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CRYSTAL CHEMISTRY OF CANCRINITE-GROUP MINERALS WITH AN *AB*-TYPE FRAMEWORK: A REVIEW AND NEW DATA.
II. IR SPECTROSCOPY AND ITS CRYSTAL-CHEMICAL IMPLICATIONS

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Abstract

We present a comparative analysis of powder infrared spectra of cancrinite-group minerals with the simplest framework, of *AB* type, from the viewpoint of crystal-chemical characteristics of extra-framework components. We provide IR spectra for typical samples of cancrinite, cancrisilite, kyanoxalite, hydroxycancrinite, depmeierite, vishnevite, pitiglianoite, balliranoite, davyne and quadridavyne, as well as the most unusual varieties of cancrinite-subgroup minerals (Ca-deficient cancrinite, H_2O-free cancrinite, intermediate members of the series cancrinite – hydroxycancrinite, cancrinite–cancrisilite, cancrinite–kyanoxalite, K-rich vishnevite, S_2-bearing balliranoite). Samples with solved crystal structures are used as reference patterns. Empirical trends and relationships between some parameters of IR spectra, compositional characteristics and unit-cell dimensions are obtained. The effect of Ca content on stretching vibrations of CO_3^{2-} is explained in the context of the cluster approach. The existence of a hydrous variety of quadridavyne is demonstrated.

Keywords: cancrinite, cancrisilite, kyanoxalite, hydroxycancrinite, depmeierite, vishnevite, pitiglianoite, balliranoite, davyne, quadridavyne, cancrinite group, infrared spectrum, crystal chemistry.

Sommaire

Nous présentons une analyse comparative des spectres infrarouges obtenus à partir de poudres de minéraux du groupe de la cancrinite ayant la charpente la plus simple, de type *AB*, du point de vue des caractéristiques cristallochimiques des composantes externes à la charpente. Nous présentons les spectres IR des exemples typiques de cancrinite, cancrisilite, kyanoxalite, hydroxycancrinite, depmeïerite, vishnévite, pitiglianoïte, balliranoïte, davyne et quadridavyne, de même que des variétés les plus inhabituelles des minéraux du sous-groupe de la cancrinite (cancrinite déficitaire en Ca, cancrinite dépourvue en H_2O, membres intermédiaires des séries cancrinite – hydroxycancrinite, cancrinite–cancrisilite, cancrinite–kyanoxalite, vishnévite riche en K, et balliranoïte porteuse de S_2). Les données décrivant les échantillons dont la structure cristalline est déjà résolue sont utilisées comme spectres de référence. Il en résulte des tracés empiriques et des relations entre certains paramètres des spectres IR, les caractéristiques compositionnelles et les dimensions de la maille élémentaire. Nous rendons compte de l'effet du Ca sur les vibrations d'étirement de CO_3^{2-} selon le concept des agrégats atomiques. Nous démontrons l'existence de la variété hydratée de la quadridavyne.

(Traduit par la Rédaction)

Mots-clés: cancrinite, cancrisilite, kyanoxalite, hydroxycancrinite, depmeïerite, vishnévite, pitiglianoïte, balliranoïte, davyne, quadridavyne, groupe de la cancrinite, spectre infrarouge, cristallochimie.

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INTRODUCTION

Infrared (IR) spectroscopy is a very effective tool for investigation of the fine crystal-chemical characteristics of minerals. This method provides direct information on the presence of different chemical groups, their local symmetry, and the presence of hydrogen bonding. The availability of reference samples characterized preliminarily by other techniques makes IR spectroscopy more informative. A representative collection of cancrinite-group minerals with an *AB*-type framework (mainly cancrinite-subgroup minerals: see Pekov *et al.* 2011) was arranged by us. It includes well-characterized representatives of almost all mineral species (except microsommite) and most important varieties from more than fifty localities. This gives us the opportunity to investigate the general relationships between crystal-chemical characteristics and parameters of IR spectra of cancrinite-subgroup members.

EXPERIMENTAL PART

The data on chemical and structural variations of the minerals studied, as well as their localities, are given in our companion paper (Pekov *et al.* 2011). In this work, preference is given to the samples with known structures (including holotype specimens where available), as well as well-characterized samples with diverse compositional and spectroscopic characteristics.

Infrared absorption spectra of cancrinite-group minerals mixed with anhydrous KBr and pelletized have been obtained using a two-beam SPECORD 75 IR spectrophotometer (Carl Zeiss, Germany) in the wavenumber range 400–3800 cm^{-1}. The IR spectrum of pure KBr disk was subtracted from the overall spectrum. Polystyrene and gaseous NH_3 were used as frequency standards. The precision of wavenumber measurement is ±1 cm^{-1}, and the mean resolution for the range of 400–1600 cm^{-1} is 0.8 cm^{-1}. In addition, the precision was checked using an ALPHA Fourier infrared spectrometer (Bruker, Germany). In separate experiments with dry mineral oil as the immersion medium, the accuracy of the IR spectrum in the ranges 3000–4000 and 1500–1800 cm^{-1} was validated.

PRIMARY EXPERIMENTAL DATA

Typical IR spectra of 18 samples (Table 1), representing varieties of ten mineral species belonging to the cancrinite subgroup, are presented in Figures 1–6. The following specific features are common of absorption bands in all samples, related to IR-active normal modes of the *AB* framework: a group of overlapping strong bands of stretching vibrations with absorption

TABLE 1. SUMMARY OF THE SAMPLES OF CANCRINITE-GROUP MINERALS STUDIED

Fig.	Mineral, variety	Empirical formula	Wavenumbers of diagnostic IR bands, cm^{-1}		
			ν_I	ν_{III}	Stretching vibrations of extra-framework anions and H_2O molecules in the wide channel
1a	Ca-deficient cancrinite	$Na_{7.1}Ca_{0.6}(Si_{6.5}Al_{5.5}O_{24})(CO_3)_{1.4}\bullet 2H_2O$	580	689	3420, 1509, 1475, 1440, 1388
1b	Typical cancrinite	$Na_{6.5}Ca_{1.2}(Si_{6.2}Al_{5.8}O_{24})(CO_3)_{1.6}\bullet 2H_2O$	579	684	1514, 1502, 1484, 1397
1c	H_2O-free cancrinite	$Na_{6.1}Ca_{1.4}K_{0.1}(Si_{6.1}Al_{5.9}O_{24})(CO_3)_{1.4}(SO_4)_{0.1}Cl_{0.1}$	582	687	1505, 1485, 1405
2a	Cancrisilite	$Na_{7.5}(Si_{7.3}Al_{4.7}O_{24})(CO_3)_{1.4}\bullet 2H_2O$	578	704	1464
2b	Ca-bearing cancrisilite	$Na_{7.4}Ca_{0.1}(Si_{7.0}Al_{5.0}O_{24})(CO_3)_{1.3}\bullet 2H_2O$	577	692	(1505), (1465)
2c	Depmeierite [a]	$Na_{7.6}K_{0.1}(Si_{6.2}Al_{5.8}O_{24})(PO_4)_{0.5}(CO_3)_{0.2}\bullet 3.35H_2O$	567	683	3350, (1478), (1392)
3a	Kyanoxalite [b]	$Na_{6.5}K_{0.1}(Si_{6.9}Al_{5.1}O_{24})(C_2O_4)_{0.5}(PO_4)_{0.1}(SO_4)_{0.1}\bullet 4.8H_2O$	573	687	3450, 1713, 1373
3b	C_2O_4-rich cancrinite	$Na_{7.1}K_{0.4}Ca_{0.1}(Si_{6.5}Al_{5.5}O_{24})(CO_3,C_2O_4)_{1.1}\bullet nH_2O$	573	688	3350, (1708), 1460, 1425, (1375)
3c	CO_3-rich kyanoxalite	$Na_{6.0}Ca_{0.3}(Si_{6.9}Al_{5.1}O_{24})(C_2O_4,CO_3)_{0.75}\bullet nH_2O$	576	687	3340, 1713, (1506), (1469), 1370
4a	K-poor vishnevite	$Na_{7.5}K_{0.1}(Si_{6.3}Al_{5.7}O_{24})(SO_4)_{0.9}(CO_3)_{0.05}\bullet nH_2O$	568	681	3520, 1184, 1160
4b	K-rich vishnevite	$Na_{4.4}K_{2.9}Ca_{0.4}(Si_{6.3}Al_{5.7}O_{24})(SO_4)_{1.1}Cl_{0.1}(CO_3)_x\bullet nH_2O$	569	681	3400, 1160
4c	Pitiglianoite [c]	$Na_{4.7}K_{2.7}Ca_{0.1}(Si_{6.1}Al_{5.9}O_{24})(SO_4)_{0.8}\bullet nH_2O$	560	680	3450, 1153
5a	Davyne	$Na_{5.4}Ca_{2.0}K_{0.8}(Si_{6.1}Al_{5.9}O_{24})Cl_{2.0}(SO_4)_{1.1}(OH)_{0.1}$	556	669	1167
5b	Balliranoite [a]	$Na_{4.7}Ca_{2.5}K_{0.7}(Si_{6.0}Al_{6.0}O_{24})Cl_{2.3}(CO_3)_{0.8}(SO_4)_{0.3}\bullet 0.1H_2O$	567	682	1519, 1410
5c	S_2-bearing balliranoite	$Na_{5.5}Ca_{2.5}K_{0.1}(Si_{6.0}Al_{6.0}O_{24})Cl_{2.0}(CO_3)_{0.7}(SO_4)_{0.3}(S_2)_{0.3}\bullet 0.4H_2O$	565	683 671	1504, 1478, 1410, 1391
6a	Hydroxycancrinite	$Na_{\sim 8}(Si_{6.5}Al_{5.5}O_{24})(OH,CO_3)_x\bullet nH_2O$ (n ≈ 3)	567	681	3440, (1400)
6b	CO_3-deficient and H_2O-rich cancrinite	$Na_{7.65}K_{0.05}(Si_{6.3}Al_{5.7}O_{24})(CO_3)_{0.9}(SO_4)_{0.1}\bullet 2.6H_2O$	570	683	(3375), 1489, 1396
6c	Quadridavyne	$Na_{3.5}Ca_{2.1}K_{1.8}(Si_{6.2}Al_{5.8}O_{24})Cl_{3.4}(SO_4)_{0.1}(CO_3)_x\bullet nH_2O$ ($x << 1$)	554	668	3435

Note: The IR spectral bands of subordinate (non-species-defining) components are given in parentheses. [a] Holotype specimens. [b] Cotype specimen. [c] Bonaccorsi & Orlandi (1996). The first column indicates the number of the figure in which the spectrum is presented.

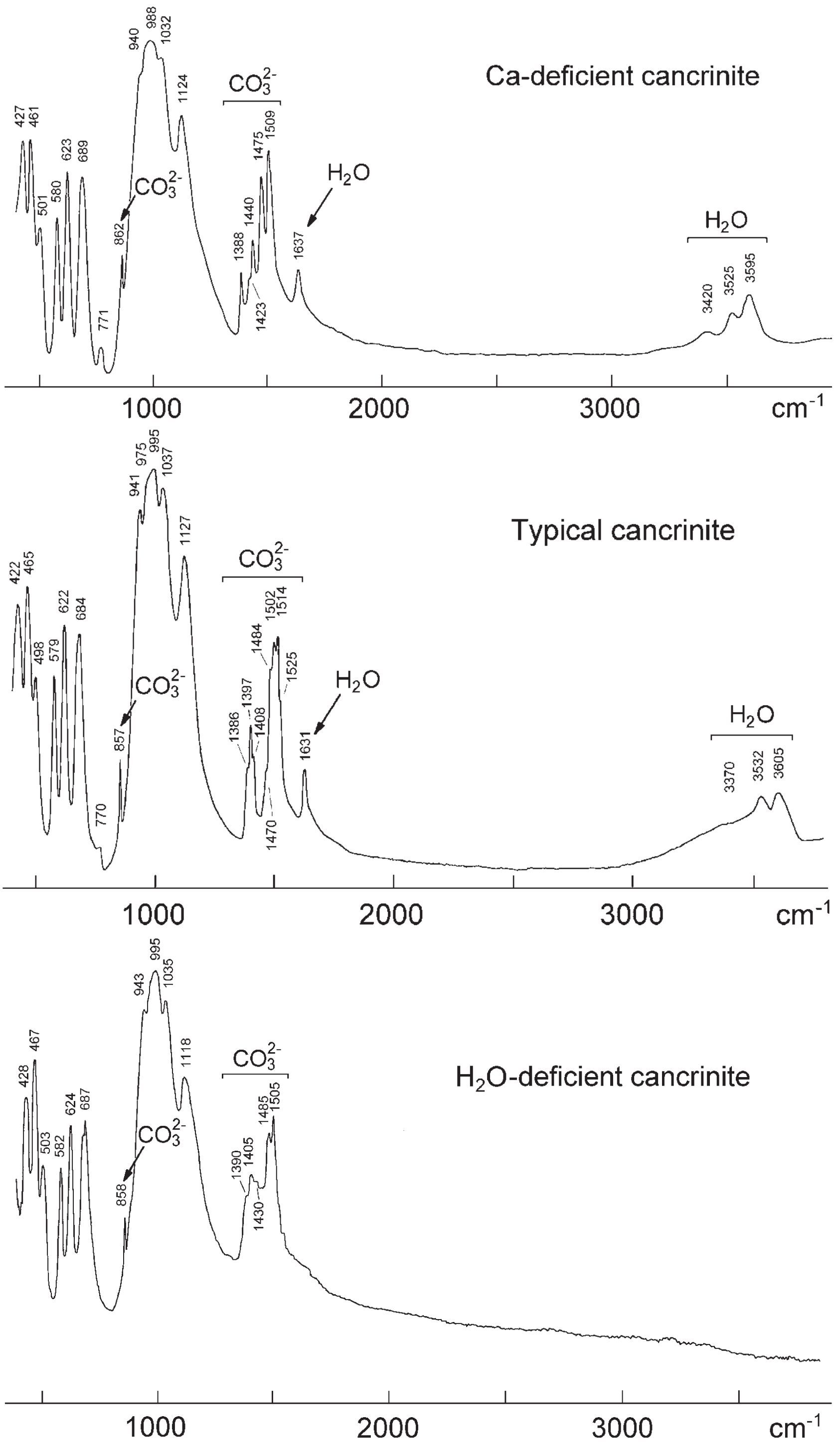

FIG. 1. IR spectra of cancrinite: a) Ca-deficient variety (Mount Koashva, Khibiny, Kola Peninsula, Russia), b) typical cancrinite (Vishnevye Mountains, southern Urals, Russia), c) H_2O-deficient cancrinite (Bellerberg, Eifel, Germany).

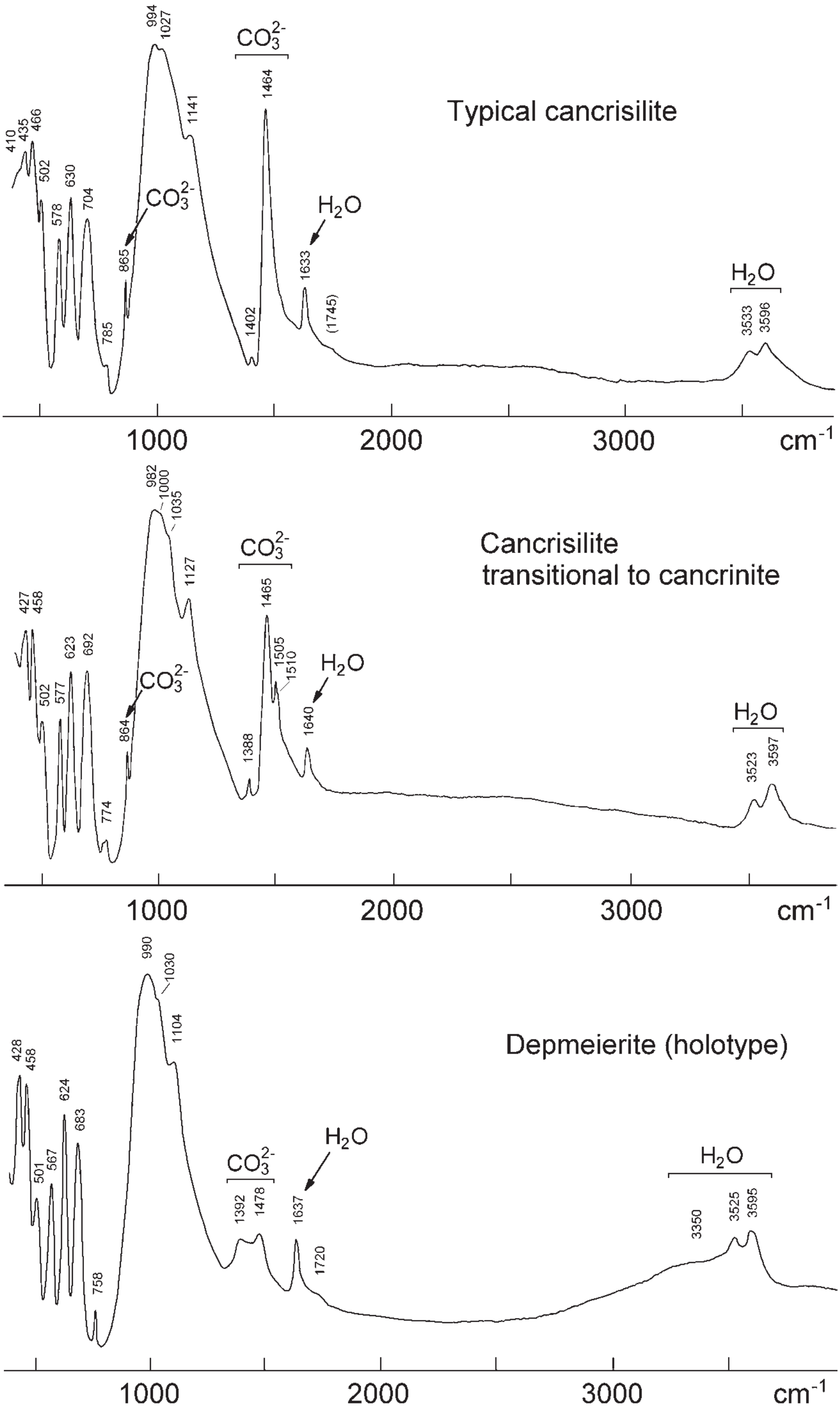

FIG. 2. IR spectra of typical cancrisilite from Mount Alluaiv, Lovozero, Kola Peninsula, Russia, sample u1631 (a), the cancrisilite variety transitional to cancrinite by composition from Mount Kukisvumchorr, Khibiny massif, Kola Peninsula, Russia (b), and the holotype specimen of depmeierite from Mount Karnasurt, Lovozero massif, Kola Peninsula, Russia (c).

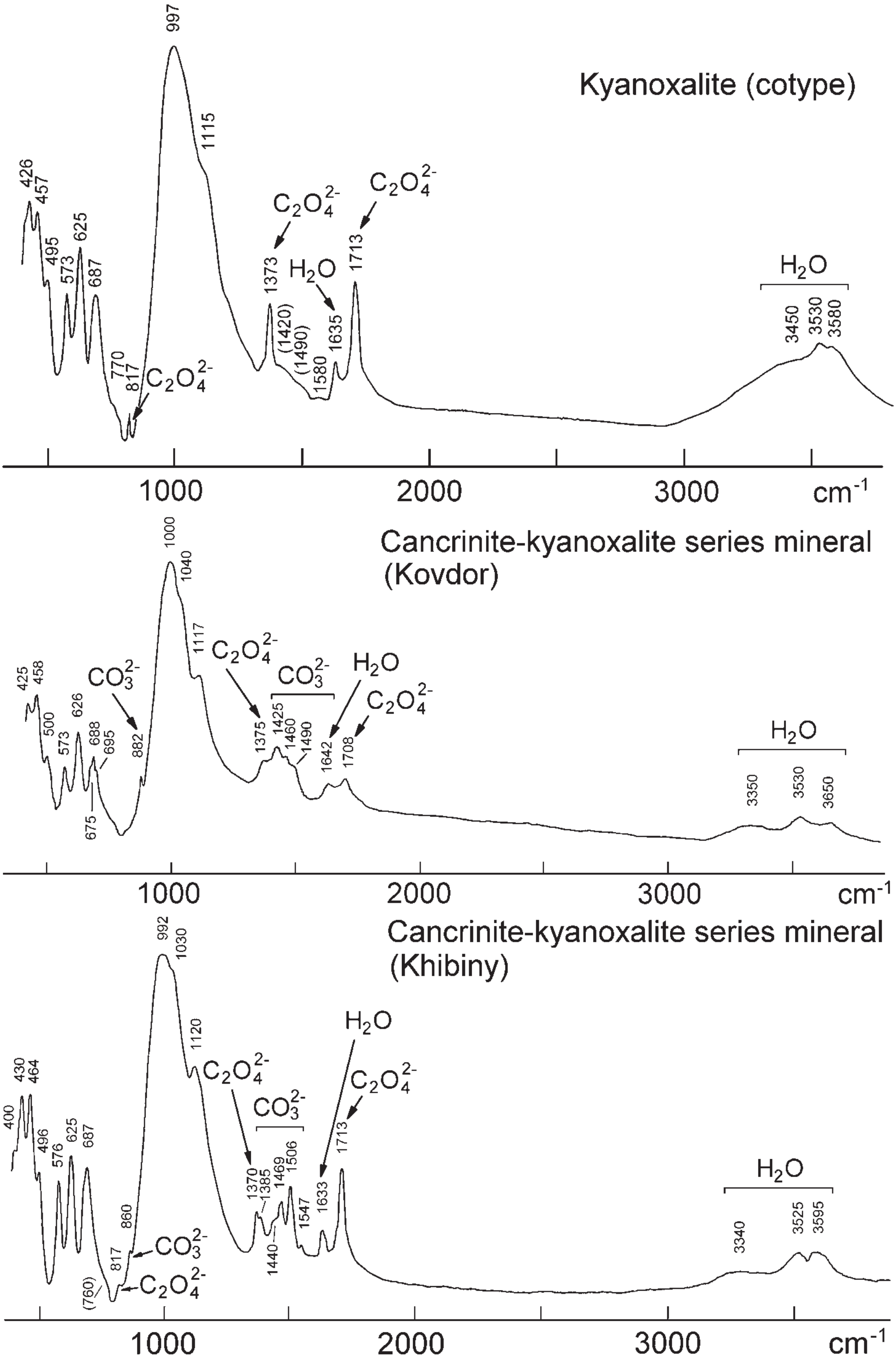

FIG. 3. IR spectra of the cotype specimen of kyanoxalite from Mount Alluaiv, Lovozero massif, Kola Peninsula, Russia (a), and minerals of the cancrinite–kyanoxalite series from Kovdor massif, Kola Peninsula, Russia (b), and from Mount Putelichorr, Khibiny massif, Kola Peninsula, Russia (c).

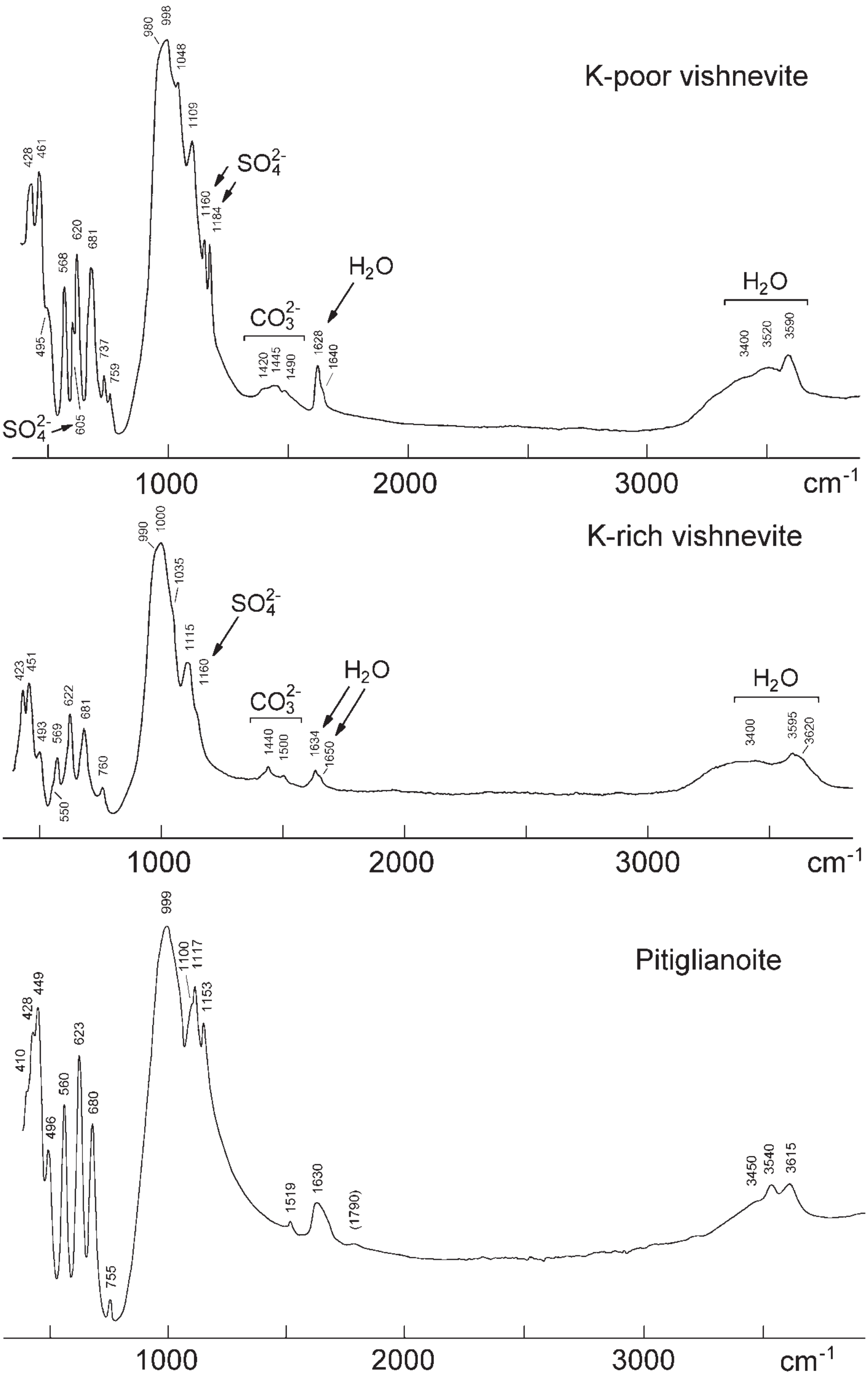

FIG. 4. IR spectra of SO_4-bearing cancrinite-group minerals: vishnevite, K-poor variety from Mount Alluaiv, Lovozero massif, Kola Peninsula, Russia (a), vishnevite, K-rich variety from Murun massif, Siberia, Russia, (b), and pitiglianoite from Monte Cavalluccio, Sacrofano volcanic complex, Latium, Italy (c).

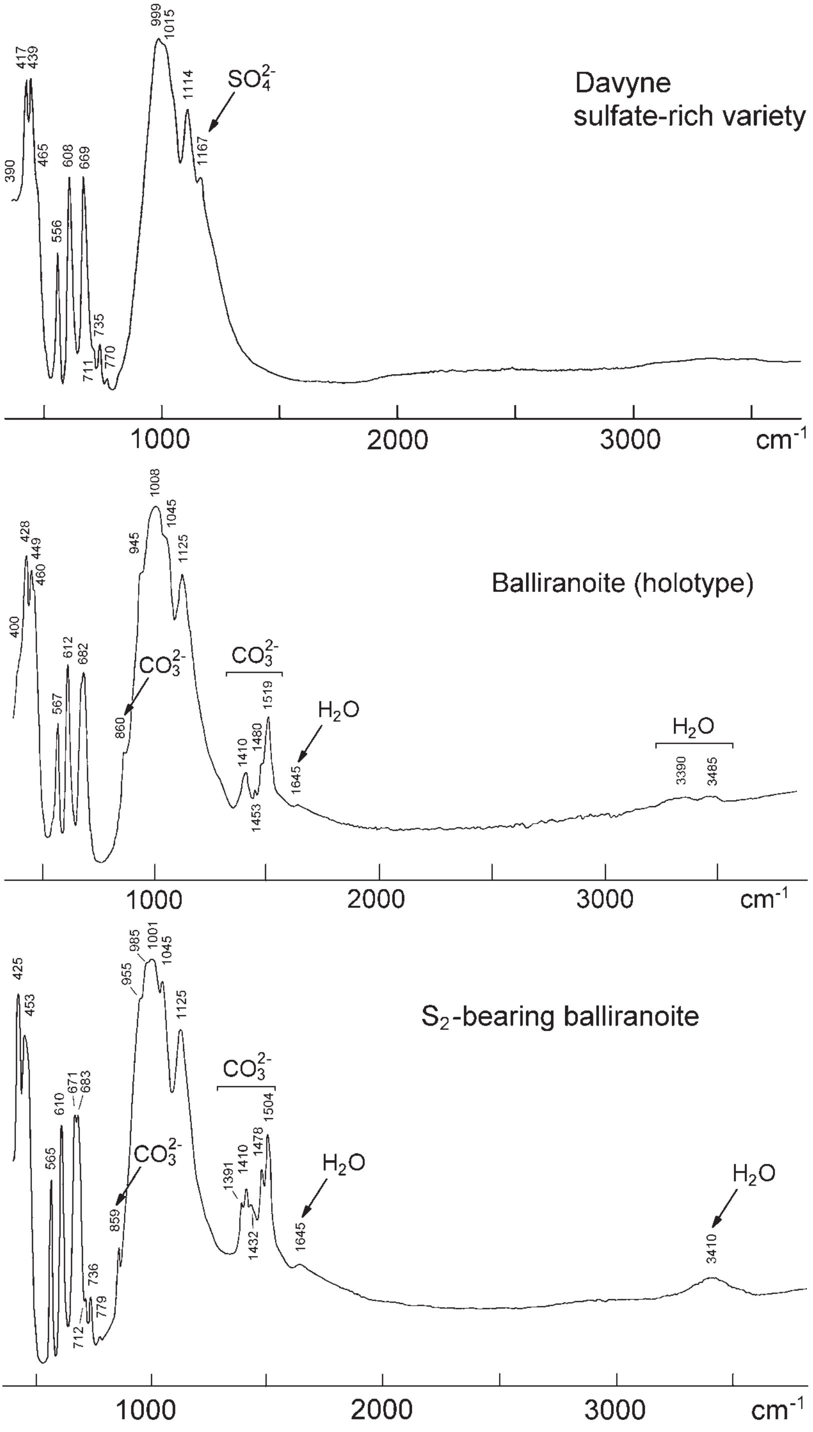

FIG. 5. IR spectra of Cl-bearing cancrinite-group minerals: sulfate-rich variety of davyne from Sar-e-Sang, Afghanistan (a), the holotype specimen of balliranoite from Monte Somma, Vesuvius, Campania, Italy (b), and the S_2-bearing variety of balliranoite from the Tultui lazurite deposit, Lake Baikal area, Siberia, Russia (c).

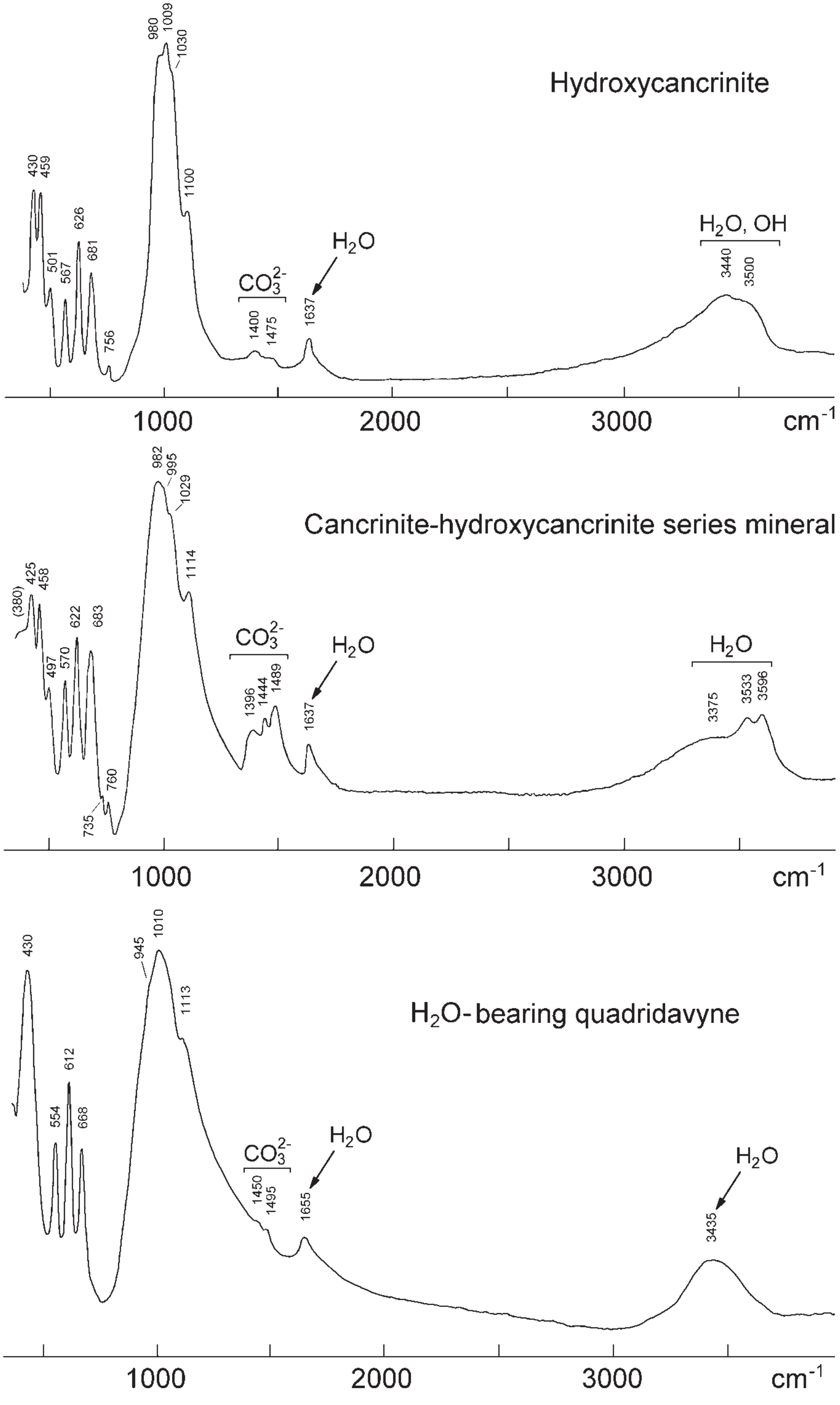

FIG. 6. IR spectra of synthetic hydroxycancrinite (a), intermediate member of the cancrinite–hydroxycancrinite series from Kovdor massif, Kola Peninsula, Russia (b), and H_2O-bearing quadridavyne from Vesuvius, Campania, Italy (c).

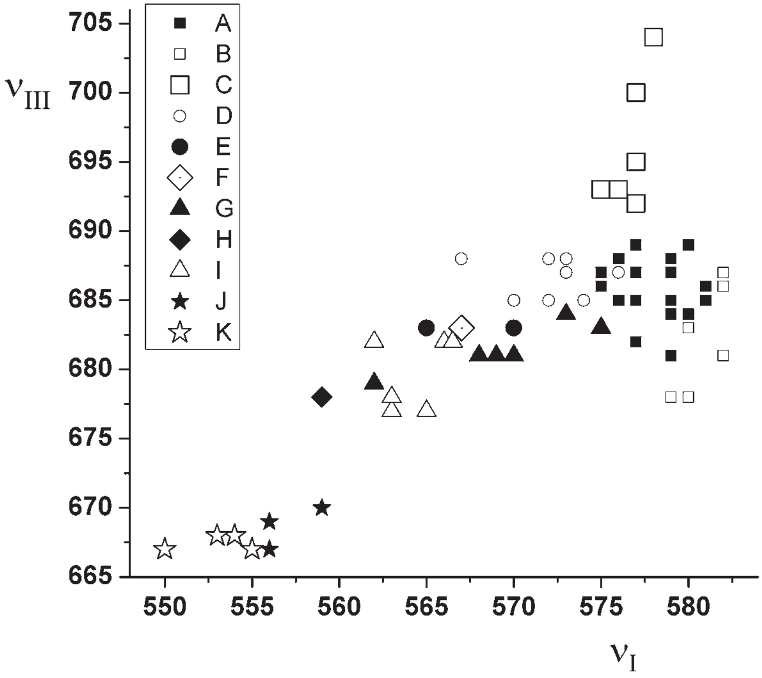

FIG. 7. Wavenumbers of absorption maxima of the bands ν_I and ν_{III} in IR spectra of cancrinite solid-solution (A), H_2O-poor cancrinite (B), cancrisilite (C), kyanoxalite and C_2O_4-rich members of the cancrinite–kyanoxalite series (D), hydroxycancrinite and a CO_3-poor member of the cancrinite–hydroxycancrinite series (E), depmeierite (F), vishnevite (G), pitiglianoite (H), balliranoite and CO_3-rich members of the davyne–balliranoite series (I), davyne (J), and quadridavyne (K).

maximum located between 988 and 1010 cm^{-1}, three narrow bands, ν_I, ν_{II} and ν_{III}, corresponding to mixed vibrations of the framework of tetrahedra (in the ranges 550–581 cm^{-1} for ν_I, 608–630 cm^{-1} for ν_{II} and 667–704 cm^{-1} for ν_{III}), and strong bands of bending vibrations of the framework observed below 500 cm^{-1}. In addition, the IR spectra of cancrinite-group minerals contain absorption bands of oxygen-bearing extra-framework anions and molecules. Their assignment is given below.

RESULTS

The IR bands of mixed vibrations of the framework in the range 500–800 cm^{-1} are very sensitive to the spatial structure of tectosilicates. Cancrinite-group minerals confirm this empirical rule: minerals with an *AB*-type framework show three distinct bands in this range, whereas members of this group with a more complex stacking of layers are characterized by more than three bands of framework mixed vibrations, each type of framework having its own characteristic set of bands. The composition of extra-framework species (cations, anions, and neutral molecules) and their arrangement in channels cause shifts of these bands, as well as the appearance of additional IR absorption maxima.

Framework vibrations

Different mineral species with an *AB*-type framework belonging to the cancrinite group are characterized by individual fields on a diagram plotted in the coordinates ν_I, ν_{III} (Fig. 7). In most cases, regions of overlap between different areas are absent.

Occasionally, in the IR spectra of minerals with an *AB*-type framework, additional splitting of the bands ν_I and ν_{III} is observed whose value does not exceed 12–13 cm^{-1}. Some samples of vishnevite display weak resonance absorption at 605 cm^{-1} (*i. e.*, near the band ν_{II}) related to bending vibrations of SO_4^{2-} anions.

In Figure 7, CO_3-rich varieties of davyne form a common domain with balliranoite; CO_3-rich varieties of vishnevite and kyanoxalite form a common domain with cancrinite.

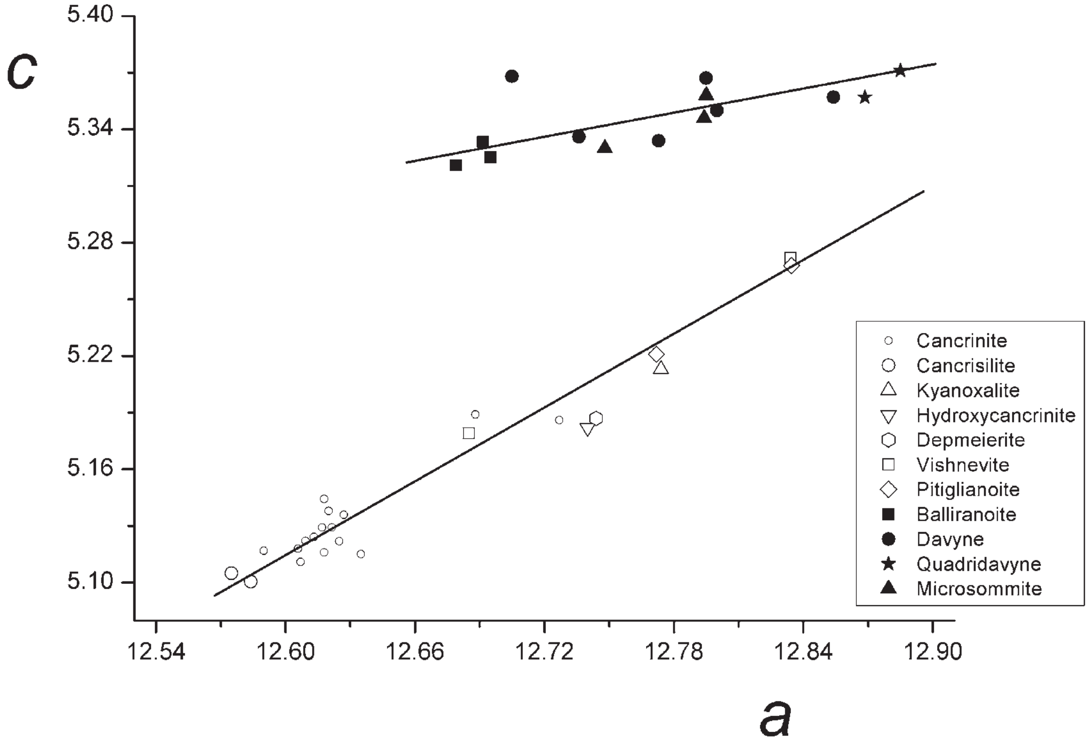

FIG. 8. Correlations between unit-cell parameters of Cl-bearing (upper correlation) and Cl-free (lower correlation) cancrinite-group minerals with an *AB*-type framework whose crystal structures are investigated. For minerals with ordered extra-framework ions, pseudo-cell parameters are used: $a^* = 0.5a\ [\sin(\pi/3)]^{-1}$ (for microsommite and pitiglianoite) and $a^{**} = 0.5a$ (for quadridavyne).

Cancrinite-group minerals with an *AB*-type framework can be subdivided into two series according to the occupant of the narrow channel: the chains ···Na–H_2O···Na–H_2O··· (lower correlation in Fig. 8) and the chains ···Ca–Cl···Ca–Cl··· (upper correlation in Fig. 8). The formation of a continuous solid-solution between members of the two series is not observed.

From the comparative analysis of diagrams given in Figures 7 and 8, one can draw the following conclusions:

1) In general, there is a positive correlation between ν_I and ν_{III} values.

2) An increase of H_2O content in the wide channel, especially if accompanied by an increase in the Si:Al ratio (transition from cancrinite to cancrisilite), results in deviations from this correlation and favors an increase of ν_{III}. In particular, this tendency is observed for cancrisilite, kyanoxalite and the H_2O-rich member of the davyne–balliranoite series.

3) Substitution of CO_3^{2-} for the larger anions SO_4^{2-}, $C_2O_4^{2-}$ or PO_4^{3-}, and substitution of Na^+ for the larger cation K^+ in the wide channel, are accompanied by the enhancement of *a* and *c* unit-cell parameters and by a lowering of ν_I and ν_{III} values.

4) Substitution of $H_2O + Na^+$ for $Cl^- + Ca^{2+}$ in the cancrinite cages results in a strong enhancement of the *c* parameter and in a lowering of both ν_I and ν_{III}.

5) The H_2O-poor varieties of cancrinite (with << 1 H_2O molecules *pfu* in the narrow channels) are characterized by somewhat lower values of ν_{III} as compared with normal varieties with ~2 molecules of H_2O *pfu*.

6) Concentration of Cl in the wide channels (transition from balliranoite and davyne to quadridavyne) results in the enhancement of *a* and in the lowering of ν_I.

Some of these regularities (namely the relationships between *a* and ν_{III}, and between K content and *a*) have been noted elsewhere (Ballirano *et al.* 1996) for davyne-type minerals.

Local vibrations of extra-framework groups

The presence of extra-framework species (molecules and anions) with polar covalent bonds, such as H_2O^0, CO_2^0, CO_3^{2-}, $C_2O_4^{2-}$ or SO_4^{2-}, can be detected in cancrinite-group minerals by characteristic IR bands corresponding to their local vibrations. The IR spectra of all cancrinite-group minerals with an *AB*-type framework and H_2O molecules in the cancrinite cages contain two bands of O–H stretching vibrations in the range of 3520–3615 cm^{-1}, corresponding to relatively weak hydrogen bonds. Absorption maxima of these bands are located in the ranges 3580–3615 and 3520–3535 cm^{-1}. According to single-crystal FTIR data for vishnevite from Latium, Italy (Della Ventura *et al.* 2007), the former band is strongly polarized for $\mathbf{E} \perp \mathbf{c}$, whereas the latter one behaves in an almost isotropic fashion. In the H_2O molecules present in the cancrinite cages, one O–H bond (corresponding to the high-frequency component) is oriented along **c**, whereas another one (with a hydrogen atom involved in stronger hydrogen bonds and corresponding to the low-frequency component in the range 3520–3535 cm^{-1}) can have different orientations. The assignment of these two bands to symmetric and asymmetric vibrations involving both O–H bonds of the H_2O molecule must be excluded because in this case, both bands would be polarized or both bands would behave isotropically. The corresponding band of H–O–H bending vibrations is located between 1628 and 1633 cm^{-1}.

In samples with $Cl^- \leq 2$ *pfu*, all chlorine is situated in cancrinite cages. In particular, in samples with $Cl^- <$ 2 *pfu* and $(H_2O + Cl^-) > 2$ *pfu*, all Cl and part of H_2O are present in cancrinite cages, amounting there to 2 *pfu* $(H_2O + Cl^-)$ in total. Excessive H_2O molecules occupy sites in the wide channel. As a result, IR spectra of most such samples contain an additional broad band of O–H stretching vibrations corresponding to strong hydrogen bonds, whose maximum is located between 3320 and 3450 cm^{-1}. The broad band at 3320 cm^{-1} present in the IR spectrum of vishnevite and predominantly polarized for $\mathbf{E} \parallel \mathbf{c}$ was assigned to additional OH groups (Della Ventura *et al.* 2007). This assignment seems questionable if one takes into account the absence of high-field-strength cations and strong acceptors of hydrogen bonds in the wide channel. Moreover, the presence of the band in the range 3320–3450 cm^{-1} is usually accompanied by a high-frequency shift of the band of H–O–H bending vibrations, or by the appearance of high-frequency shoulder of this band indicating the presence of different H_2O molecules.

In the IR spectrum of cancrinite investigated by Della Ventura *et al.* (2009), both bands (at 3602 and 3531 cm^{-1}) have the same polarization and correspond to H_2O molecules involved in bifurcated hydrogen bonds.

An almost anhydrous cancrinite-like mineral, with the chains ···Na–□···Na–□··· in narrow channels formed by cancrinite cages was discovered by us in effusive rocks of Bellerberg, Eifel volcanic area, Germany (Chukanov *et al.* 2009a). Its IR spectrum is characterized by the absence of bands of H_2O in the range 1600–3700 cm^{-1} and rather poor resolution of the bands of CO_3 groups in the range 1390–1505 cm^{-1} (Fig. 1c). We believe that this mineral is a product of the thermal dehydration of common H_2O-bearing cancrinite.

As shown by Hassan *et al.* (2006), the dehydration of cancrinite starts at a temperature of 200°C and is completed at 625°C. Discontinuities of first derivatives of the dependences of unit-cell parameters *a* and *c* on temperature at 504°C are caused by a structural transformation consisting of the disordering of [Ca–CO_3] clusters and their vacancies. Anhydrous cancrinite with an almost constant occupancy-factor for CO_3 is stable in the temperature interval 625–952°C.

The structure refinement of pitiglianoite at 457°C shows that all H_2O was released from the narrow channel (Bonaccorsi *et al.* 2007). The relatively low temperature of dehydration of pitiglianoite can have both a steric and an energetic origin. Indeed, pitiglianoite, as compared with cancrinite, is characterized by larger unit-cell parameters (Fig. 8) and a higher wavenumber of the low-frequency component of the doublet of O–H stretching vibrations (of 3540 cm^{-1}), corresponding to a weaker hydrogen bond (Fig. 3c).

Although the accepted formula of quadridavyne $[(Na,K)_6Cl_2](Ca_2Cl_2)(Si_6Al_6O_{24})$, does not contain H_2O, some varieties of this mineral show a relatively strong broad band at 3430–3440 cm^{-1} and a distinct band at 1650–1660 cm^{-1}, both corresponding to H_2O molecules in the wide channel (Fig. 6c).

Della Ventura *et al.* (2005) provided IR spectroscopic evidence for the presence of CO_2 molecules in channels of pitiglianoite from Monte Cavalluccio, Sacrofano volcanic complex, Latium, Italy, using single-crystal micro-FTIR technique. Asymmetric O–C–O vibrations give a very weak narrow band at 2351 cm^{-1} that is strongly polarized for $\mathbf{E} \perp \mathbf{c}$, indicating that linear CO_2 molecules form almost at a right angle with the **c** axis. The estimated content of CO_2 in the sample studied is about 0.06 wt%. The release of CO_2 from pitiglianoite starts at temperatures >250° and is complete at ~450°C.

The carbonate anion is the most common carbon-bearing extra-framework species in cancrinite-group minerals. Ideally, the anion CO_3^{2-} is planar and has the D_{3h} symmetry. Thus its three modes are active in an IR spectrum: $\nu_2(A''_2)$ (out-of-plane non-degenerate bending mode, typical wavenumber range is 840–880 cm^{-1}), $\nu_3(E')$ (doubly degenerate asymmetric stretching mode; corresponding bands are usually observed in the range 1370–1530 cm^{-1}), and $\nu_4(E')$ (doubly degenerate in-plane bending mode, typical wavenumber range is 690–750 cm^{-1}). The stretching mode $\nu_1(A'_1)$ (non-degenerate stretching vibrations with wavenumbers ~1050–1090 cm^{-1}) can be active only where the D_{3h} symmetry of the anion CO_3^{2-} is distorted.

Most samples of cancrinite whose crystal structures have been investigated have two or four localized sites of carbonate groups (Pekov *et al.* 2011). Their

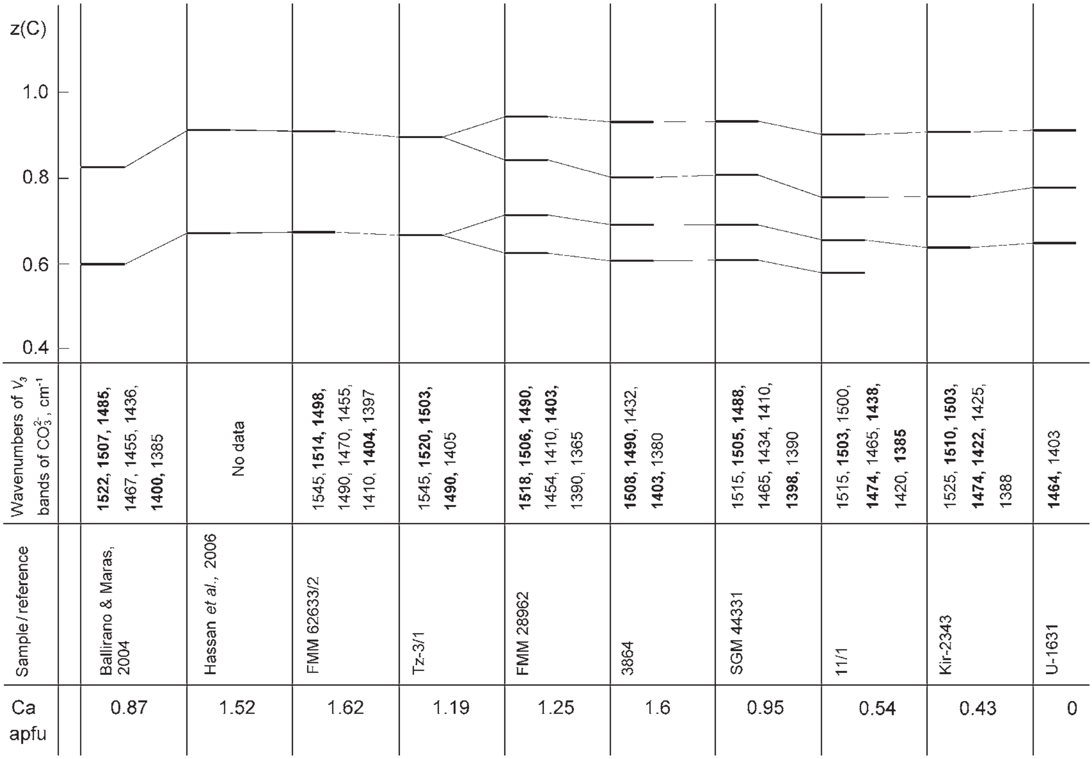

Fig. 9. The values of the *z* coordinate of CO_3 groups and wavenumbers of ν_3 bands in cancrinite and cancrisilite. Wavenumbers of the strongest bands are given in bold type.

location is shown schematically in Figure 9. Only Ca-poor sample kir2343 (transitional to cancrisilite by composition) has three sites of carbonate groups that are close to that localized in cancrisilite sample u1631. In "disordered cancrinite" (Ballirano & Maras 2004), the groups CO_3^{2-} occupy two sites surrounded by three extra-framework cations that occupy the site *A* split into two subsites, *A*' and *A*". There are several tens of variants of the distribution of extra-framework cations and vacancies between these subsites around each carbonate group, hence there are several tens of local situations that can be realized for the groups CO_3^{2-}. However, owing to the overlap of individual bands and low statistical weight of some local situations, only eight absorption maxima and shoulders (inflection points) are observed on the spectral curve of this sample in the region of ν_3(E') vibrations.

The content of Ca in cancrinite is the most important factor in determining characteristics of the IR spectrum in the range of C–O stretching vibrations. In the IR spectrum of Ca-free cancrisilite, only one strong band of C–O stretching vibrations is observed at $\nu_3^* = 1464$ cm^{-1}. An enrichment in Ca from 0 to 0.54 *apfu* is accompanied by the shift of the band ν_3^* toward 1474 cm^{-1} and by the appearance and growth of additional ν_3 bands, the most intense of which are observed in the ranges 1385–1422 and 1500–1510 cm^{-1}. All these minerals (including cancrisilite) have CO_3^{2-} groups having *z* coordinates in the ranges 0.64–0.66, 0.76–0.78 and 0.90–0.915. An additional CO_3^{2-} group with a *z* coordinate of 0.58 exists in the sample with a Ca content equal to 0.54 *apfu.*

Samples with intermediate contents of Ca have CO_3^{2-} groups with $z = 0.60–0.61$ and $z = 0.81–0.825$; additional CO_3^{2-} groups with $z = 0.69$ and $z = 0.935$ are present in "disordered cancrinite" (Ballirano & Maras 2004). For these samples, the maximum of the band ν_3^* is located at 1485–1488 cm^{-1}.

Further increase of Ca content is accompanied by the subsequent high-frequency shift of the band ν_3^* to 1490–1498 cm^{-1} (for samples with $Ca_{1.19–1.62}$). In high-calcium samples, two sites of carbonate groups are present, with $z = 0.67–0.68$ and $z = 0.90–0.92$. Each of these sites can be split into two subsites (Fig. 9).

A gradual shift of the band ν_3^* from 1474 to 1498 cm^{-1} with an increase of Ca content in cancrinite from 0.43 to 1.62 *apfu* indicates that this band reflects local situations in which Ca coordinates the group CO_3^{2-}. At low Ca contents, the clusters $Na_2Ca(CO_3)$ are mainly isolated from each other, *i.e.*, in most cases the neighboring clusters are $Na_3(CO_3)$. At high contents of Ca, there are linear sequences $C_{Na}(C_{Ca})_nC_{Na}$ of Ca-bearing clusters C_{Ca} confined by Ca-free ones, which results in the generation of chain vibrations due to the resonance between ν_3-type vibrations of neighboring $Na_2Ca(CO_3)$ clusters. This vibrational problem was solved by us earlier (Loghinov *et al.* 1979, Chukanov & Kumpanenko 1988). The solution of a secular equation results in the following analytical expression for the dependence of the wavenumber ν_3* of the IR-active band of chain vibrations on *n*:

$$\nu_3{}^*(n)^2 = \nu_3{}^*(1)^2 + d{\cdot}\cos[\pi:(n+1)]$$

where $\nu_3{}^*(1) = 1474$ cm^{-1} is the wavenumber of the ν_3 mode of an isolated cluster; the parameter *d* is the element of the dynamic matrix corresponding to the resonance interaction between ν_3 modes of neighboring $Na_2Ca(CO_3)$ clusters. The value *d* can be estimated from the condition $\nu_3{}^*(\infty)^2 = 1474^2 + d$, where $\nu_3{}^*(\infty) \approx 1498$ cm^{-1} is limiting ν_3* value for high-calcium cancrinite.

The IR spectra of all $CO_3{}^{2-}$-rich cancrinite-group minerals contain a narrow single band $\nu_2(A''_2)$ with a maximum located typically between 857 and 865 cm^{-1}. This band is not relevant as a diagnostic tool.

Oxalate groups, $C_2O_4{}^{2-}$, were first detected in cancrinite-group minerals by us using IR spectroscopy. The presence of these groups in species-defining amount in kyanoxalite was confirmed by the combination of various methods, including single-crystal structural investigation, anionic chromatography, thermogravimetry and IR-controlled data on the oxidation of $C_2O_4{}^{2-}$ to $CO_3{}^{2-}$ in channels (Chukanov *et al.* 2009b, Olysych *et al.* 2011).

The absorption bands of oxalate groups in the IR spectra of kyanoxalite and $C_2O_4{}^{2-}$-bearing cancrinite (Fig. 3) are observed in the ranges 1702–1713 cm^{-1} (anti-symmetric C–O stretching mode of carboxylate groups –COO), 1369–1373 cm^{-1} (symmetric C–O stretching mode of carboxylate groups), and ~817 cm^{-1} (bending vibrations of carboxylate groups). The C–C stretching vibrations of oxalate anions are inactive in the IR spectra because the dipole moment of this bond is equal to 0.

Sulfate groups, $SO_4{}^{2-}$, present in major amounts in cancrinite-group minerals with an *AB*-type framework, can be detected by the presence of absorption maxima or shoulders in the range 1150–1190 cm^{-1} corresponding to asymmetric S–O stretching vibrations of SO_4 tetrahedra (Fig. 4). Rarely, a band of bending vibrations of SO_4 tetrahedra is observed near 605 cm^{-1} (Fig. 4a). However, in most cases, the SO_4 bending bands, as well as the SO_4 stretching bands below 1150 cm^{-1}, are masked by stronger bands of the framework. For the same reason (*i.e.*, overlap with strong bands of the framework), absorption maxima of phosphate groups, $PO_4{}^{3-}$, are unobserved in the IR spectrum of depmeierite.

CONCLUSIONS

1) For cancrinite-group minerals with an *AB*-type framework (cancrinite, cancrisilite, kyanoxalite, hydroxycancrinite, depmeierite, vishnevite, pitiglianoite, balliranoite, davyne, quadridavyne), a powder IR spectrum is an important diagnostic tool. A comprehensive collection of IR spectra of well-studied reference samples presented in the paper makes it possible to identify mineral species and some important varieties of these minerals, including anhydrous cancrinite, low- and high-calcium cancrinite, K-rich and K-poor vishnevite, as well as intermediate members of solid-solution series between different mineral species.

2) A positive correlation between the parameters ν_I and ν_{III} is established in the series of minerals with different extra-framework anions; both parameters increase in the sequence: $Cl^- \rightarrow SO_4{}^{2-}, PO_4{}^{3-}, OH^- \rightarrow C_2O_4{}^{2-} \rightarrow CO_3{}^{2-}$. Deviations from this correlation to higher or lower values of ν_{III} is connected with higher or lower contents of H_2O, respectively.

3) The same sequence $Cl^- \rightarrow SO_4{}^{2-}, PO_4{}^{3-}, OH^- \rightarrow C_2O_4{}^{2-} \rightarrow CO_3{}^{2-}$, as well as the replacement of extra-framework cations in the sequence K → Ca → Na, correspond to a decrease in the unit-cell parameter *c*.

4) A gradual shift of the band ν_3* of asymmetric C–O stretching vibrations from 1474 to 1498 cm^{-1} with an increase in Ca content in cancrinite from 0.43 to 1.62 *apfu* is interpreted in the context of the cluster approach.

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