

## MALEEVITE, $\text{BaB}_2\text{Si}_2\text{O}_8$ , AND PEKOVITE, $\text{SrB}_2\text{Si}_2\text{O}_8$ , NEW MINERAL SPECIES FROM THE DARA-I-PIOZ ALKALINE MASSIF, NORTHERN TAJIKISTAN: DESCRIPTION AND CRYSTAL STRUCTURE

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### ABSTRACT

Maleevite, ideally  $\text{BaB}_2\text{Si}_2\text{O}_8$ , and pekovite, ideally  $\text{SrB}_2\text{Si}_2\text{O}_8$ , are two new mineral species found in boulders in the moraine of the Dara-i-Pioz glacier, the Alai range, Tien Shan, Garmskii district, northern Tajikistan. Both minerals occur as anhedral equant crystals from 0.5 to 2 mm in diameter. Crystals of both minerals are white to transparent with a white streak and a vitreous luster. Maleevite occurs in aegirine – microcline – quartz pegmatite in syenites with arfvedsonite, polyolithionite, reedmergnerite, cesium-kupletskite, hyalotekite, albite, dusmatovite, pyrochlore, tadjhikite, tienshanite, sogdianite, stillwellite-(Ce), leucosphenite, leucophanite, willemite, danburite, zektzerite, berezanskite, baotite, cappelenite-(Y) and an unknown Y–Ca silicate. Pekovite occurs in a rock consisting mainly of quartz with subordinate pectolite, aegirine, stillwellite-(Ce), polyolithionite, leucosphenite and reedmergnerite. More rarely, turkestanite, galena, calcite, kapitsaite-(Y), neptunite, sugilite, baratovite, bismuth, sphalerite, fluorite, pyrochlore, fluorapatite, and zeravshanite occur in the same rock. Pekovite commonly forms intergrowths with pectolite, quartz, strontian fluorite and aegirine. Maleevite fluoresces intense blue in short-wave ultraviolet light. Maleevite and pekovite show no cleavage, have a Mohs hardness of 7, and are brittle with uneven fracture. The observed and calculated densities are as follows: maleevite,  $D(\text{obs.}) = 3.78(1)$ ,  $D(\text{calc.}) = 3.79$ ; pekovite,  $D(\text{obs.}) = 3.35(2)$ ,  $D(\text{calc.}) = 3.36$  g/cm<sup>3</sup>. Maleevite is colorless in transmitted light, biaxial negative, with  $\alpha$  1.649(2),  $\beta$  1.656(2),  $\gamma$  1.656(2),  $2V(\text{obs.}) = 5(3)^\circ$ ,  $2V(\text{calc.}) = 0^\circ$ . Pekovite is colorless in transmitted light, biaxial negative, with  $\alpha$  1.597(2),  $\beta$  1.627(3),  $\gamma$  1.632(2),  $2V(\text{obs.}) = 43(3)^\circ$ ,  $2V(\text{calc.}) = 44^\circ$ . Both maleevite and pekovite are orthorhombic, with space-group symmetry  $Pnma$ ,  $Z = 4$ , and the following unit-cell dimensions: maleevite:  $a$  8.141(2),  $b$  8.176(2),  $c$  9.038(2) Å,  $V$  601.6(2) Å<sup>3</sup>; pekovite:  $a$  8.155(2),  $b$  7.919(1),  $c$  8.921(2) Å,  $V$  576.1(2) Å<sup>3</sup>. The strongest seven lines in the X-ray powder-diffraction patterns [ $d$  (in Å)/( $hkl$ )] are: maleevite: 3.62(10)(210), 2.021(7)(033), 6.07(6)(011), 3.39(6)(121), 2.83(5)(013), 2.481(4)(131), 4.86(3)(111); pekovite: 3.62(10)(210), 3.51(9)(112), 2.786(9)(103,013,122), 3.31(8)(121), 1.982(7)(232), 5.94(6)(011), 3.01(6)(202). Chemical analysis by electron microprobe gave: maleevite:  $\text{SiO}_2$  34.86,  $\text{B}_2\text{O}_3$  19.92,  $\text{BaO}$  43.64,  $\text{PbO}$  0.42, sum 98.84 wt.% (maleevite can contain up to 16.08 wt.% PbO); pekovite:  $\text{SiO}_2$  41.56,  $\text{B}_2\text{O}_3$  23.39,  $\text{SrO}$  34.15,  $\text{CaO}$  0.38, sum 99.48 wt.%. The resulting empirical formulae on the basis of 8 anions are as follows: maleevite:  $(\text{Ba}_{0.99}\text{Pb}_{0.01})\text{B}_{1.99}\text{Si}_{2.01}\text{O}_8$ ; pekovite:  $(\text{Sr}_{0.97}\text{Ca}_{0.02})\text{B}_{1.97}\text{Si}_{2.02}\text{O}_8$ . The crystal structures of both minerals were solved by direct methods and refined to  $R_1$  indices of 2.2 (maleevite) and 3.2% (pekovite) based on 879 (maleevite) and 705 (pekovite) observed unique reflections. In the crystal structures of maleevite and pekovite, there are two tetrahedrally coordinated sites: the  $T(1)$  site is occupied by boron with  $\langle T(1)\text{--O} \rangle = 1.473$  (maleevite) and 1.474 (pekovite) Å; the  $T(2)$  site is occupied by silicon with  $\langle T(2)\text{--O} \rangle = 1.617$  (maleevite) and 1.619 (pekovite) Å. Tetrahedra form a framework with channels extending along [010]. The topology of the framework is identical to that of danburite,  $\text{CaB}_2\text{Si}_2\text{O}_8$ . In the crystal structure of maleevite, Ba can be regarded as [7]- or [10]-coordinated, with  $\langle \text{Ba--O} \rangle = 2.749$  or 2.863 Å; in the crystal structure of pekovite, Sr can be regarded as [7]- or [9]-coordinated, with  $\langle \text{Sr--O} \rangle = 2.582$  or 2.693 Å. In danburite, Ca is [7]- or [9]-coordinated,  $\langle \text{Ca--O} \rangle = 2.460$  or 2.585 Å. Maleevite and pekovite are the Ba and Sr analogues of danburite.

**Keywords:** maleevite, pekovite, new mineral species, danburite, crystal structure, chemical analysis, Dara-i-Pioz, Tien Shan, Tajikistan.

### SOMMAIRE

La maleevite, de formule idéale  $\text{BaB}_2\text{Si}_2\text{O}_8$ , et la pékovite, de formule idéale  $\text{SrB}_2\text{Si}_2\text{O}_8$ , sont des nouvelles espèces découvertes dans des blocs d'une moraine du glacier Dara-i-Pioz, dans la chaîne de montagnes Alai, Tien Shan, district de Garmskii, dans le nord du Tadjikistan. Les cristaux des deux minéraux sont équidimensionnels et xénomorphes, et entre 0.5 to 2

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mm de diamètre. Ils sont blancs ou transparents, avec un rayure blanche et un éclat vitreux. La maleevite, trouvée dans un bloc de pegmatite à aegyrine – microcline – quartz dans une syénite, est associée à arfvedsonite, polyolithionite, reedmergnerite, césium-kupletskite, hyalotékite, albite, dusmatovite, pyrochlore, tadjzhikite, tienshanite, sogdianite, stillwellite-(Ce), leucosphénite, leucophanite, willémitte, danburite, zektzérîte, bérézanskite, baotite, cappelénite-(Y) et un silicate à Y–Ca méconnu. La pékovite se présente dans une roche faite surtout de quartz, avec pectolite, aegyrine, stillwellite-(Ce), polyolithionite, leucosphénite et reedmergnerite comme phases accessoires. Plus rares dans la même roche sont: turkestanite, galène, calcite, kapitsaïte-(Y), neptunite, sugilite, baratovite, bismuth, sphalérite, fluorite, pyrochlore, fluorapatite, et zeravshanite. La pékovite forme une intercroissance avec pectolite, quartz, fluorite strontifère et aegyrine. La maleevite montre une fluorescence bleue intense en lumière ultraviolette à courte longueur d'onde. La maleevite et la pékovite ne montrent aucun clivage, possèdent une dureté de Mohs de 7, et sont cassantes, avec une fracture inégale. Les densités observées et calculées sont comme suit: maleevite,  $D(\text{obs.}) = 3.78(1)$ ,  $D(\text{calc.}) = 3.79$ ; pékovite,  $D(\text{obs.}) = 3.35(2)$ ,  $D(\text{calc.}) = 3.36 \text{ g/cm}^3$ . La maleevite est incolore en lumière transmise, biaxe négative, avec  $\alpha 1.649(2)$ ,  $\beta 1.656(2)$ ,  $\gamma 1.656(2)$ ,  $2V(\text{obs.}) = 5(3)^\circ$ ,  $2V(\text{calc.}) = 0^\circ$ . La pékovite est incolore en lumière transmise, biaxe négative, avec  $\alpha 1.597(2)$ ,  $\beta 1.627(3)$ ,  $\gamma 1.632(2)$ ,  $2V(\text{obs.}) = 43(3)^\circ$ ,  $2V(\text{calc.}) = 44^\circ$ . Les deux minéraux sont orthorhombiques, groupe spatial  $Pnma$ ,  $Z = 4$ , avec les dimensions de la maille suivantes: maleevite:  $a 8.141(2)$ ,  $b 8.176(2)$ ,  $c 9.038(2) \text{ \AA}$ ,  $V 601.6(2) \text{ \AA}^3$ ; pékovite:  $a 8.155(2)$ ,  $b 7.919(1)$ ,  $c 8.921(2) \text{ \AA}$ ,  $V 576.1(2) \text{ \AA}^3$ . Les sept raies les plus intenses du spectre de diffraction X (méthode des poudres) [ $d$  (en  $\text{\AA}$ )] ( $hkl$ ) sont: maleevite: 3.62(10)(210), 2.021(7)(033), 6.07(6)(011), 3.39(6)(121), 2.83(5)(013), 2.481(4)(131), 4.86(3)(111); pékovite: 3.62(10)(210), 3.51(9)(112), 2.786(9)(103,013,122), 3.31(8)(121), 1.982(7)(232), 5.94(6)(011), 3.01(6)(202). Une analyse chimique effectuée avec une microsonde électronique a donné: maleevite:  $\text{SiO}_2 34.86$ ,  $\text{B}_2\text{O}_3 19.92$ ,  $\text{BaO} 43.64$ ,  $\text{PbO} 0.42$ , somme 98.84% (la maleevite peut contenir jusqu'à 16.08%  $\text{PbO}$ ); pékovite:  $\text{SiO}_2 41.56$ ,  $\text{B}_2\text{O}_3 23.39$ ,  $\text{SrO} 34.15$ ,  $\text{CaO} 0.38$ , somme 99.48% (poids). Les formules empiriques qui en résultent, sur une base de huit anions, sont comme suit: maleevite:  $(\text{Ba}_{0.99}\text{Pb}_{0.01})\text{B}_{1.99}\text{Si}_{2.01}\text{O}_8$ ; pékovite:  $(\text{Sr}_{0.97}\text{Ca}_{0.02})\text{B}_{1.97}\text{Si}_{2.02}\text{O}_8$ . Nous avons résolu la structure cristalline des deux minéraux par méthodes directes et nous les avons affinés jusqu'à un résidu  $R_1$  de 2.2 (maleevite) et 3.2% (pékovite) en utilisant 879 (maleevite) et 705 (pékovite) réflexions uniques observées. Dans ces structures, il y a deux sites à coordinence tétraédrique: le site  $T(1)$  contient le bore, avec  $\langle T(1)-O \rangle = 1.473$  (maleevite) et 1.474 (pékovite)  $\text{\AA}$ ; le site  $T(2)$  contient le silicium, avec  $\langle T(2)-O \rangle = 1.617$  (maleevite) et 1.619 (pékovite)  $\text{\AA}$ . Les tétraèdres sont agencés en trame avec des canaux le long de  $[010]$ . La topologie de cette trame est identique à celle de la danburite,  $\text{Ca B}_2\text{Si}_2\text{O}_8$ . Dans la structure de la maleevite, on peut considérer la coordinence du Ba égale à [7] ou [10], avec  $\langle \text{Ba}-O \rangle$  égal à 2.749 ou 2.863  $\text{\AA}$ ; dans la structure de la pékovite, on peut considérer la coordinence du Sr égale à [7] ou [9], avec  $\langle \text{Sr}-O \rangle$  égal à 2.582 ou 2.693  $\text{\AA}$ . Dans la danburite, le Ca possède une coordinence [7] ou [9], et  $\langle \text{Ca}-O \rangle$  est égal à 2.460 ou 2.585  $\text{\AA}$ . La maleevite et la pékovite sont les analogues de la danburite, à dominance de Ba et de Sr, respectivement.

(Traduit par la Rédaction)

**Mots-clés:** maleevite, pékovite, nouvelles espèces minérales, danburite, structure cristalline, analyse chimique, Dara-i-Pioz, Tien Shan, Tadjikistan.

## INTRODUCTION

Maleevite, ideally  $\text{Ba B}_2\text{Si}_2\text{O}_8$ , and pekovite, ideally  $\text{Sr B}_2\text{Si}_2\text{O}_8$ , are new minerals isostructural with danburite,  $\text{Ca B}_2\text{Si}_2\text{O}_8$  (Phillips *et al.* 1974). They were discovered in the moraine of the Dara-i-Pioz glacier, the Alai range, Tien Shan, northern Tajikistan. The homovalent isomorphous substitution  $\text{Ca} \leftrightarrow \text{Sr} \leftrightarrow \text{Ba}$  is fairly common in several groups of minerals, *e.g.*, the aragonite group, the barite group, the apatite group, the feldspar group.

These two new minerals were approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association. Maleevite (IMA 2002–027) is named after the Bulgarian mineralogist Mikhail Naidenovitch Maleev (born 1940), a well-known expert on the morphology of crystals and mineral systematics. Pekovite (IMA 2003–035) is named after the Russian mineralogist Igor Viktorovich Pekov (born 1967), a well-known expert on the mineralogy of alkaline rocks. The holotype specimens have been deposited in the collection of the A.E. Fersman Mineralogical Museum, Russian Academy of Science, Moscow,

Russia. Here, we report the new mineral description and crystal chemistry of pekovite and maleevite.

## OCCURRENCE

Maleevite and pekovite were found in rocks collected by the authors (LAP and AAA) and V.Yu. Karpenko and M.V. Khvorov. The glacier descends from the southern slope of the Igla Mountain (5301.2 m above sea level), which is situated at the intersection of the Turkestan, Alai and Zeravshan mountain ranges. Fragments of alkaline rocks and pegmatites of the upper Dara-i-Pioz massif occur in the moraine of the glacier. The massif is known for very high contents of boron (Dusmatov 1968). The mineralogical consequence of this fact is the widespread and varied occurrence of boron minerals. Currently, there are 17 boron-bearing mineral species known from the Upper Dara-i-Pioz massif, and seven minerals, tienshanite, tadjzhikite-(Y), tadjzhikite-(Ce), kapitsaite-(Y), "calciborasilite", maleevite and pekovite were first described from this massif. Note that along with maleevite and pekovite, danburite also occurs at the Dara-i-Pioz, and it contains only trace amounts of B and Sr.

Maleevite was found in a single slightly rounded block of pegmatite in syenite,  $1 \times 0.8 \times 0.7$  m in dimensions. This pegmatite is a medium- to coarse-grained leucocratic rock that consists mainly of quartz, microcline and aegirine. Arfvedsonite, polyolithionite, reedmergnerite, cesium-kupletskite, hyalotekite, albite, dusmatovite, pyrochlore, tadzhikite, tienshanite, sogdianite, stillwellite-(Ce), leucosphenite, leuco-

phanite, willemite, danburite, zektzerite, berezanskite, baotite, cappelenite-(Y) and an unknown Y-Ca silicate are less abundant. Maleevite occurs as anhedral equant crystals from 0.5 to 2 mm in diameter, and rarely as tabular grains in quartz (Fig. 1).

Pekovite was found in a block of quartz. These blocks are rounded to various degrees and vary from 0.2 to 2.0 m in diameter. The genesis of these quartz

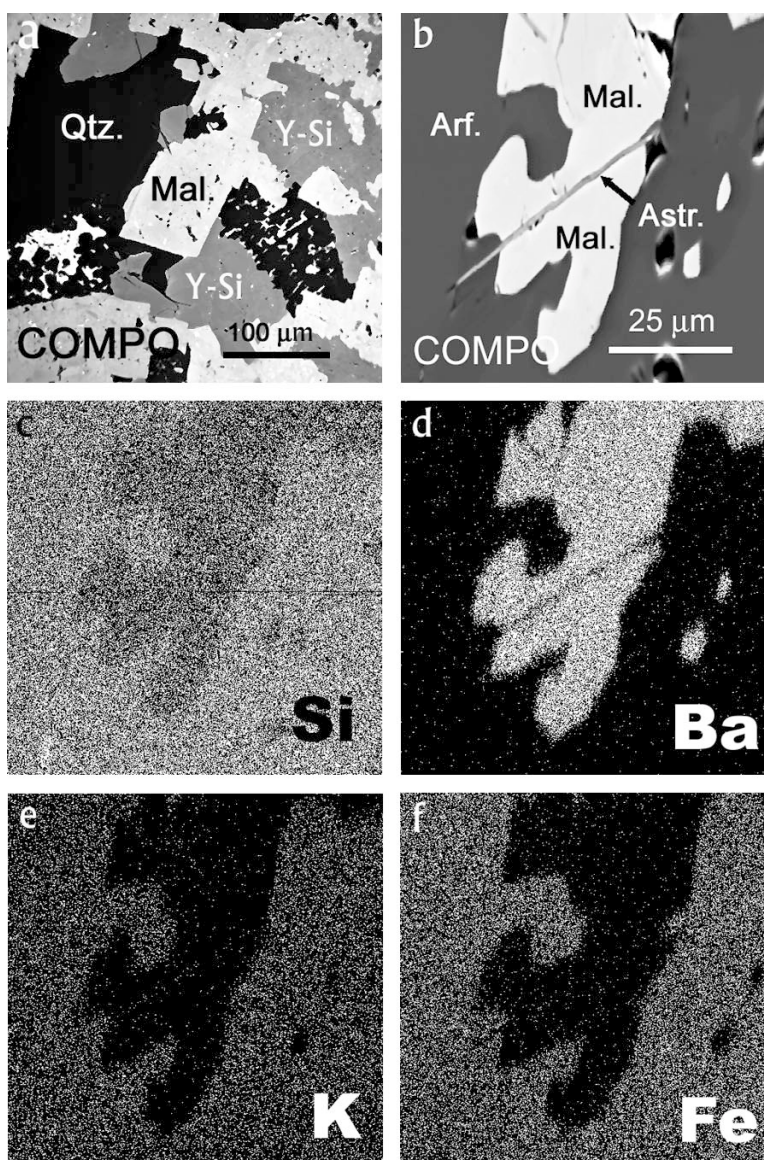


FIG. 1. (a) An intergrowth of maleevite (Mal) and quartz (Qtz) and unknown Y-silicate (Y-Si); (b) maleevite (Mal) in arfvedsonite and astrophyllite (Astr); (c, d, e, f) images using characteristic X-ray radiation for Si, Ba, K and Fe.

blocks is not clear; they could be fragments of quartz cores of pegmatites or fragments of veins. Unfortunately, none of these quartz blocks show contacts with other rocks. Because of the very intensely rugged relief, no bedrock of this type has yet been described. These quartz blocks consist mainly of medium- to coarse-grained granulated quartz with disseminated large plates of polyolithionite, crystals of microcline, pockets of pale-yellow to pink reedmergnerite, randomly distributed, usually idiomorphic and almost black aegirine crystals, rare lenticular crystals of stillwellite-(Ce), grass-green crystals of leucosphenite, purple-pink plates of sogdianite, dark green elongate prismatic crystals of turkestanite with a high content of  $U^{4+}$  and  $H_2O$ , and polymineralic pockets lined mainly by pectolite. Galena, calcite, kapitsaite-(Y), neptunite, sugilite, pyrochlore, eudialite-group minerals, tadzhikite, baratovite, native bismuth, sphalerite, fluorite, fluorapatite, fluorapophyllite, zeravshanite and several unknown Cs-minerals are less abundant in the quartz blocks. Pekovite occurs as anhedral equant grains from 0.05 to 0.2 mm, commonly intergrown with pectolite, quartz, highly strontian fluorite and aegirine (Fig. 2).

#### PHYSICAL AND OPTICAL PROPERTIES

Crystals of both minerals are macroscopically white and colorless in small grains and thin chips. They are colorless in transmitted light, with a white streak and a vitreous, slightly greasy luster. Maleevite fluoresces bright blue in short-wave ultraviolet light. They show no cleavage, and are brittle with an uneven fracture. The Mohs hardness is 7 for maleevite and 6.5–7 for pekovite. For maleevite, the micro-indentation hardness is 1018 (15 measurements, range 997–1139)  $kg/mm^2$ , and the VHN load is 50 g (the mineral cracks with a larger VHN load); for pekovite, the mean is 953 (14 measurements, range 905–990)  $kg/mm^2$ , and the VHN load is 100 g. The micro-indentation hardness for both minerals was measured with a PMT-3 instrument, calibrated with NaCl. The observed and calculated densities are as follows: maleevite,  $D(obs.) = 3.78(1)$ ,  $D(calc.) = 3.79$ ; pekovite,  $D(obs.) = 3.35(2)$ ,  $D(calc.) = 3.36 g/cm^3$ ; density was measured by microflotation in Clerici solution.

Maleevite is biaxial negative with  $2V = -5(3)^\circ$ . The low accuracy of  $2V$  results from the very low birefringence:  $\alpha$  1.649(2),  $\beta$  1.656(2),  $\gamma$  1.656(2). Pekovite is

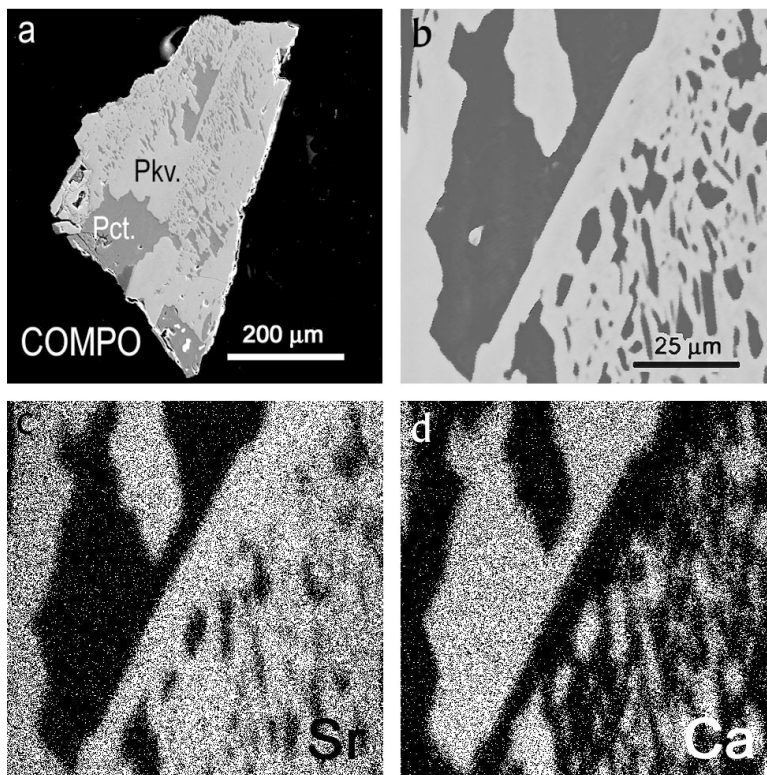


FIG. 2. An intergrowth of pekovite (Pkv) and pectolite (Pct): (a) BSE image; (c) a fragment of the previous image; (c, d) images with characteristic X-ray radiation for Sr and Ca.

biaxial negative,  $2V = -43(3)^\circ$  (measured with the Federov stage). The optical dispersion is medium,  $v > r$ . In immersion liquids, pekovite appears as lath-like grains forming subparallel intergrowths. Elongate grains show straight extinction, and the axis coincides with the direction of elongation. We found only two grains of pekovite (out of many examined) suitable for optical measurement. Unfortunately, we could not measure  $\beta$  because of the insufficient thickness of the grains. We measured  $\alpha$  and  $\gamma$  with a spindle stage:  $\alpha$  1.597(2),  $\beta_{\text{calc}}$  1.627(2),  $\gamma$  1.632(2).

#### CHEMICAL COMPOSITION

Chemical analysis of maleevite and pekovite (Table 1) was done with a JEOL JXA-50A electron microprobe with an energy-dispersion spectrometer and three wavelength-dispersion spectrometers operating at 20 kV and 20 nA for all elements except boron. The following standards and crystals were used: Si, Ca:  $K\alpha$ , danburite; Ba:  $L\alpha$ , barite; Pb:  $M\alpha$ , crocoite; Sr:  $L\alpha$ ,  $\text{SrSO}_4$ . The amount of boron was measured at 10 kV and 90 nA with an STE crystal and  $K\alpha$  X-rays. The differentiated mode of the discriminator was used. Danburite was used as the standard for boron, and was included in the same mount as maleevite and pekovite. Data were reduced using the  $\phi(\rho Z)$  procedure of Pouchou & Pichoir (1985). Infrared spectra (Fig. 3) show the absence of ( $\text{H}_2\text{O}$ ) in maleevite and pekovite. Colorimetric examination with beryllon-2 showed that no beryllium is present. The chemical compositions and formulae calculated on the basis of eight atoms of oxygen are shown in Table 1. Empirical formulae ( $\text{Ba}_{0.99}\text{Pb}_{0.01}\text{B}_{1.99}\text{Si}_{2.01}\text{O}_8$  (based on composition 1, Table 1) and ( $\text{Sr}_{0.97}\text{Ca}_{0.02}\text{B}_{1.97}\text{Si}_{2.03}\text{O}_8$  are close to the end-member formulae  $\text{BaB}_2\text{Si}_2\text{O}_8$  and  $\text{SrB}_2\text{Si}_2\text{O}_8$ .

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND FORMULA (*apfu*) FOR MALEEVITE AND PEKOVITE

	Maleevite			Pekovite	
$\text{SiO}_2$	34.86	35.68	33.33	33.31	41.56
$\text{B}_2\text{O}_3$	19.92	20.67 *	19.32 *	19.29 *	23.39
BaO	43.64	43.15	36.12	32.38	—
SrO	—	—	—	—	34.15
CaO	—	—	—	—	0.38
PbO	0.42	1.14	9.63	16.08	—
Total	98.84	100.65	98.40	101.06	99.48
Si	2.01	2.01	2.00	1.99	2.02
B	1.99	2.00	2.00	2.00	1.97
Ba	0.99	0.95	0.85	0.76	—
Sr	—	—	—	—	0.97
Pb	0.01	0.02	0.16	0.26	—
Ca	—	—	—	—	0.02
Sum	1.00	0.97	1.01	1.02	0.99

— : not detected

\*: calculated

Table 1 shows major replacement of Ba by Pb in maleevite. Extensive  $\text{Ba} \leftrightarrow \text{Pb}^{2+}$  solid-solution is fairly common in minerals from Dara-i-Pioz: (1) there are two varieties of hyalotekite, barium and lead, and we believe that there are two distinct mineral species; (2) kaptisaite-(Y) contains significant amounts of Pb; (3) cappelenite-(Y) with a high content of Pb has been found recently. Unfortunately, Pb-rich maleevite occurs as extremely fine grains and we could not measure any physical properties for it.

The Gladstone–Dale constant (Mandarino 1981) is 0.007 (superior) for maleevite and 0.022 (excellent) for pekovite.

#### INFRARED SPECTROSCOPY

The infrared spectra of both minerals were measured using a Specord 75 IR spectrometer (as KBr disks). The principal absorptions in the infrared spectrum are as follows: maleevite: 1149, 1093, 1012, 957, 943, 865,

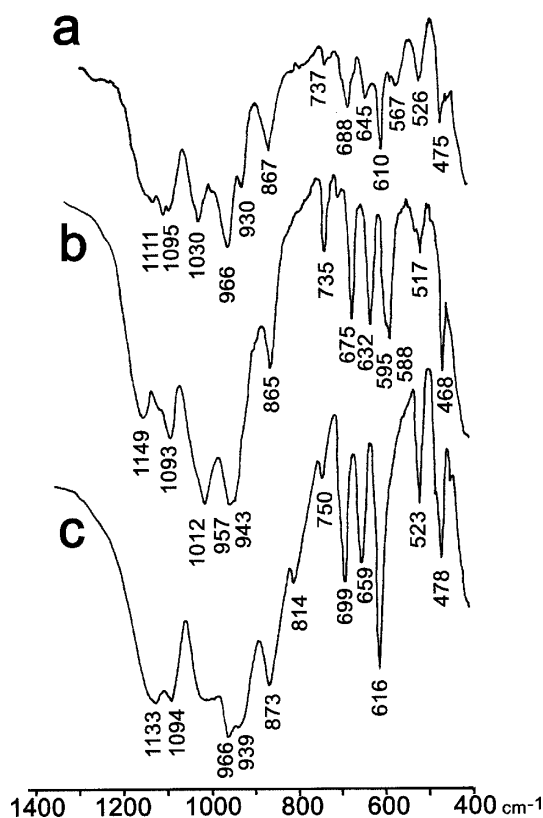


FIG. 3. Infrared spectra of: (a) pekovite, (b) maleevite, and (c) danburite from Dal'negorsk, Russia.



735, 675, 632, 592, 527, 517, 468  $\text{cm}^{-1}$ ; pekovite: 1111, 1095, 1030, 966, 930, 867, 737, 688, 645, 610, 567, 526, 475  $\text{cm}^{-1}$ . Both spectra are similar to that of danburite (Ferraro 1982), but all three are quite distinct (Fig. 3).

#### X-RAY POWDER DIFFRACTION

The powder-diffraction patterns for maleevite and pekovite were recorded with a 114-mm-diameter Debye-Scherrer camera using Mn-filtered  $\text{FeK}\alpha$  X-radiation. Quartz was used as an internal standard. Note that we observed an unusual phenomenon: the X-ray film was blackened in the camera owing to the very bright luminescence of maleevite when exposed to X-rays, even for small samples with a diameter of less than 0.1 mm. To avoid this effect, we had to screen the film with black paper. For pekovite, there was no such complication. Table 2 shows the X-ray powder-diffraction data.

#### SINGLE-CRYSTAL X-RAY DIFFRACTION

Single crystals of maleevite and pekovite were attached to glass fibers and mounted on a Siemens P4 automated four-circle diffractometer equipped with  $\text{MoK}\alpha$  X-radiation and a serial detector. Twenty-five reflections over the ranges  $6.7 < 2\theta < 24.9$  (maleevite) and  $10.3 < 2\theta < 27.8^\circ$  (pekovite) were centered, and the unit-cell dimensions (Table 3) were refined by least-squares from the resultant setting angles. Intensity data

TABLE 2A. X-RAY DIFFRACTION POWDER PATTERN FOR MALEEVITE

$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$
6	6.07	6.063	0 1 1	1	1.514	1.516	0 4 4
3	4.86	4.863	1 1 1	"	"	1.513	5 2 0
10	3.62	3.644	2 1 0	1	1.475	1.480	3 1 5
6	3.39	3.387	1 2 1	2	1.437	1.438	2 5 2
3	3.03	3.024	2 0 2	"	"	1.437	0 5 3
5	2.83	2.827	0 1 3	2	1.334	1.335	5 3 2
2	2.74	2.748	2 2 1	"	"	"	2 2 6
1	2.604	2.609	0 3 1	"	"	1.333	4 1 5
4	2.481	2.485	1 3 1	1	1.257	1.257	5 2 4
1	2.419	2.422	2 0 3	2	1.215	1.216	4 4 4
1	2.323	2.324	1 2 3	"	"	1.215	6 3 0
3	2.244	2.243	1 3 2	2	1.189	1.189	5 3 4
2	2.085	2.083	2 2 3	1	1.179	1.178	2 2 7
7	2.021	2.021	0 3 3	1	1.162	1.162	2 5 5
1	1.929	1.929	4 1 1	"	"	"	2 4 6
1	1.880	1.881	3 3 1	1	1.122	1.122	2 6 4
1	1.827	1.827	2 4 0	"	"	"	6 4 1
2	1.758	1.765	0 1 5	1	1.107	1.107	3 5 5
3	1.688	1.686	4 0 3	"	"	"	3 4 6
"	"	1.690	4 2 2	1	1.067	1.067	5 2 6
1	1.650	1.652	2 0 5	1	1.060	1.060	4 6 3
"	"	"	4 1 3	1	1.042	1.042	4 5 5
3	1.603	1.603	1 5 0	"	"	"	4 4 6
1	1.566	1.572	5 1 1	1	1.014	1.014	1 8 0
"	"	1.562	2 4 3	1	0.985	0.985	2 8 1
				1	0.947	0.947	3 6 6

were collected in  $\theta$ - $2\theta$  scan-mode at a fixed scan-rate of  $2.0^\circ$   $2\theta/\text{min}$ . Totals of 1988 (maleevite) and 1910 (pekovite) reflections were measured over the range  $4 < 2\theta < 60.06^\circ$  (maleevite) and  $60.08^\circ$  (pekovite). One standard reflection was monitored every fifty-eight reflections; there was no significant change in its intensity during data collection. Psi-scan data were measured on 11 reflections out to  $60^\circ$   $2\theta$  at increments of  $5^\circ$ , and an absorption correction, with the crystal modeled as a triaxial ellipsoid, reduced  $R(\text{azimuthal})$  from 10.8 to 2.6% (maleevite) and from 6.5 to 2.6% (pekovite). The data were corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors; of the 939 (maleevite) and 903 (pekovite) unique reflections, 879 (maleevite) and 705 (pekovite) were considered as observed [ $|F_o| > 4\sigma F$ ].

TABLE 2B. X-RAY DIFFRACTION POWDER PATTERN FOR PEKOVITE

$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$l_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$
4	6.01	6.019	1 0 1	1	1.604	1.604	5 0 1
6	5.94	5.922	0 1 1	1	1.599	1.597	3 3 3
3	4.79	4.791	1 1 1	2	1.581	1.581	3 2 4
10	3.62	3.625	2 1 0	1	1.527	1.528	2 4 3
9	3.51	3.508	1 1 2	1	1.517	1.517	4 3 2
8	3.31	3.308	1 2 1	3	1.476	1.476	2 5 0
6	3.01	3.009	2 0 2	2	1.466	1.468	1 5 2
3	2.960	2.961	0 2 2	"	"	1.466	3 1 5
9	2.786	2.794	1 0 3	1	1.427	1.429	5 2 2
"	"	2.784	0 1 3	2	1.417	1.418	4 3 3
"	"	2.783	1 2 2	2	1.398	1.398	0 5 3
6	2.706	2.707	2 2 1	1	1.376	1.376	2 1 6
1	2.600	2.600	3 0 1	1	1.353	1.353	4 4 2
2	2.531	2.531	0 3 1	"	"	1.353	3 5 1
4	2.469	2.470	3 1 1	1	1.34	1.340	6 1 0
3	2.417	2.418	1 3 1	1	1.325	1.325	5 3 2
2w	2.401	2.403	2 0 3	"	"	1.325	6 1 1
"	"	2.396	2 2 2	1	1.320	1.320	0 6 0
1	2.322	2.321	3 0 2	1	1.299	1.299	5 1 4
2	2.231	2.230	0 0 4	"	"	1.299	3 3 5
5	2.189	2.189	1 3 2	1	1.282	1.283	6 1 2
2w	2.175	2.174	3 2 1	"	"	1.282	4 4 3
1	2.152	2.151	1 0 4	1	1.258	1.258	0 1 7
1	2.075	2.076	1 1 4	"	"	1.257	5 3 3
5	2.055	2.054	2 2 3	1	1.247	1.247	5 4 1
4	2.003	2.003	3 2 2	1	1.243	1.244	1 1 7
7w	1.982	1.985	2 3 2	"	"	1.244	2 6 1
"	"	1.980	0 4 0	"	"	1.243	3 5 3
1	1.927	1.928	4 1 1	2	1.235	1.235	2 3 6
2	1.881	1.881	1 4 1	"	"	1.235	6 2 2
3	1.853	1.852	3 3 1	1	1.221	1.221	6 1 3
1	1.810	1.810	0 4 2	1	1.208	1.208	6 3 0
1	1.766	1.767	1 4 2	1	1.200	1.200	1 2 7
5	1.742	1.743	1 0 5	1	1.179	1.180	6 2 3
"	"	1.743	3 3 2	"	"	1.178	5 3 4
"	"	1.741	0 1 5	1	1.166	1.166	3 5 4
1	1.722	1.724	3 0 4	"	"	1.166	6 3 2
1	1.703	1.702	1 1 5	2w	1.149	1.150	4 2 6
2	1.685	1.685	3 1 4	"	"	1.148	6 1 4
1w	1.680	1.681	4 0 3	"	"	1.147	3 6 2
"	"	1.679	4 2 2	1	1.142	1.143	7 1 1
1	1.667	1.668	1 3 4	"	"	1.142	3 1 7
1	1.644	1.645	4 1 3				

### Structure refinement

Scattering curves for neutral atoms were taken from the International Tables for Crystallography (1992). The SHELXTL v. 5.1 system of programs (Sheldrick 1997) was used for this work. Using the atom coordinates of danburite,  $\text{Ca B}_2 \text{Si}_2 \text{O}_8$  (Phillips *et al.* 1974), the re-

finements converged to  $R_1$  indices of 2.2% (maleevite) and 3.4% (pekovite). Site-scattering refinement for the A site using the scattering curves of Ba and Sr showed that it is completely occupied by Ba in maleevite and by Sr in pekovite.  $R$  indices are given in Table 3, and are expressed as percentages. Positional and displacement parameters are given in Table 4, selected interatomic distances in Table 5, and bond valences for maleevite and pekovite are given in Table 6. The parameters for pekovite are very similar to those of the synthetic analogue (Berger *et al.* 1996). Observed and calculated structure-factors for both structures are available from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

### DESCRIPTION OF THE STRUCTURE

#### Coordination of the cations

There are two sites that are tetrahedrally coordinated by oxygen atoms. The  $T(1)$  site is occupied by B with  $\langle T(1)\text{--O} \rangle = 1.473$  (maleevite) and  $1.474 \text{ \AA}$  (pekovite); the  $T(2)$  site is occupied by Si with  $\langle T(2)\text{--O} \rangle = 1.617$  (maleevite) and  $1.619 \text{ \AA}$  (pekovite). There is one A site in this structure type. There are seven A–O bonds ranging from 2.623 to 2.794  $\text{\AA}$  and three bonds ranging from 3.060 to 3.162  $\text{\AA}$  in the crystal structure of maleevite. The coordination number for Ba can be considered as either [7] or [10], with  $\langle \text{Ba--O} \rangle = 2.749$  or  $2.863 \text{ \AA}$  (Table 5) and corresponding ionic radii of 1.38 or 1.52  $\text{\AA}$  (Shannon 1976). In the crystal structure of pekovite, seven A–O bonds range from 2.509 to 2.608  $\text{\AA}$ , there

TABLE 3. MISCELLANEOUS STRUCTURE-REFINEMENT INFORMATION

	Maleevite	Pekovite
$a$ (Å)	8.141(2)	8.155(2)
$b$	8.176(2)	7.919(1)
$c$	9.038(2)	8.921(1)
$V$ (Å <sup>3</sup> )	601.5(2)	576.1(2)
Space group	$Pnma$	
$Z$	4	
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	3.789	3.376
Absorption coefficient (mm <sup>-1</sup> )	7.01	9.68
$F(000)$	632	559.1
crystal size (mm)	0.10 x 0.12 x 0.16	0.03 x 0.04 x 0.10
radiation	MoK $\alpha$	
maximum $2\theta$ (°)	60.06	60.08
$R(\text{int})$ (%)	3.1	4.6
Total no. of reflections	1988	1910
Unique reflections	939	903
$F_o > 4\sigma F$	879	705
Refinement method	least-squares on $F^2$ ; fixed weights $1/\sigma(F)$	
Goodness of fit on $F^2$	1.089	1.029
Final $R_1$ index (%) [ $F_o > 4\sigma F$ ]	2.2	3.4
$R_1$ index (%) (all data)	2.3	4.8
$wR_2$ (%)	5.5	9.2

TABLE 4. ATOM POSITIONS AND DISPLACEMENT FACTORS

MALEEVITE										
	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
A	0.38853(3)	1/4	0.08357(2)	0.01426(15)	0.01121(13)	0.01087(14)	0	0.00045(7)	0	0.01211(10)
T(1)	0.2711(4)	0.0855(3)	0.4117(3)	0.0086(12)	0.0073(11)	0.0064(11)	0.0004(8)	0.0001(9)	−0.0002(9)	0.0074(5)
T(2)	0.07232(9)	0.93355(8)	0.18988(7)	0.0093(3)	0.0088(3)	0.0069(3)	−0.0000(2)	−0.0001(3)	−0.0002(3)	0.00831(19)
O(1)	0.2181(3)	0.9538(2)	0.07000(18)	0.0134(9)	0.0167(9)	0.0068(8)	−0.0005(6)	0.0029(7)	−0.0028(8)	0.0123(4)
O(2)	0.1458(3)	0.9685(2)	0.35401(19)	0.0132(8)	0.0119(8)	0.0077(8)	−0.0002(6)	−0.0020(7)	−0.0032(7)	0.0110(4)
O(3)	0.4293(3)	0.0653(2)	0.3369(2)	0.0119(8)	0.0114(8)	0.0113(8)	0.0009(6)	0.0021(7)	0.0013(7)	0.0115(4)
O(4)	0.4966(4)	3/4	0.3126(3)	0.0123(13)	0.0089(11)	0.0136(12)	0	−0.0008(10)	0	0.0116(5)
O(5)	0.2083(3)	1/4	0.3807(3)	0.0096(12)	0.0083(11)	0.0126(11)	0	−0.0018(10)	0	0.0101(5)
PEKOVITE										
	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
A	0.38756(7)	1/4	0.07841(7)	0.0129(3)	0.0037(3)	0.0103(3)	0	−0.0005(2)	0	0.00898(19)
T(1)	0.2650(5)	0.0808(5)	0.4153(5)	0.0083(18)	0.0000(16)	0.0063(17)	−0.0006(17)	0.0007(16)	−0.0007(14)	0.0049(8)
T(2)	0.06105(13)	0.94094(14)	0.19163(12)	0.0082(5)	0.0006(4)	0.0061(5)	−0.0002(4)	−0.0001(4)	−0.0002(4)	0.0050(2)
O(1)	0.2002(4)	0.9833(4)	0.0688(3)	0.0137(14)	0.0047(12)	0.0071(13)	−0.0018(12)	0.0021(12)	−0.0033(11)	0.0085(6)
O(2)	0.1344(3)	0.9637(4)	0.3597(3)	0.0114(13)	0.0044(12)	0.0055(13)	−0.0002(11)	−0.0012(11)	−0.0017(11)	0.0071(6)
O(3)	0.4103(3)	0.0725(4)	0.3207(3)	0.0113(13)	0.0007(12)	0.0106(13)	−0.0005(11)	0.0033(11)	0.0015(10)	0.0075(6)
O(4)	0.4924(5)	3/4	0.3277(5)	0.0127(19)	0.0001(16)	0.010(2)	0	0.0019(17)	0	0.0077(8)
O(5)	0.1951(5)	1/4	0.4127(5)	0.0078(18)	0.0046(17)	0.013(2)	0	0.0026(18)	0	0.0086(8)

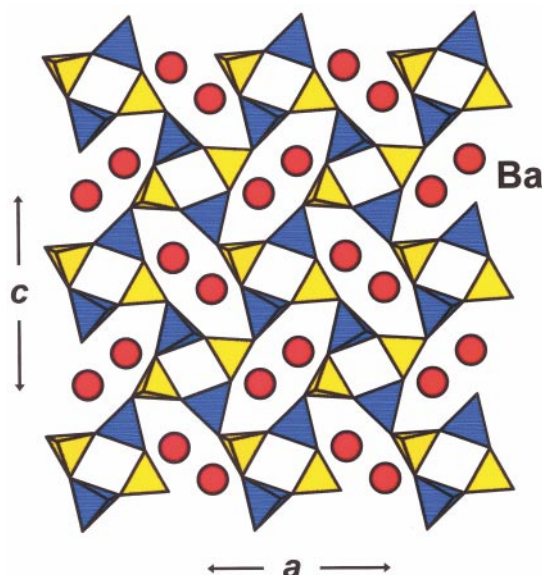


FIG. 4. The *ac* projection of the crystal structures of maleevite. *T*(1) = (*Bφ*<sub>4</sub>) tetrahedra are yellow, *T*(2) = (SiO<sub>4</sub>) tetrahedra are blue; Ba atoms are shown as crimson circles.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

	Maleevite	Pekovite	Danburite*
<i>T</i> (1)–O(1)	1.469(3)	1.488(5)	1.479(1)
<i>T</i> (1)–O(2)	1.493(3)	1.497(5)	1.498(1)
<i>T</i> (1)–O(3)	1.463(3)	1.456(5)	1.461(1)
<i>T</i> (1)–O(5)	<u>1.466(3)</u>	<u>1.456(4)</u>	<u>1.456(1)</u>
< <i>T</i> (1)–O>	1.473	1.474	1.474
<i>T</i> (2)–O(1)	1.615(2)	1.613(3)	1.617(1)
<i>T</i> (2)–O(2)	1.625(2)	1.624(3)	1.624(1)
<i>T</i> (2)–O(3)	1.605(2)	1.615(3)	1.611(1)
<i>T</i> (2)–O(4)	<u>1.623(1)</u>	<u>1.622(2)</u>	<u>1.614(1)</u>
< <i>T</i> (2)–O>	1.617	1.619	1.617
<i>T</i> (1) <sub>a</sub> –O(1)– <i>T</i> (2)	132.4(2)	133.5(3)	132.4(1)
<i>T</i> (1) <sub>b</sub> –O(2)– <i>T</i> (2)	133.1(2)	129.6(3)	126.3(1)
<i>T</i> (1)–O(3)– <i>T</i> (2) <sub>c</sub>	141.6(2)	133.5(3)	128.1(1)
<i>T</i> (2) <sub>d</sub> –O(4)– <i>T</i> (2) <sub>e</sub>	135.3(2)	137.6(3)	136.8(1)
<i>T</i> (1)–O(5)– <i>T</i> (1)	<u>133.1(3)</u>	<u>133.9(4)</u>	<u>130.6(1)</u>
< <i>T</i> –O– <i>T</i> >	135.1	133.6	130.8
**A–O(1) x2	2.794(2)	2.608(3)	2.496(1)
A–O(2)a x2	2.752(2)	2.590(3)	2.452(1)
A–O(3) x2	2.763(2)	2.585(3)	2.467(1)
A–O(5)d	<u>2.623(3)</u>	<u>2.509(4)</u>	<u>2.399(1)</u>
<A–O> [7]	2.749	2.582	2.462
A–O(2)e x2	3.162(2)	3.082(3)	3.020(1)
A–O(5)	<u>3.060(3)</u>	<u>3.370(4)</u>	<u>3.479(1)</u>
<A–O> [10]	2.863	[9] 2.693	[9] 2.585

\* Phillips *et al.* (1974)

\*\*A = Ba (maleevite), Sr (pekovite), Ca (danburite)

a:  $-x + \frac{1}{2}$ ,  $-y + 1$ ,  $-z - \frac{1}{2}$ ; b:  $x$ ,  $y + 1$ ,  $z$ ; c:  $x + \frac{1}{2}$ ,  $y - 1$ ,  $-z + \frac{1}{2}$ ; d:  $x + \frac{1}{2}$ ,  $y$ ,  $-z + \frac{1}{2}$ ; e:  $x + \frac{1}{2}$ ,  $-y + \frac{3}{2}$ ,  $-z + \frac{1}{2}$ ; f:  $x$ ,  $-y + \frac{1}{2}$ ,  $z$ .

are two bonds of 3.082 Å and an A–O(5) separation of 3.370 Å. The latter is too long to be considered as a bond (bond valence = 0.04 valence units, *vu*), and the coordination number for Sr can be considered as either [7] or [9], with <Sr–O> = 2.582 or 2.693 Å (Table 5) and corresponding ionic radii of 1.21 or 1.31 Å (Shannon 1976).

#### Structure topology

In the crystal structure of maleevite and pekovite, *T*(1) and *T*(2) tetrahedra form four-membered rings, which are connected in a framework topologically identical to that of danburite, Ca B<sub>2</sub> Si<sub>2</sub>O<sub>8</sub> (Phillips *et al.* 1974). In the framework, channels extend along [010]. The channels accommodate the A site. Figure 4 shows the crystal structure of maleevite viewed down [010]; the frameworks in danburite and pekovite are identical. The Ba atom in maleevite has a coordination number of [10]: the bond A–O(5)g of 3.060 Å is characteristic only for the maleevite structure (Figs. 5a, b). In danburite and pekovite, where the A cation has a coordination number of [9], this particular bond is 3.479 and 3.370 Å, *i.e.*, much longer compared to other bonds in the coordination polyhedra (Figs. 5c–f). Increase of the ionic radius of the A cation from 1.18 Å for [9]-coordinated Ca in danburite to 1.52 Å for [10]-coordinated Ba in maleevite results in

- (1) an increase in <A–O> for [CN] = 7;
- (2) the appearance of an additional bond, A–O(5) in maleevite (Fig. 5a);

TABLE 6. BOND-VALENCE (*vu*) TABLES\*

MALEEVITE				
	A = Ba	<i>T</i> (1)	<i>T</i> (2)	Σ
O(1)	0.25 <sup>±2</sup> <sub>1</sub>	0.74	1.04	2.03
O(2)	0.28 <sup>±2</sup> <sub>1</sub> [7] 0.11 <sup>±2</sup> <sub>1</sub> [10]	0.70	1.01	2.05 [7] 2.16 [10]
O(3)	0.27 <sup>±2</sup> <sub>1</sub>	0.76	1.07	2.10
O(4)			1.02 <sup>±2</sup> <sub>–</sub>	2.04
O(5)	0.39 [7] 0.13 [10]	0.76 <sup>±2</sup> <sub>–</sub>		1.94 [7] 2.04 [10]
Σ	1.99 [7] 2.34 [10]	2.96	4.14	
PEKOVITE				
	A = Sr	<i>T</i> (1)	<i>T</i> (2)	Σ
O(1)	0.25 <sup>±2</sup> <sub>1</sub>	0.73	1.02	2.00
O(2)	0.27 <sup>±2</sup> <sub>1</sub> 0.08 <sup>±2</sup> <sub>1</sub>	0.71	1.00	1.98 [7] 2.06 [9]
O(3)	0.27 <sup>±2</sup> <sub>1</sub>	0.80	1.02	2.09
O(4)			1.00 <sup>±2</sup> <sub>–</sub>	2.00
O(5)	0.33	0.80 <sup>±2</sup> <sub>–</sub>		1.93
Σ	1.91 [7] 2.07 [9]	3.04	4.04	

\* bond-valence parameters from Brown (1981)



(3) as a result of (2), the  $T(1)$ –O(5) bond increases in length, and the framework angle  $T(1)$ –O(5)– $T(1)_f$  increases.

(4) From danburite to maleevite *via* pekovite, the  $b$  and  $c$  cell parameters increase 5.8 and 3.3%, respec-

tively (Table 7). The  $b$  dimension increases more than the  $c$  dimension as the channels, which occlude large cations, extend along  $b$ . The  $a$  dimension increases from danburite to pekovite by 1.4%, and does not change significantly from pekovite to maleevite.

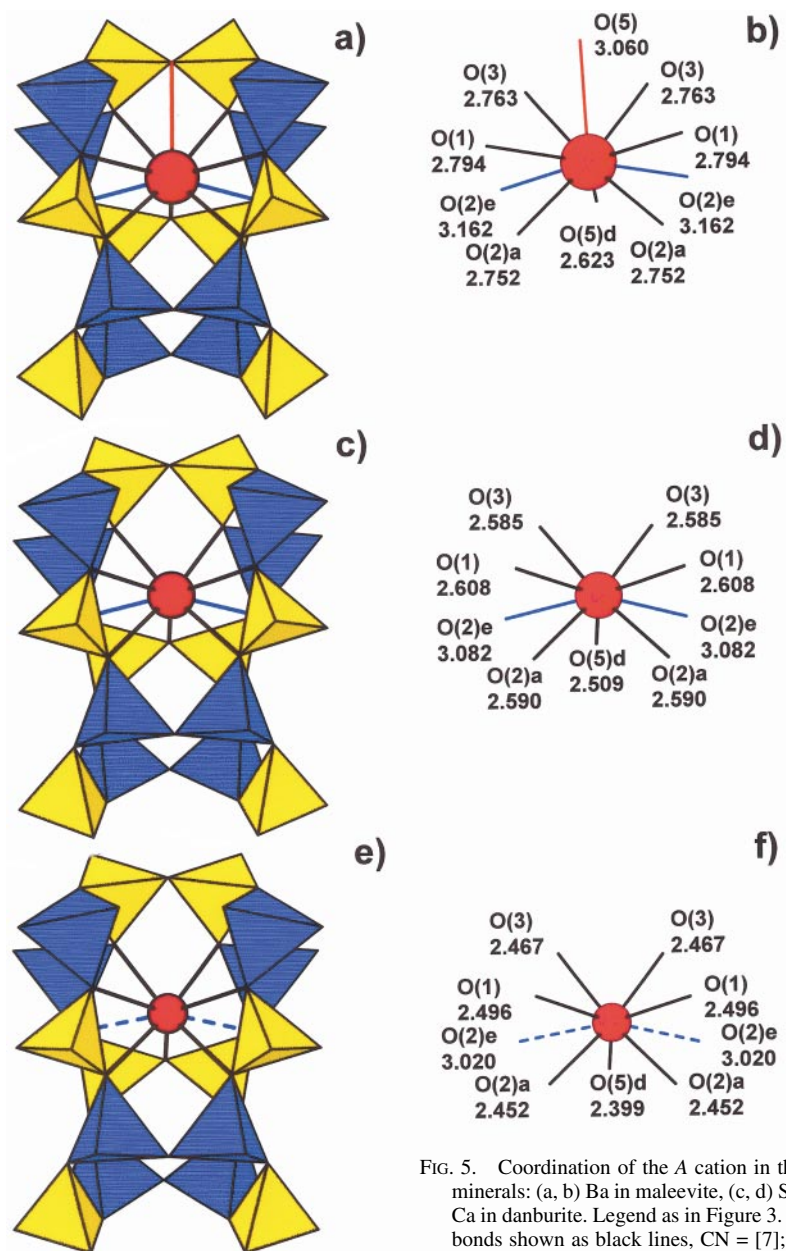


FIG. 5. Coordination of the A cation in the danburite-group minerals: (a, b) Ba in maleevite, (c, d) Sr in pekovite, (e, f) Ca in danburite. Legend as in Figure 3. Seven shorter A–O bonds shown as black lines, CN = [7]; two longer bonds, A–O(2)e, shown as blue lines, solid for maleevite and pekovite and dashed for danburite, CN = [9]; the A–O(5) bond in maleevite is shown as a solid red line.

ON THE ISOMORPHOUS SUBSTITUTION  $\text{Ca} \leftrightarrow \text{Sr} \leftrightarrow \text{Ba}$ 

Similar to danburite, pekovite and maleevite, Ca, Sr and Ba analogues occur in several mineral groups. In the aragonite group, they are carbonates: aragonite,  $\text{CaCO}_3$ , strontianite,  $\text{SrCO}_3$ , and witherite,  $\text{BaCO}_3$  (de Villiers 1971). In the apatite group, they are Cl-phosphates: chlorapatite, ideally  $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$  (Hughes *et al.* 1989), strontium "chlorapatite",  $\text{Sr}_5(\text{PO}_4)_3\text{Cl}$  (Sudarsanan & Young 1974), and alforsite,  $\text{Ba}_5(\text{PO}_4)_3\text{Cl}$  (Hata *et al.* 1979); and (OH)- or F-phosphates: hydroxylapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$  (Sudarsanan & Young 1969), strontium-apatite,  $(\text{Sr}_{3.656}\text{Ca}_{1.35})(\text{PO}_4)_3\text{F}$  (Pushcharovskii *et al.* 1987), and  $\text{Ba}_5(\text{PO}_4)_3\text{F}$  (Mathew *et al.* 1979). In the barite group, they are sulfates: barite,  $\text{BaSO}_4$  (Jacobsen *et al.* 1998), and celestine,  $\text{SrSO}_4$  (Hawthorne & Ferguson 1975a). Anhydrite,  $\text{CaSO}_4$  (Hawthorne & Ferguson 1975b) is isochemical but not isostructural with barite and celestine. In the feldspar group, they are aluminosilicates: anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$  (Kempster *et al.* 1962), slawsonite, ideally  $\text{SrAl}_2\text{Si}_2\text{O}_8$  (Griffen *et al.* 1977), celsian,  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (Griffen & Ribbe 1976) and paracelsian,  $\text{BaAl}_2\text{Si}_2\text{O}_8$  (Chiari *et al.* 1985). Figure 6(a–f) shows the variation in  $\langle\text{A–O}\rangle$  (Å) as a function of constituent cation radius at the A site for the minerals listed in Table 8.

Corresponding lead minerals and synthetic compounds are also considered here: cerussite  $\text{Pb}(\text{CO}_3)$  (Sahl 1974), the synthetic OH-analogue of pyromorphite,  $\text{Pb}_5(\text{PO}_4)_3(\text{OH})$  (Barinova *et al.* 1998), pyromorphite,  $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$  (Mashimoto & Matsumoto 1998), and two synthetic Pb-"feldspars",  $\text{PbAl}_2\text{Si}_2\text{O}_8$  (Benna *et al.* 1996).

TABLE 7. COMPARATIVE TABLE

	Maleevite	Pekovite	Danburite
Chemical formula	$\text{BaB}_2\text{Si}_2\text{O}_8$	$\text{SrB}_2\text{Si}_2\text{O}_8$	$\text{CaB}_2\text{Si}_2\text{O}_8$
Space group	<i>Pnma</i>	<i>Pnma</i>	<i>Pnma</i>
<i>a</i> (Å)	8.141	8.155	8.038
<i>b</i>	8.176	7.919	7.730
<i>c</i>	9.038	8.921	8.752
<i>V</i> (Å <sup>3</sup> )	601.5	576.1	543.8
<i>Z</i>	4	4	4
Intense X-ray	6.07(6)	6.01(4)	3.65(4)
powder-diffraction	3.62(10)	5.94(6)	3.57(10)
lines	3.39(6)	3.62(10)	3.44(4)
<i>d</i> (Å), ( <i>h</i> )	3.03(3)	3.51(9)	2.961(8)
	2.83(5)	2.31(8)	2.743(7)
	2.74(2)	3.01(6)	2.729(4)
	2.244(3)	2.786(9)	2.655(6)
	2.021(7)	2.706 (6)	2.140(4)
	1.688(3)	1.198(7w)	
Density (g/cm <sup>3</sup> )	3.79	3.36	2.94
Optic sign	biaxial (–)	biaxial (–)	biaxial (–)
2 <i>V</i> (°)	5	43	88
$\alpha$	1.649	1.597	1.63
$\beta$	1.656	1.627	1.633
$\gamma$	1.656	1.632	1.636

There is a linear correlation between  $\langle\text{A–O}\rangle$  and  $r_A$  for danburite, pekovite, maleevite for coordination numbers of both [7] and [9] (Fig. 6a), and for the aragonite-group minerals with a coordination number of [9] (Fig. 6b, Table 8). Within each of these groups, the minerals are of the same structure-type, *i.e.*, they retain the same space-group, *Pnma* and *Pmcn*, respectively (Table 8), and have the same bond topology. There is a linear correlation between  $\langle\text{A–O}\rangle$  and  $r_A$  for the apatite-group minerals (Figs. 6c, d). For this group, we consider  $\langle\text{A–O}\rangle$  distances for the A site that is surrounded solely by  $\text{O}^{2-}$  ligands, and differentiate between Cl- and (F,OH)-dominant species. Strontium-apatite has lower symmetry, *P6<sub>3</sub>*, in contrast to *P6<sub>3</sub>/m* for the majority of the apatite-group minerals. Nevertheless,  $\langle\text{A}(1)\text{–O}\rangle$  and  $\langle\text{A}(2)\text{–O}\rangle$  fit the linear correlation between  $\langle\text{A–O}\rangle$  and  $r_A$  for the F and (OH) species of the apatite group (Fig. 4c).

The situation is quite different for sulfate minerals of the form  $\text{A}^{2+}\text{SO}_4$  and for the feldspar-group minerals. There is a linear correlation for the barite-group minerals (space group *Pnma*) (Fig. 6e). The isochemical Ca analogue, anhydrite (space group *Amma*), does not fit this correlation (Fig. 6e). Figure 6f shows  $\langle\text{A–O}\rangle$  versus  $r_A$  for several minerals of the feldspar group. Anorthite,  $\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8$ , is triclinic, and there are 4 A sites in its structure, with  $\langle\text{A–O}\rangle$  in the range 2.495–2.544 Å (Table 8). Where the space symmetry increases (*P2<sub>1</sub>/a* for slawsonite,  $\text{SrAl}_2\text{Si}_2\text{O}_8$ , and paracelsian,  $\text{BaAl}_2\text{Si}_2\text{O}_8$ ; *I2/c* for celsian,  $\text{BaAl}_2\text{Si}_2\text{O}_8$ , and synthetic  $\text{PbAl}_2\text{Si}_2\text{O}_8$ ; *C2/m* for another polymorph of synthetic  $\text{PbAl}_2\text{Si}_2\text{O}_8$ ), there is only one A site in the crystal structure. As indicated in Figure 6f, the slopes of the trends for the space groups *I2/c* and *P2<sub>1</sub>/a* are the same, but the trends are displaced from each other. Moreover, other structures with different space-groups (but the same bond-topology) are displaced from the trends for *I2/c* and *P2<sub>1</sub>/a*.

Shannon & Prewitt (1969) showed that the effective ionic radius of a cation depends on its charge, coordination number and the type of ligand. In a specific group of isostructural minerals, the type of ligand and (usually) the coordination number are constant and hence one expects a linear relation between mean bond-lengths and the radii of the constituent cations. This relation is used extensively in crystal chemistry, and accounts for the linearity of the relations in Figures 6a–d. It is apparent from Figure 6e that difference in structure-type produces non-linearity in this type of relation. Difference in space-group symmetry within an isochemical group exhibiting the same bond-topology also produces non-linearity in this type of relation (Fig. 6f). We suggest that this latter type of non-linearity is an expression of structural strain. If considered from a bond-valence perspective, the geometrical details of a specific bond-topology are constrained by (1) the need to conform as closely as possible to the valence-sum rule (Brown 1981, Hawthorne 1994, 1997), and (2) the spatial con-

TABLE 8. SELECTED Ba, Sr, Pb<sup>2+</sup> and Ba MINERALS AND SYNTHETIC ANALOGUES

Mineral	Formula	Space group	Z	a (Å)	b (Å)	c (Å)	Cation	A-site CN	r <sub>A</sub> (Å)	<A-O> (Å)	Ref.
Danburite	Ca <sub>2</sub> B <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>Pnma</i>	4	8.038(3)	7.730(2)	8.752(5)	Ca	7 9	1.06 1.18	2.462 2.585	(1)
Pekovite	Sr <sub>2</sub> B <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>Pnma</i>	4	8.155(2)	7.919(1)	8.921(1)	Sr	7 9	1.21 1.31	2.582 2.693	(2)
Maleevite	Ba <sub>2</sub> B <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>Pnma</i>	4	8.141(2)	8.176(2)	9.038(2)	Ba	7 9	1.38 1.47	2.749 2.841	(2)
Aragonite	Ca (CO <sub>3</sub> )	<i>Pmcn</i>	4	4.9614(3)	7.9671(4)	5.7407(4)	Ca	9	1.18	2.528	(3)
Strontianite	Sr (CO <sub>3</sub> )	<i>Pmcn</i>	4	5.090(2)	8.358(2)	5.997(4)	Sr	9	1.31	2.636	(3)
Cerussite	Pb (CO <sub>3</sub> )	<i>Pmcn</i>	4	5.1800(7)	8.492(3)	6.134(3)	Pb <sup>2+</sup>	9	1.35	2.692	(4)
Witherite	Ba (CO <sub>3</sub> )	<i>Pmcn</i>	4	5.3126(5)	8.8958(5)	6.4284(5)	Ba	9	1.47	2.807	(3)
Hydroxylapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	<i>P6<sub>3</sub>/m</i>	2	9.424(4)	—	6.879(4)	Ca	9	1.18	2.554	(5)
Strontium-apatite	(Sr,Ca) <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	<i>P6<sub>3</sub></i>	2	9.565(8)	—	7.115(3)	(Sr <sub>0.3</sub> Ca <sub>0.7</sub> ) (Sr <sub>0.75</sub> Ca <sub>0.25</sub> )	9 9	1.22 1.28	2.604 2.633	(6)
synthetic	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (OH)	<i>P6<sub>3</sub>/m</i>	2	9.774(1)	—	7.291(1)	Pb <sup>2+</sup>	9	1.35	2.724	(7)
synthetic	Ba <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	<i>P6<sub>3</sub>/m</i>	2	10.153(2)	—	7.733(1)	Ba	9	1.47	2.824	(8)
Chlorapatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (Cl <sub>0.88</sub> F <sub>0.09</sub> )	<i>P6<sub>3</sub>/m</i>	2	9.9579	—	6.7762	Ca	9	1.18	2.549	(9)
synthetic	Sr <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	<i>P6<sub>3</sub>/m</i>	2	9.859(1)	—	7.206(2)	Sr	9	1.31	2.669	(10)
Pyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	<i>P6<sub>3</sub>/m</i>	2	10.022(3)	—	7.348(9)	Pb <sup>2+</sup>	9	1.35	2.714	(11)
synthetic analogue of alforsite	Ba <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	<i>P6<sub>3</sub>/m</i>	2	10.284(2)	—	7.651(3)	Ba	9	1.47	2.824	(12)
Anhydrite	Ca (SO <sub>4</sub> )	<i>Amma</i>	4	6.993(2)	6.995(2)	6.245(1)	Ca	8	1.12	2.469	(13)
Celestine	Sr (SO <sub>4</sub> )	<i>Pnma</i>	4	8.360(1)	5.352(1)	6.858(1)	Sr	8	1.26	2.682	(14)
Anglesite	Pb (SO <sub>4</sub> )	<i>Pnma</i>	4	8.4723(11)	5.3973(8)	6.9549(9)	Pb <sup>2+</sup>	8	1.29	2.727	(15)
Barite	Ba (SO <sub>4</sub> )	<i>Pnma</i>	4	8.8790(18)	5.4540(11)	7.1540(14)	Ba	8	1.38	2.803	(15)
Anorthite *	Ca Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>P2<sub>1</sub></i>	2	8.1768	12.8768	14.169	Ca	7	1.06	2.544 2.495 2.499 2.538	(16)
Slawsonite **	(Sr,Ca) Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>P2<sub>1</sub>/a</i>	14	8.888(2)	9.344(2)	8.326(3)	(Sr <sub>0.87</sub> Ca <sub>0.13</sub> )	7	1.19	2.63	(17)
synthetic***	Pb Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>C2/m</i>	4	8.428(1)	13.054(2)	7.174(2)	Pb <sup>2+</sup>	7	1.23	2.757	(18)
synthetic†	Pb Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>I2/c</i>	8	8.388(1)	13.067(2)	14.327(2)	Pb <sup>2+</sup>	7	1.23	2.722	(18)
Celsian††	Ba Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>I2/c</i>	8	8.622(4)	13.078(6)	14.411(8)	Ba	7	1.38	2.862	(19)
Paracelsian†††	Ba Al <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	<i>P2<sub>1</sub>/a</i>	4	9.065(3)	9.568(1)	8.578(5)	Ba	7	1.38	2.803	(20)

\*  $\alpha = 93.17^\circ$ ,  $\beta = 115.85^\circ$ ,  $\gamma = 91.22^\circ$ ; \*\*  $\beta = 90.33(2)^\circ$ ; \*\*\*  $\beta = 115.32(1)^\circ$ ; †  $\beta = 115.19(1)^\circ$ ; ††  $\beta = 115.09(2)^\circ$ ; †††  $\beta = 90.01(4)^\circ$

References: (1) Phillips *et al.* (1974); (2) this work; (3) De Villiers (1971); (4) Sahl (1974); (5) Sudarsanan & Young (1969); (6) Pushcharovskii *et al.* (1987); (7) Barinova *et al.* (1998); (8) Mathew *et al.* (1979); (9) Hughes *et al.* (1989); (10) Sudarsanan & Young (1974); (11) Mashimoto & Matsumoto (1998); (12) Hata *et al.* (1979); (13) Hawthorne & Ferguson (1975b); (14) Hawthorne & Ferguson (1975a); (15) Jacobsen *et al.* (1998); (16) Kempster *et al.* (1962); (17) Griffen *et al.* (1977); (18) Benna *et al.* (1996); (19) Griffen & Ribbe (1976); (20) Chiari *et al.* (1985).

straints of its space-group symmetry (whatever the specific symmetry adopted by particular arrangement of atoms under consideration). The geometrical details of a structure can thus be seen as a compromise between these two constraints, and the atomic arrangement will incorporate strain that is a reflection of the disparity between a geometry that exactly satisfies the valence-sum rule and a geometry that obeys the constraints of its space-group symmetry.

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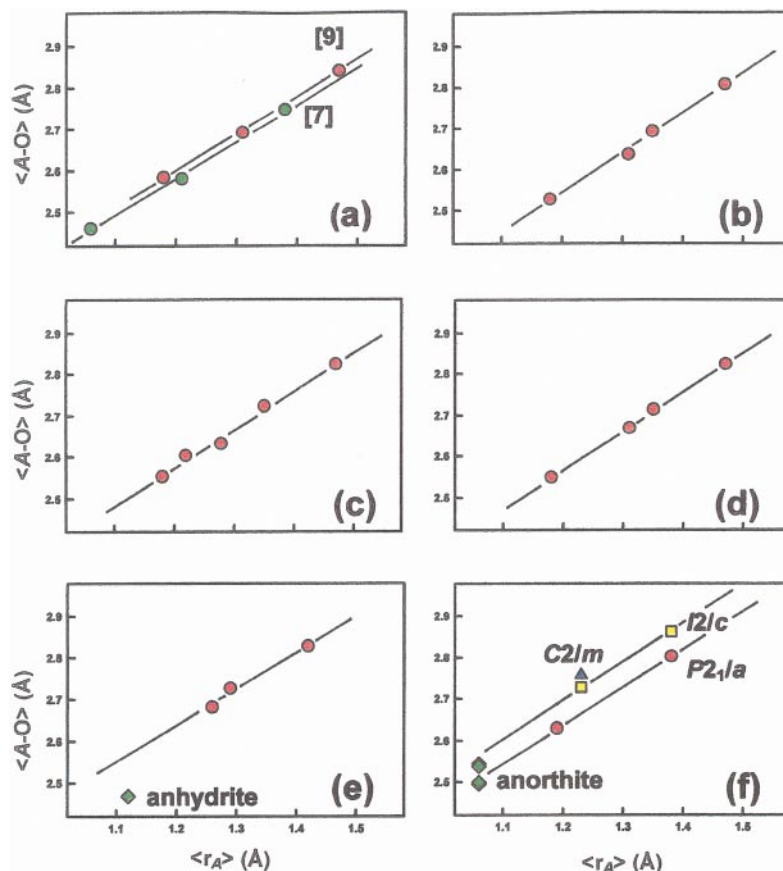


FIG. 6. Variation in  $\langle A-O \rangle$  as a function of constituent-cation radius at the A site for Ca, Sr,  $Pb^{2+}$  and Ba-dominant minerals: (a) danburite – pekovite – maleevite (green circles, [7]-coordinated; red circles, [9]-coordinated); (b) aragonite – strontianite – cerussite – witherite, CN = [9]; (c) hydroxylapatite – strontium apatite – “OH-pyromorphite” (synthetic) – “Ba-F-apatite”, CN = [9]; (d) chlorapatite – “strontium chlorapatite” (synthetic) – pyromorphite – alforsite, CN = [9]; (e) anhydrite (green squares), celestine – anglesite – barite (red circles), CN = [8]; (f) anorthite (P1, green diamonds), slawsonite – paracelsian (P2<sub>1</sub>/a, red circles), synthetic  $Pb_2Al_2Si_2O_8$  – celsian (I2/c, yellow squares),  $Pb_2Al_2Si_2O_8$  (C2/m, black triangle).

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