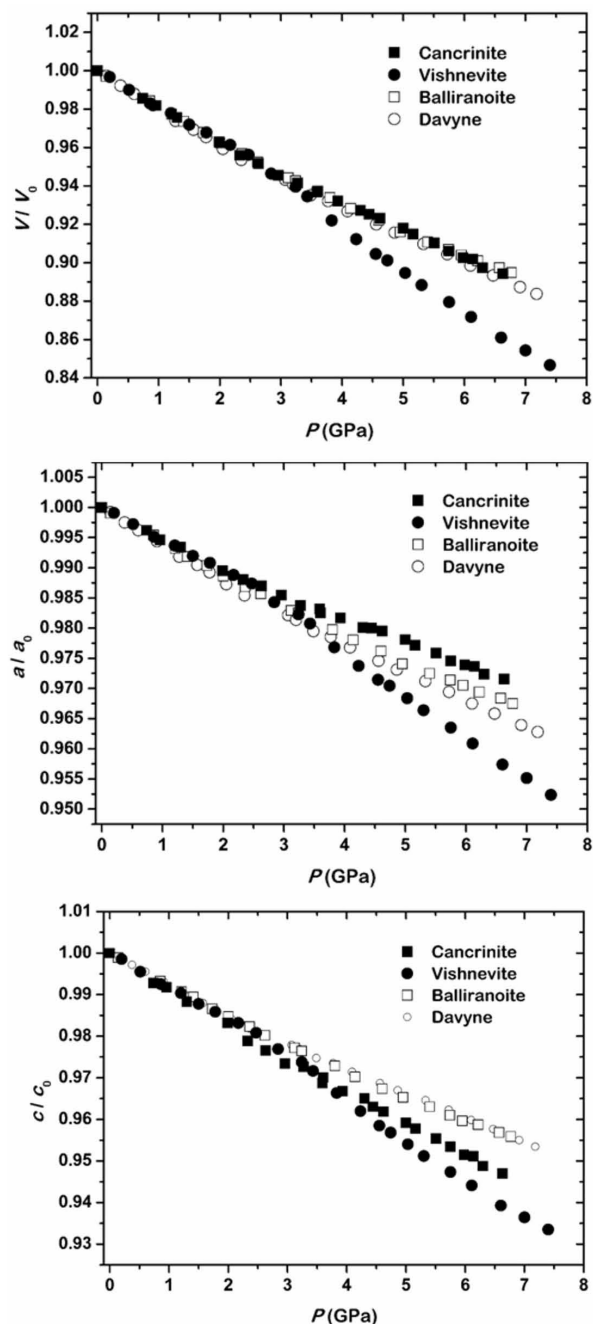


FIGURE 4. The pressure-induced evolution of the unit-cell volume, and a and c cell edges of cancrinite (Lotti et al. 2012), vishnevite (Lotti 2014), balliranoite (Lotti et al. 2014b), and davyne (Lotti et al. 2014a).

framework silicates (Gatta 2008, 2010; Gatta and Lee 2014). Moreover, all the members of the group share the same elastic anisotropy scheme, where the most compressible direction, along the c crystallographic axis, corresponds to the stacking of S6R-layers (Fig. 1). Besides the similar anisotropy scheme, the calculated $K_a:K_c$ ratios (Table 2) suggest a different behavior for the cancrinite- and the davyne-subgroup minerals, with elastic anisotropy more pronounced in the former.

If the P -induced elastic response of davyne and balliranoite is virtually identical within estimated standard deviations (Fig. 4; Table 2; Lotti et al. 2014a, 2014b), a comparison of the cancrinite and vishnevite behaviors shows a different scenario. Vishnevite clearly shows a significant increase in compressibility, related to a structural re-arrangement of the channel population (Lotti 2014) at $P > 3.43$ GPa. In cancrinite, an apparent softening is observed at higher pressures ($P > 4.62$ GPa; Lotti et al. 2012) by the evolution of the unit-cell parameters with P , but without any significant change in the evolution of structural parameters at the atomic scale. For both cancrinite and vishnevite, the change in the elastic behavior at high pressure leads to an increase of the elastic anisotropy (Table 2). Nevertheless, the elastic parameters reported in Table 2 suggest that the minerals of this subgroup share the same bulk compressibility and elastic anisotropy at ambient conditions and, more generally, in the low- P regime (Fig. 4).

The same conclusion is valid for the synthetic hydroxycancrinite (Table 2), a cancrinite-subgroup compound studied at high-pressure by Oh et al. (2011). It is worth noting that Oh et al. (2011) also reported a subtle discontinuity in the P - V data between 1.9 and 2.5 GPa, although not supported by structural data. The only other compound of the cancrinite group studied at high pressure is the synthetic $\text{Na}_6\text{Cs}_2[\text{Ga}_6\text{Ge}_6\text{O}_{24}]\cdot\text{Ge}(\text{OH})_6$ (Gatta and Lee 2008), which is the only one with a non-aluminosilicate framework studied at high pressure. To the different composition of the tetrahedral framework is likely ascribable the reported higher bulk compressibility (Table 2). The pronounced compression in the low- P regime of the $(\text{Ga},\text{Ge})\text{O}_4$ tetrahedra is, at least partially, responsible for the lower K_0 and for the elastic stiffening with increasing pressure (as suggested by the higher K'), if compared to the natural compounds all showing a “quasi-rigid” Si- or Al-tetrahedra.

All the cancrinite-group compounds studied at high pressure were found to be stable up to the highest pressures investigated (Table 2), with no hints of structural collapse or amorphization. In particular, davyne and balliranoite showed stability up to ~ 7 GPa without phase transitions or change of the compressional behavior (Lotti et al. 2014a, 2014b).

THERMAL BEHAVIOR OF CANCRINITE-GROUP MINERALS

Several studies have been devoted to the high-temperature behavior of cancrinite-group compounds. We will provide a brief overview of the behavior of natural samples, starting from the in situ single-crystal X-ray diffraction study of cancrinite sensu stricto performed by Gatta et al. (2014), who reported a very slow dehydration process at 748 K, which took 12 days to reach structural relaxation. Similarly, Sirbescu and Jenkins (1999) reported a thermogravimetric analysis of a synthetic sample of cancrinite (0.06 K/min average heating rate), which needed 10 days to fully dehydrate at 1058 K, with an intense weight-loss peak in the range 570–770 K. These results are in good agreement with the structure refinement performed by Gatta et al. (2014) at T above the dehydration temperature (i.e., 748 K), showing the presence of residual H_2O molecules within the *can* unit cages. It is worth noting the stability, or metastability, of the “quasi-anhydrous” cancrinite reported by Gatta et al. (2014) at least in

TABLE 2. Thermo-elastic parameters of cancrinite-group minerals

		P -range (GPa)	β_{V0} (GPa ⁻¹)	K_{V0} (GPa)	K'_{V0}	T -range (K)	$\alpha_{V(293\text{ K})}$ (10 ⁻⁵ K ⁻¹)		
	Reference								
Cancrinite	a	0.0001–4.62	0.022(1)	45(2)	6(1)				
	a	5.00–6.63	0.025(1)	40(2)	4				
	b					298–769	4.2(4)		
	c					100–293	3.8(7)		
	d					303–748	4.88(8)		
Vishneville	d					748–823	3.1(6)		
	e	0.20–2.47	0.020(2)	49(4)	5.4(33)				
Balliranoite	e	3.83–7.40	0.033(3)	30(3)	2.6(5)				
	f	0.0001–6.77	0.021(1)	48(3)	4.0(10)				
Davyne ($P6_3$)	g					108–293	4.6(4)		
	h	0.38–7.18	0.0215(5)	46.5(11)	3.7(3)				
	i					110–293	4.2(4)		
Davyne ($P6_3/m$)	j					293–449	5.4(6)*		
	j					503–948	3.0(1)*		
	j					293–829	2.7(2)*		
Microsommitte ($P6_3$)	j					293–423	5.5(4)*		
Microsommitte ($P6_3/m$)	j					503–947	1.9(2)*		
Hydroxycancrinite†	k	0.0001–6.1	0.0213(4)	46.9(9)	4.0(4)				
Na ₆ Cs ₂ [Ga ₆ Ge ₆ O ₂₄]-Ge(OH) ₆ †	l	0.0001–5.01	0.029(2)	35(2)	11(1)				
		P -range (GPa)	β_{00} (GPa ⁻¹)	K_{00} (GPa)	K'_{00}	T -range (K)	$\alpha_{00(293\text{ K})}$ (10 ⁻⁵ K ⁻¹)		
Cancrinite	a	0.0001–4.62	0.0064(7)	52(6)	11(4)				
	a	5.00–6.63	0.0057(4)	58(4)	4				
	b					298–769	0.90(8)		
	c					100–293	0.7(2)		
	d					303–748	1.16(3)		
Vishneville	d					748–823	0.6(3)		
	e	0.20–2.47	0.0060(4)	56(4)	7.3(32)				
Balliranoite	e	3.83–7.40	0.0083(6)	40(3)	1.8(4)				
	f	0.0001–6.77	0.0062(5)	54(4)	4.6(14)				
Davyne ($P6_3$)	g					108–293	1.4(2)		
	h	0.38–7.18	0.0066(1)	50.3(9)	4.0(3)				
	i					110–293	1.4(1)		
Davyne ($P6_3/m$)	j					293–449	1.69(8)*		
	j					503–948	1.32(6)*		
	j					293–829	1.34(7)		
Microsommitte ($P6_3$)	j					293–423	1.6(1)*		
Microsommitte ($P6_3/m$)	j					503–947	0.86(4)*		
Hydroxycancrinite†	k	0.0001–6.1	0.0062(6)*	54(5)*	4*				
Na ₆ Cs ₂ [Ga ₆ Ge ₆ O ₂₄]-Ge(OH) ₆ †	l	0.0001–5.01	0.0083(4)	40(2)	11(1)				
		P -range (GPa)	β_{c0} (GPa ⁻¹)	K_{c0} (GPa)	K'_{c0}	K_{00}/K_{c0}	T -range (K)	$\alpha_{c0(293\text{ K})}$ (10 ⁻⁵ K ⁻¹)	α_{c0}/α_{00}
Cancrinite	a	0.0001–4.62	0.0098(6)	34(2)	2.8(8)	1.53			
	a	5.00–6.63	0.016(1)	20.6(14)	4	2.82			
	b						298–769	2.3(2)	2.55
	c						100–293	2.1(3)	3.00
	d						303–748	2.58(8)	2.22
Vishneville	d						748–823	1.9(5)	3.17
	e	0.20–2.47	0.0090(5)	37(2)	5.0(20)	1.51			
Balliranoite	e	3.83–7.40	0.021(4)	16(3)	3.6(5)	2.50			
	f	0.0001–6.77	0.0083(4)	40(2)	3.3(6)	1.35			
Davyne ($P6_3$)	g						108–293	1.7(2)	1.21
	h	0.38–7.18	0.0083(1)	40.3(7)	3.2(2)	1.25			
	i						110–293	1.6(1)	1.14
Davyne ($P6_3/m$)	j						293–449	1.6(4)	0.95
	j						503–948	0.3(1)	0.23
	j						293–829	0.11(3)*	0.08
Microsommitte ($P6_3$)	j						293–423	1.6(4)	1.00
Microsommitte ($P6_3/m$)	j						503–947	0.2(1)	0.23
Hydroxycancrinite†	k	0.0001–6.1	0.0101(9)*	33(3)*	4*	1.64			
Na ₆ Cs ₂ [Ga ₆ Ge ₆ O ₂₄]-Ge(OH) ₆ †	l	0.0001–5.01	0.0108(3)	31(1)	7.4(8)	1.29			

Notes: β_{V0} is the isothermal compressibility coefficient, K_{V0} and K'_{V0} are the isothermal bulk modulus and its P -derivative, respectively, and $\alpha_{V(293\text{ K})}$ is the thermal expansion coefficient of the unit-cell volume; β_{00} , K_{00} , K'_{00} and $\alpha_{00(293\text{ K})}$ are the co-respective axial coefficients (with $j = a, c$). References: a = Lotti et al. (2012); b = Hassan et al. (2006); c = Gatta et al. (2012a); d = Gatta et al. (2014); e = Lotti et al. (2014b); f = Lotti et al. (2014b); g = Gatta et al. (2013b); h = Lotti et al. (2014a); i = Gatta et al. (2013a); j = Bonaccorsi et al. (1995); k = Oh et al. (2010); l = Gatta and Lee (2008).

* Calculated from published data; † synthetic compounds.

the range 748–823 K, above which a broadening of the diffraction peaks suggested an impending decomposition or a severe deterioration of the long-range order of the crystal. Interestingly, the dehydration was reported to be irreversible at the timescale

of the experiment, as confirmed by the diffraction data collected after the high- T ramp. The dehydration of a natural cancrinite was also reported by Isupova et al. (2010) by in situ single-crystal X-ray diffraction at 623 K, above which a dehydrated form was

reported to be crystalline at least up to 823 K. An irreversible dehydration was also reported by Ballirano et al. (1995), on basis of an ex situ single-crystal X-ray diffraction experiment at room- T on a cancrinite sample previously heated up to 873 K.

These experimental observations may be coupled with the findings of natural partially anhydrous cancrinite crystals in volcanic alkaline rocks at the Eifel region, for which Zubkova et al. (2011) suggested the loss of H_2O in response to the roasting of the crystals during the effusive process. The high- T behavior of a natural cancrinite, showing superstructure reflections along the c -axis, was also studied by Hassan et al. (2006) by in situ synchrotron X-ray powder diffraction, reporting a discontinuity in the evolution of the unit-cell parameters at 777 K and a complete dehydration at 898 K. Loss of CO_2 was reported to occur at 1223 K by Hassan (1996a) on the basis of a TG-DTG analysis of a natural cancrinite, which was observed to melt at 1528 K. Sirbescu and Jenkins (1999) reported unchanged CO_3^{2-} signals from ex situ infrared analysis of previously heated synthetic cancrinite up to 1153 K, where decomposition to a mixture of nepheline + hauyne was observed.

To the best of our knowledge, no high-temperature studies of the SO_4^{2-} end-member of the cancrinite subgroup (i.e., vishnevite) are available in the open literature. However, the high- T behavior of the K-rich pitiglianoite was performed by Bonaccorsi et al. (2007) by in situ single-crystal X-ray diffraction and FTIR spectroscopy. These authors reported a unit-cell expansion up to 499 K, followed by a dehydration process with unit-cell contraction in the range 499–676 K and a further expansion between 676 and 914 K. The dehydration was coupled with a partial and irreversible migration of the channel- K^+ cations into the *can* cages and cage- Na^+ into the channel sites, which likely played a role in the minor re-adsorption of H_2O observed with decreasing temperature. These data point out the significant influence of the extraframework constituents on the P - T -induced transformations of cancrinite-group minerals. The presence of CO_2 molecules, along with SO_4^{2-} anions, within the structural channels was confirmed by FTIR spectra, which suggested, as reported by Bonaccorsi et al. (2007), a full loss of CO_2 at $T \geq 723$ K.

The major difference between the high- T behavior of the cancrinite- and davyne-subgroup minerals can be found in the (nominally) anhydrous nature of the latter. Bonaccorsi et al. (1995) reported the high- T study of both $P6_3$ -davyne and $P6_3$ -microsommitte, by in situ single-crystal X-ray diffraction, observing a similar thermal expansion with a clear discontinuity in the evolution of the cell parameters and a decrease of the thermal expansivity along the c -axis (Table 2) at 473 (for davyne) and 433 K (for microsommitte). This discontinuity is due to the displacive phase transition to the $P6_3/m$ space group, induced by the expansion of the dzc chains, via tetrahedral tilting, to the geometric limit for which the inter-tetrahedral O3-O4-O3 angle is 180° (O3-O3-O3 in space group $P6_3/m$, Fig. 5). This symmetry-constraint prevents a further expansion of the dzc chains by tetrahedral tilting and is responsible for the decrease of the thermal expansivity along the [0001] direction.

Bonaccorsi et al. (1995) also reported the high- T behavior of a davyne sample with $P6_3/m$ symmetry at room conditions, for which insignificant thermal expansion along the c -axis was observed even at the low-temperature regime (Table 2). The

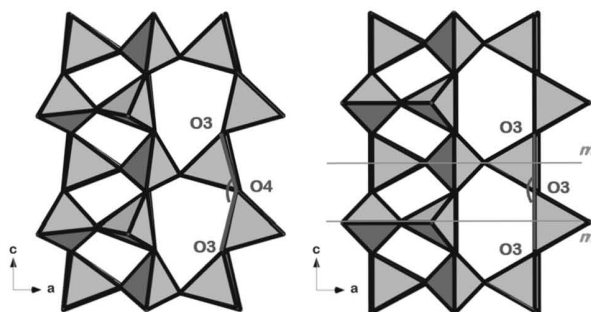


FIGURE 5. The inter-tetrahedral O3-O4-O3 angle in $P6_3$ davyne (left) is symmetry-induced to O3-O3-O3 = 180° in $P6_3/m$ davyne (right), for the presence of mirror planes at $z = 0.25$ and 0.75 .

high- T behavior of microsommitte was later studied by Bonaccorsi et al. (2001), by in situ single-crystal X-ray diffraction and Monte Carlo simulation, to define the order-disorder processes of the extraframework population. The authors reported a full disorder (i.e., in response to a complete microsommitte-to-davyne structure transformation) at the critical temperature of 1023 K.

If the T -induced dehydration may act as a destabilizing factor affecting the cancrinite-subgroup compounds, in the nominally anhydrous davyne-subgroup minerals a potential source of thermal instability is represented by the T -induced phase transition to the $P6_3/m$ space group, which hinders the deformation mechanisms able to accommodate the structural expansion along the c -axis via tetrahedral tilting.

When not affected by dehydration processes, all minerals of the cancrinite group show comparable bulk thermal expansivities (Hassan et al. 2006; Gatta et al. 2012a, 2013a, 2013b, 2014), and the stacking direction of the 6-rings layers ([0001]-axis) is the most expandable one. Two different anisotropic patterns can be defined for the minerals belonging to the two subgroups, more pronounced for cancrinite-subgroup minerals (Table 2).

MECHANISMS OF CRYSTAL STRUCTURE DEFORMATION AT NON-AMBIENT CONDITIONS

Mechanisms of framework deformation

The different coordination environment of the Na^+ cation, compared with that of Ca^{2+} (Fig. 2), leads to a framework contraction of cancrinite and vishnevite in the (0001) plane already at room conditions. Moreover, beside the different ditrigonal character of the $\text{S6R} \perp [0001]$ (Fig. 1), a different configuration of the channel voids is also observed among the cancrinite-group minerals. In cancrinite subgroup, the $\sim 1:1$ ratio of the symmetry-independent O1-O1_{12R} and O3-O4_{12R} diameters (Fig. 6) gives an almost circular shape of the section perpendicular to the c axis; in davyne subgroup, a markedly hexagonal section occurs (Fig. 1), with a smaller effective pore width (sensu Baerlocher et al. 2007). In addition, the presence of $[\text{Ca-Cl}]^+$ clusters in the cages and/or SO_4^{2-} anions (with associated K^+ cations) in the channels leads to an expansion of the dzc chains along [0001] already at room conditions. As a consequence, the dzc chains are more expanded in vishnevite than cancrinite and in davyne than balliranoite.

The different extraframework population in cancrinite- and davyne-subgroup members is not only the source for the differ-

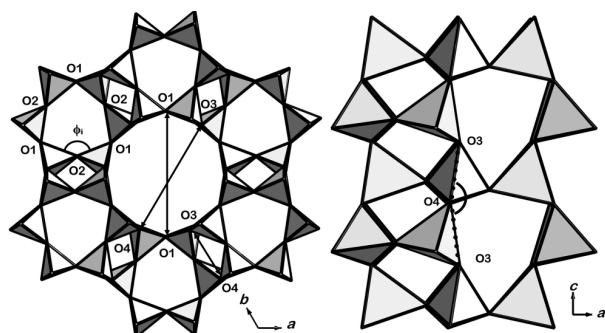


FIGURE 6. The [CAN] framework of cancrinite viewed down [0001] (left) and two base-sharing *can* units (right) showing the relevant structural parameters (diameters and angles) reported in Tables 3¹ and 4¹.

ent framework configurations at ambient conditions, but also the cause of the different distortion mechanisms in response to temperature or pressure. In the following paragraphs, we provide a model of the structural evolution of cancrinite-group minerals at non-ambient conditions, on the basis of the high-*P* studies of Lotti (2014) and Lotti et al. (2012, 2014a, 2014b) and the low-

and high-*T* studies of Bonaccorsi et al. (1995, 2007), Hassan et al. (2006), Isupova et al. (2010), and Gatta et al. (2012a, 2013a, 2013b, 2014).

The analysis of the *T*- and *P*-induced evolution of the Si-O-Al inter-tetrahedral angles shows that two distinct trends can be defined for the cancrinite- and davyne-subgroup minerals, respectively. In cancrinite subgroup, all the four symmetry-independent Si-O-Al angles vary with *T* or *P* (Fig. 7, Tables 3¹ and 4¹). In davyne subgroup, no significant variations of the Si-O2-Al angle are observed and the Si-O1-Al angle always shows the greatest change with *T* or *P* (Fig. 7, Tables 3¹ and 4¹). These different trends are the basis for different deformation mechanisms in the two subgroups.

The framework deformation along [0001] is controlled by the tilting of the tetrahedra forming the *dzc* chains, around the O3 and O4 hinges (Figs. 1 and 5), which correlates with the Si-O3-Al and Si-O4-Al inter-tetrahedral angles. The behavior of these angles with *P* and *T* does not show any significant dif-

¹ Deposit item AM-16-25282, Tables 3 and 4. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to <http://www.minsocam.org/MSA/AmMin/TOC/>).

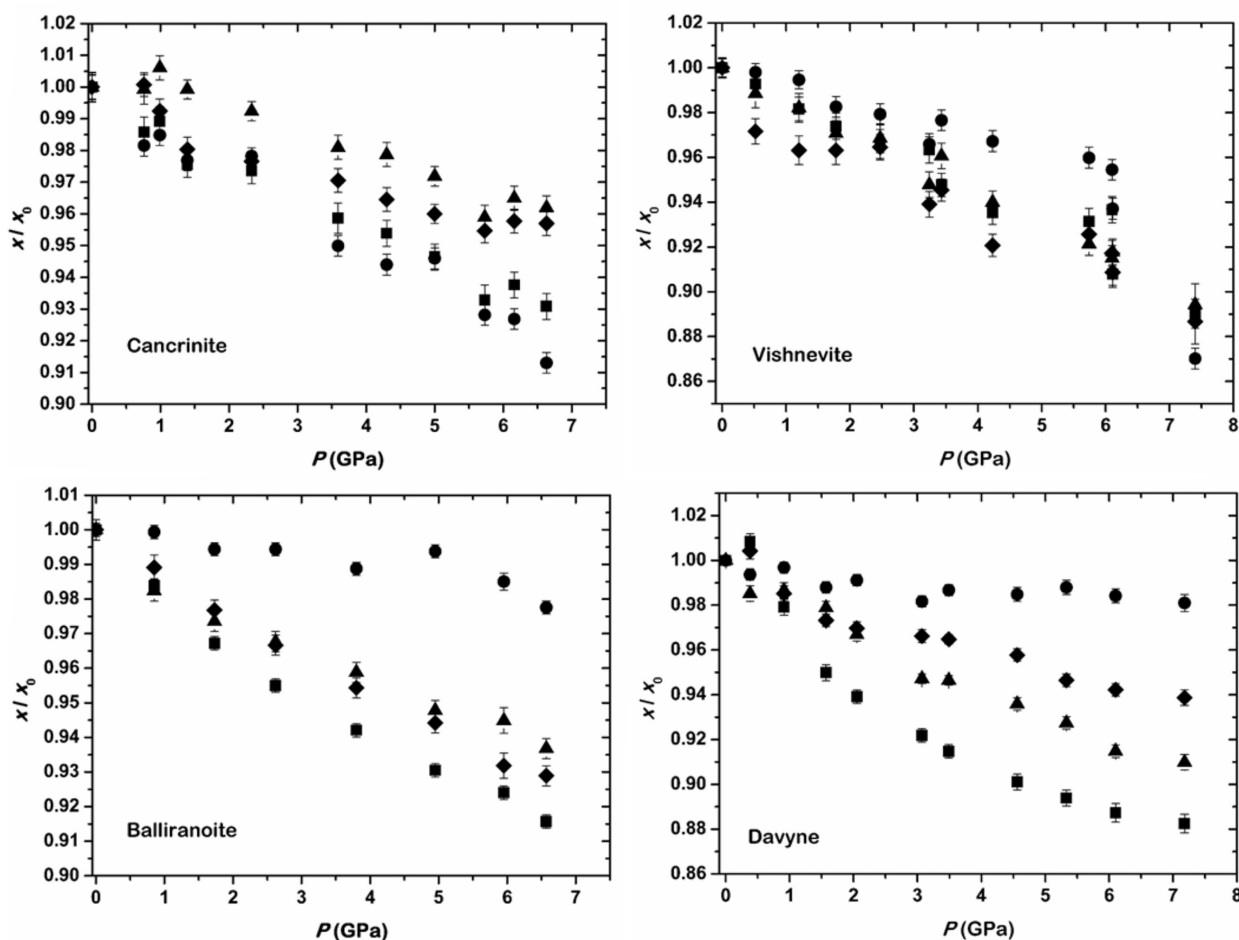


FIGURE 7. The pressure-induced evolution of the inter-tetrahedral Si-O1-Al (squares), Si-O2-Al (circles), Si-O3-Al (triangles), and Si-O4-Al (diamonds) angles of cancrinite (Lotti et al. 2012), vishnevite (Lotti 2014), balliranoite (Lotti et al. 2014b), and davyne (Lotti et al. 2014a).

ference between the two subgroups of minerals (Tables 3¹ and 4¹). The same deformation mechanism accommodates the strain along the *c*-axis: the expansion or compression of the *dzc* chains is well described by the change in the O3-O4-O3 angle (Figs. 5 and 6; Tables 3¹ and 4¹). When the maximum expansion limit of 180° is reached, the displacive phase transition from the *P*6₃ to the *P*6₃/*m* space group occurs (Bonaccorsi et al. 1995). Similarly, the reverse transition occurs when pressure is applied to a davyne sample showing *P*6₃/*m* symmetry at room conditions (Lotti et al. 2014a).

The main differences between the two subgroups are in the mechanisms accommodating the strain within the (0001) plane, mainly governed by the tilting of the tetrahedra around the O1 and O2 hinges, correlated with the Si-O1-Al and Si-O2-Al inter-tetrahedral angles. In cancrinite and vishnevite, a strong variation in the ditrigonal shape of the S6R⊥[0001] occurs in response to *T* and *P*, and the bulk compression/expansion is accommodated by both the S4Rs (along O3-O4) and by the channels (along O1-O1) (Fig. 6; Tables 3¹ and 4¹). In contrast, balliranoite and davyne show less intense “ditrigonalization” of the cage bases, and the compression/expansion on the (0001) plane is mainly accommodated by the channel diameters (Fig. 6; Tables 3¹ and 4¹). Overall, for all the studied minerals, the contribution of the channel voids to the bulk compressibility/expansivity was found to be significantly higher than that of the *can* cages (Lotti 2014).

Behavior of extraframework population at non-ambient conditions

The high-*P* and low-*T* studies of cancrinite (Lotti et al. 2012; Gatta et al. 2012a) and vishnevite (Lotti 2014) showed, in response to pressure or low temperature, a compression of the first tetrahedral shell of the Na-coordination environment into the cage (involving three O2 and the closer Ow sites) and an anisotropic expansion of the second shell (Tables 3¹ and 4¹). In other words, the distortion of the bipyramidal polyhedron is further enhanced in a “compressive” regime (i.e., high-*P* and low-*T*), leading to an increasingly tetrahedral form of the Na-coordination. In contrast, only minor changes occur for the Ca-O bonds in balliranoite and davyne at the same conditions (Tables 3¹ and 4¹; Gatta et al. 2013a, 2013b; Lotti et al. 2014a, 2014b). This markedly different behavior reflects the different evolution with *T* and *P* of the Si-O2-Al inter-tetrahedral angle between the two subgroups (Tables 3¹ and 4¹). In fact, the inhibited tetrahedral rotation around the O2 hinge (Fig. 6) in davyne-subgroup minerals prevents the migration of this oxygen toward the Ca²⁺ cation and, as a consequence, a significant compression of the Ca-O2 bonds (Fig. 2). Such a different behavior may be ascribed to the nature of the cage cations and their different coordination configuration: the longer Ca-O bond lengths, if compared to Na-O ones, can explain the less pronounced compression of the Ca-O2 bonds (than the Na-O2) in response to the applied *P* (or low-*T*), leading to different framework deformation mechanisms than those observed in Na-members.

The analysis of the high-temperature behavior of cancrinite showed the same mechanisms previously observed at low-*T* and high-*P*, but opposite in sign, at least at temperatures below the start of dehydration (Table 4¹; Hassan et al. 2006; Isupova et al. 2010; Gatta et al. 2014). In response to dehydration, an inversion

in the *T*-induced trend of the Si-O2-Al inter-tetrahedral angle can be observed from the HT studies of Isupova et al. (2010) and Gatta et al. (2014) (Table 4¹), likely to minimize both the Na-O1 and Na-O2 bond lengths to counterbalance the loss of H₂O-oxygen atoms. This mechanism concurs to the stability (or metastability) of the observed quasi-anhydrous form of cancrinite in Nature.

The compression/expansion of the chemical bonds of the channel cations (*M*-O_{framework}, *M* = Na, Ca, K) is strictly related to the distortion of the *dzc* chains along [0001]. In cancrinite, balliranoite and davyne, no substantial change in the coordination of channel cations and anions was observed at non-ambient conditions (Gatta et al. 2012a, 2013a, 2013b; Lotti et al. 2012, 2014a, 2014b). Therefore, for these minerals, the channel extraframework population apparently does not have a significant effect on the behavior in response to the applied temperature or pressure. In contrast, a re-arrangement of the channel population apparently occurs in vishnevite at *P* ≥ 3.43(4) GPa, coupled with a significant increase in compressibility (Lotti 2014). In vishnevite, a displacement of the SO₄²⁻ tetrahedra around the 6₃-axis is followed by a significant migration of the Na⁺ cations toward the center of the channel. However, the marked increase in compressibility and the unusually short K-O bonds suggest a metastable nature of the observed high-*P* configuration of vishnevite (Lotti 2014). Nevertheless, these data show that even the channel constituents, and in particular the cations bonding environment, might control the behavior and the stability of some cancrinite-group species at non-ambient conditions. This is also substantiated by the high-*T* behavior of pitiglianoite (Bonaccorsi et al. 2007), for which, at temperatures above the dehydration process, an irreversible Na⁺/K⁺ cationic exchange occur between channels and cages, with the larger cations occupying the *can* units in the new high-*T* structural configuration.

IMPLICATIONS

The studies performed during the last decade on the behavior of cancrinite-group minerals at non-ambient conditions, and here reviewed, allowed the experimental determination of the thermo-elastic parameters of the most important end-members of this group (Table 2), whose implementation in the thermodynamic data sets can be used for a better modeling of the complex equilibria relating to natural rocks. Often, thermodynamic data (here isothermal compressibility or isobaric thermal expansivity) are “estimated,” when not known experimentally (e.g., Holland and Powell 2011), giving rise to potentially crude results.

The crystal chemistry of cancrinite-group minerals is somehow unique: they are among the few silicates that contain structurally incorporated H₂O and anionic groups as CO₃²⁻, C₂O₄²⁻, SO₄²⁻, or Cl⁻. Their open-frameworks allow also additional molecules to be entrapped into the cavities, including CO₂. Della Ventura et al. (2007, 2008) reported, on the basis of infrared spectroscopic analyses, the presence of strong rim-to-core inhomogeneities in the volatile composition of cancrinite-group minerals due to a CO₂/CO₃²⁻ substitution, pointing out the sensitivity of these compounds to the physical-chemical conditions of the crystallization environments and suggesting their potential application as geochemical markers.

The high-*T* experiments made on the cancrinite group

show that the anhydrous forms keep their crystallinity even at 800–900 K, which is very high temperature for microporous structures. High-*T* studies of cancrinite *sensu stricto* (e.g., Sirbescu and Jenkins 1999; Gatta et al. 2014) report slow kinetics of dehydration under equilibrium conditions, if compared to other hydrous microporous silicates, e.g., zeolites. Dehydration may likely occur under non-equilibrium conditions in xenoliths involved in volcanic processes. Nevertheless, the stability, or metastability, of the anhydrous (or partially hydrous) form of cancrinite is reported in the literature (e.g., Ballirano et al. 1995; Hassan et al. 2006; Gatta et al. 2014) and is also confirmed by its occurrence in xenoliths within alkaline basalts (Zubkova et al. 2011). The experiments on the *T*-induced dehydration of cancrinite under equilibrium conditions (Sirbescu and Jenkins 1999; Gatta et al. 2014) suggests that this process would occur at temperatures not lower than 650–750 K, at 0.0001 GPa. The combined effect of *P* and *T* on the behavior of cancrinite-group minerals is basically unknown, and this, on one hand, hinders a deep discussion on the petrological implications but, on the other hand, should act as a stimulus for new experiments in this direction. The sub-solidus stabilities of some cancrinite-group minerals were studied by Edgar (1964), who reported that cancrinite and hydroxycancrinite were still stable at 1070 K and 0.13 GPa *P*(H₂O), suggesting that, at a high-enough carbonate fugacity, cancrinite should be stable at liquidus conditions.

The experimental findings of the host-guest interactions and of the structural deformation mechanisms at high *T* and *P* show the relevant role played by the extraframework constituents, and in particular of the cage population (Fig. 2), on the behavior of cancrinite-group minerals at non-ambient conditions. The *T*-induced mutual migration of K and Na between channels and cages in pitiglianoite, at temperature above the dehydration process (Bonaccorsi et al. 2007), suggests the potential high-thermal stability of the K-bearing members of the group, which should be further investigated at high-*T* conditions. The modeling of the host-guest interactions at non-ambient conditions provides a more robust background for the potential application of these compounds in several technological fields: for example, by defining the high-*T* stability for a safe use of hydrous cancrinite-subgroup compounds as solid storage-materials of alkaline wastes or for tailoring preparation processes (Bao et al. 2005; Riley et al. 2012). Common precipitation of cancrinite-group compounds were also reported from caustic nuclear waste solutions (e.g., Buck and McNamara 2004; Rivera et al. 2011; Wang and Um 2013). The knowledge of the host-guest interactions in cancrinite-group materials with the structural cages occupied by large monovalent cations (e.g., K⁺, Cs⁺, Rb⁺) is still poor, as well as their behavior under *T* or *P*. This configuration is shown only by tiptopite (which contains K⁺) among the mineralogical species, but the synthesis of several Cs-cancrinites has successfully been reported (e.g., Colella and de' Gennaro 1989; Norby et al. 1991; Lee et al. 2000; Fechtelkord et al. 2001; Bieniok et al. 2005; Gatta and Lee 2008), whose thermal (and compressional) stability is still unknown. The confinement of Cs⁺ (or Rb⁺) cations inside the *can* units, with their small effective pore widths (*sensu* Baerlocher et al. 2007), suggests the potential application of cancrinite-group minerals as nuclear waste storage materials, as recently reported for other classes of microporous materials (e.g.,

Gatta et al. 2008b, 2009a, 2009b, 2012b; Sanchez-Valle et al. 2010). In this light, experiments on the thermo-elastic behavior, *P-T* phase stability and chemical stability (by leaching processes) of Cs-cancrinites are necessary, for their potential utilization.

The behavior at non-ambient conditions of the cancrinite-group minerals shows, beside the potential destabilizing effects of temperature (e.g., dehydration in the cancrinite subgroup, *P*₆₃-to-*P*₆/*m* phase transition in the compounds of davyne subgroup), a high-*P* stability (at room-*T*), which is quite surprising if we consider their microporous nature. The *P*-induced stability is the effect of a structural flexibility, which in turn is based mainly on tilting of rigid tetrahedra around O atoms that behave as hinges. In cancrinite-group minerals, the *P*-induced tilting of tetrahedra usually leads to continuous re-arrangements of the framework without any phase transition. As observed in other classes of open-framework silicates (e.g., zeolites), flexibility and microporosity do not necessarily imply high compressibility: the cancrinite-group minerals are less or similarly compressible than other rock-forming minerals (e.g., α -quartz, Angel et al. 1997; Na-rich feldspars, Benusa et al. 2005; tri- and di-octahedral micas, Zanazzi and Pavese 2002). In this light, the high-*P* experimental findings on cancrinite-group minerals, here reviewed, corroborate the conclusion of Gatta (2008) on zeolites, which can also be extended to this group of feldspathoids: “porous does not mean soft.”

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