

## THE CRYSTAL CHEMISTRY OF THE EUDIALYTE GROUP

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## ABSTRACT

Seventeen crystals of eudialyte (*sensu lato*) differing in provenance and showing a wide range of chemical compositions, were chosen for crystal-structure analysis and electron-microprobe analysis, supplemented with thermogravimetric analysis, infrared analysis, Mössbauer and optical absorption spectroscopy on selected samples. The structure consists of layers of six-membered rings of  $[M(1)O_6]$  octahedra linked together by  $[M(2)O_n]$  polyhedra sandwiched between two pseudocentrosymmetrically related layers of three-membered and nine-membered silicate rings forming a 2:1 composite layer. The 2:1 composite layers are cross-linked by Zr in octahedral coordination and are related to one another in accordance with the rhombohedral symmetry. This open structure is filled with  $[Na\phi_n]$  polyhedra in which Na may have various coordinations. The silicate network is relatively uniform in composition. The Zr site usually has a small amount of Ti.  $M(1)$  is normally occupied mostly by Ca; the main substitutions are Mn, REE and Y. In one crystal, more than 50% Ca is replaced by Mn and REE, resulting in an ordering in two distinct sites,  $M(1a)$  (Mn) and  $M(1b)$  (Ca + REE), and the symmetry reduced to  $R\bar{3}$ .  $M(2)$  is either a four-fold Fe-dominated site, or a five-fold site, usually Mn-dominated.  $M(3)$  and  $Si(7)$  are two central sites of the two crystallographically distinct nine-membered silicate rings, and related by the substitution  $^{[6]}M(3) + ^{[4]}Si(7) \rightleftharpoons 2^{[4]}Si(7)$ .  $M(3)$  is dominated by Nb (or W), and  $Si(7)$ , by (Si,Al). Na is present in five distinct sites (acentric eudialyte) of which the  $Na(4)$  site is particularly prone to incorporation of heavy elements such as REE and Sr. The  $O(19)$  site plays a key role in the structure, being the ligand shared by the  $M(3)$ ,  $M(2,5)$  and  $Na(4)$  sites. The degree of acentricity is strongly correlated with the chemical elements in specific atomic sites. Eudialyte *sensu stricto* represents the most centrosymmetric structure,  $R\bar{3}m$ . As substitutions such as  $Si \Rightarrow (Nb,W)$ ,  $Fe \Rightarrow Mn$ ,  $(Ca,Na) \Rightarrow (REE,Sr)$  take place, the structures become more and more noncentrosymmetric,  $R3m$ . The  $R3$

eudialyte has an incongruously low  $|E^2 - 1|$  value as a result of merohedral twinning. A complete formula for eudialyte requires structural data. An acceptable empirical formula,  $\text{Na}_{15}[\text{M}(1)]_6[\text{M}(2)]_3\text{Zr}_3[\text{M}(3)](\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH},\text{H}_2\text{O})_3 \text{X}_2$ , can be calculated on the basis of 29 (Si,Al,Zr,Ti,Hf,Nb,W,Ta) *apfu* ( $Z = 3$ ).

*Keywords:* eudialyte, kentbrooksit, crystal chemistry, single-crystal X-ray diffraction, electron-microprobe analysis.

KHOMYAKOVITE AND MANGANOKHOMYAKOVITE, TWO NEW MEMBERS OF THE EUDIALYTE GROUP FROM MONT SAINT-HILAIRE, QUEBEC, CANADA

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ABSTRACT

Khomyakovite, ideally  $\text{Na}_{12}\text{Sr}_3\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{W}(\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH},\text{H}_2\text{O})_3(\text{OH},\text{Cl})_2$  and manganokhomyakovite, ideally  $\text{Na}_{12}\text{Sr}_3\text{Ca}_6\text{Mn}_3\text{Zr}_3\text{W}(\text{Si}_{25}\text{O}_{73})(\text{O},\text{OH},\text{H}_2\text{O})_3(\text{OH},\text{Cl})_2$  are two new members of the eudialyte group from Mont Saint-Hilaire, Quebec. They occur as orange to orange-red, pseudo-octahedral crystals ranging in size from 0.5 mm (khomyakovite) to 5 mm (manganokhomyakovite). Associated minerals include, for khomyakovite: analcime, annite, calcite, natrolite, pyrite, and titanite, and for manganokhomyakovite: aegirine, albite, analcime, annite, cerussite, galena, kupletskite, microcline, molybdenite, natrolite, pyrite, pyrrhotite, sodalite, sphalerite, titanite, wöhlerite and zircon. Both minerals are transparent to translucent, with a vitreous luster and white streak. They are brittle, with a hardness of 5–6 (Mohs scale). They have no cleavage, no parting and an uneven fracture. They are uniaxial negative, for khomyakovite:  $\omega = 1.6279(5)$  and  $\epsilon = 1.6254(5)$ , and for manganokhomyakovite:  $\omega = 1.629(1)$  and  $\epsilon = 1.626(2)$ . They are trigonal, space group  $R\bar{3}m$ . For khomyakovite:  $a$  14.2959(8),  $c$  30.084(3) Å,  $V$  5324.6(7) Å<sup>3</sup>, and for manganokhomyakovite:  $a$  14.282(3),  $c$  30.12(1) Å,  $V$  5320(3) Å<sup>3</sup>,  $Z = 3$ . The strongest X-ray powder-diffraction lines, measured for manganokhomyakovite [ $d$  in Å ( $I$ )( $hkl$ )], are 11.500(90)(101), 9.535(70)(012), 6.452(50)(104), 6.072(50)(021), 5.735(50)(202), 3.406(50)(131), 3.213(50)(208), 3.167(50)(217), 2.980(100)(315) and 2.856(80)(404). The infrared spectrum of manganokhomyakovite is given. An electron-microprobe analysis of the khomyakovite crystal used for single-crystal work gave Na<sub>2</sub>O 11.35, K<sub>2</sub>O 0.52, MgO 0.04, CaO 10.42, MnO 1.63, FeO 4.33, SrO 8.45, Al<sub>2</sub>O<sub>3</sub> 0.09, La<sub>2</sub>O<sub>3</sub> 0.21, Ce<sub>2</sub>O<sub>3</sub> 0.18, SiO<sub>2</sub> 43.70, TiO<sub>2</sub> 0.11, ZrO<sub>2</sub> 10.62, HfO<sub>2</sub> 0.18, Nb<sub>2</sub>O<sub>5</sub> 1.33, Ta<sub>2</sub>O<sub>5</sub> 0.02, WO<sub>3</sub> 3.80, Cl 0.67, H<sub>2</sub>O 0.87, O ≡ Cl 0.15, total 98.37 wt.%. The proportion of H<sub>2</sub>O was calculated by stoichiometry from the structure analysis. The empirical formula of khomyakovite, based on 78.70 anions as determined in the structure analysis, is  $(\text{Na}_{12.26}\text{Ca}_{0.33}\text{K}_{0.38}\text{Sr}_{0.13}\text{REE}_{0.08})_{\Sigma 13.05}(\text{Sr}_{2.78}\text{Na}_{0.22})_{\Sigma 3}\text{Ca}_6(\text{Fe}_{2.05}\text{Mn}_{0.78}\text{Mg}_{0.03})_{\Sigma 2.86}(\text{Zr}_{2.94}\text{Ti}_{0.05}\text{Hf}_{0.03})_{\Sigma 3.02}(\text{W}_{0.56}\text{Nb}_{0.34})_{\Sigma 0.90}(\text{Si}_{24.78}\text{Al}_{0.06})_{\Sigma 24.84}\text{O}_{73}(\text{O},\text{OH},\text{H}_2\text{O})_{\Sigma 3.70}(\text{OH}_{1.36}\text{Cl}_{0.64})_{\Sigma 2}$ . For manganokhomyakovite,

an average of four electron-microprobe analyses gave Na<sub>2</sub>O 10.37 (10.05–10.59), K<sub>2</sub>O 0.41 (0.37–0.45), CaO 10.20 (10.08–10.35), MnO 4.21 (3.91–4.38), FeO 2.58 (2.40–2.65), SrO 9.17 (8.63–9.63), Al<sub>2</sub>O<sub>3</sub> 0.02 (0.00–0.05), La<sub>2</sub>O<sub>3</sub> 0.12 (0.00–0.27), Ce<sub>2</sub>O<sub>3</sub> 0.20 (0.00–0.30), SiO<sub>2</sub> 42.98 (42.51–43.39), TiO<sub>2</sub> 0.02 (0.00–0.07), ZrO<sub>2</sub> 10.43 (10.40–10.50), HfO<sub>2</sub> 0.17 (0.16–0.19), Nb<sub>2</sub>O<sub>5</sub> 1.58 (1.35–2.05), Ta<sub>2</sub>O<sub>5</sub> 0.03 (0.00–0.05), WO<sub>3</sub> 4.48 (3.66–4.83), Cl 0.84 (0.78–0.89), H<sub>2</sub>O 0.83, O = Cl 0.19, total 98.45 wt. %. The proportion of H<sub>2</sub>O was calculated by stoichiometry from the crystal-structure relationship with khomyakovite, confirmed by TGA and IR data. The empirical formula of manganokhomyakovite, based on 78.70 anions as found in the crystal structure of khomyakovite, is (Na<sub>11.51</sub>K<sub>0.30</sub>Ca<sub>0.25</sub>Sr<sub>0.04</sub>REE<sub>0.07</sub>)<sub>Σ12.17</sub> Sr<sub>3</sub> Ca<sub>6</sub> (Mn<sub>2.04</sub>Fe<sub>1.23</sub>)<sub>Σ3.27</sub> (Zr<sub>2.91</sub>Hf<sub>0.03</sub>Ti<sub>0.01</sub>)<sub>Σ2.95</sub> (W<sub>0.66</sub>Nb<sub>0.41</sub>Ta<sub>0.01</sub>)<sub>Σ1.08</sub> (Si<sub>24.60</sub>Al<sub>0.01</sub>)<sub>Σ24.61</sub> O<sub>73</sub> (O,OH,H<sub>2</sub>O)<sub>3.70</sub> (OH<sub>1.19</sub>Cl<sub>0.81</sub>)<sub>Σ2</sub>. For khomyakovite,  $D_{\text{calc.}} = 3.14 \text{ g/cm}^3$ , and for manganokhomyakovite,  $D_{\text{calc.}} = 3.17 \text{ g/cm}^3$ ,  $D_{\text{meas.}} = 3.13(3) \text{ g/cm}^3$ . Both minerals possess the eudialyte structure. Single-crystal data for khomyakovite show that W dominates over Nb in  $M(3)$ , and Sr over Na in  $Na(4)$ .  $M(2)$  is dominated by Fe in khomyakovite, and by Mn in manganokhomyakovite.

*Keywords:* khomyakovite, manganokhomyakovite, eudialyte, new mineral species, crystal structure, Mont Saint-Hilaire, Quebec.

## LABUNTSOVITE: SOLID SOLUTION AND FEATURES OF THE CRYSTAL STRUCTURE

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## ABSTRACT

Our study of solid solution in labuntsovite and related monoclinic minerals is based on chemical and electron-microprobe data for 44 samples (19 published and 25 new). The crystal structures of three samples with distinct compositions, recently refined, are here compared with the published structural data. Correlations between the composition and infrared spectral parameters for labuntsovite and labuntsovite-type minerals were determined. The general formula of minerals with labuntsovite structure ( $Z = 1$ ) is  $A1_4A2_4A3_{4-2x} [M2_x(H_2O)_{2x}] [M1_8(O,OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ , where  $0 < x < 2$ ,  $A1 = Na, Ca, G$ ;  $A2 = K, Na, H_3O, G$ ,  $A3 = K, Ba, Sr, H_3O, G$ ,  $M1 = Ti, Nb$ ;  $M2 = Mn^{2+}, Fe^{2+}, Mg, Zn, G$ , usually,  $n \approx 8$ . Correlations are observed among some components (large cations such as K, Ba, etc.,  $R^{2+}$  octahedrally coordinated cations, total number of octahedral

cations). The *A3* and *M2* positions are linked and occupied according to alternative mechanisms, e.g.,  $A3 [(2K)] + M2 [G] \leftrightarrow A3 [2H_2O] + M2 [Mn,Fe,Mg]$ . Four subgroups of monoclinic labuntsovite-type minerals are distinguished. 1) There are those with the labuntsovite structure and a predominance of vacancies in the *M2* octahedra; more than 50% of the *A3* sites are occupied by large cations. 2) There are minerals with the labuntsovite structure having a predominance of Fe, Mg, Mn, or Zn in the *M2* positions (linking octahedra) and a predominance of H<sub>2</sub>O in the *A3* position; their formula is:  $Na_4K_4(K,Ba...)_{4-2x} [R^{2+}_x(H_2O)_{2x}] [Ti_8(O,OH)_8] [Si_4O_{12}]_4 \cdot nH_2O$ , where  $1 < x < 2$ , and  $R = Mn, Fe, Mg, Zn$ . 3) There are minerals with vacant *M2* positions and more than three positions of extra-framework cations (vuoriyarvite and its analogues). An extensive solid-solution involving Ti and Nb, Na and K is typical for these phases. 4) Finally, there are minerals with the kuzmenkoite structure, which show a predominance of Mn, Fe, Mg, or Zn in the *M2* positions, and two positions of extra-framework cations. A low content of Na is typical for minerals of this subgroup. Their formula ( $Z = 1$ ) is:  $K_4G_4 [(Mn,Fe...)_2(H_2O)_4] [(Ti,Nb)_8(OH,O)_8] [Si_4O_{12}]_4 \cdot nH_2O$ .

*Keywords:* labuntsovite, chemical composition, solid solution, crystal structure.

COPARSITE,  $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ , A NEW MINERAL SPECIES FROM THE TOLBACHIK VOLCANO, KAMCHATKA PENINSULA, RUSSIA

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ABSTRACT

Coparsite, ideally  $\text{Cu}_4\text{O}_2[(\text{As},\text{V})\text{O}_4]\text{Cl}$ , occurs in the fumarole “Yadovitaya” (= “Poisonous”) in the North Breach of the great fissure Tolbachik eruption (1975–1976), Kamchatka Peninsula, Russia. It occurs as black or dark grey crystals, tabular on (100), elongate in the [010] direction, with well-developed {100}, {110} and {101} forms. Associated minerals are euchlorine, tolbachite, kamchatkite, ponomarevite, minerals from the klyuchevskite–alumoklyuchevskite solid-solution series, hematite, tenorite and vanadian lammerite. The grains of coparsite are found as small black inclusions in emerald-green euchlorine. The mineral has a metallic luster and a brown streak. Non-fluorescent. It is very brittle and thus does not allow measurements of hardness. Cleavage is perfect on the (100) plane. Coparsite is orthorhombic, space group *Pbcm*,  $a$  5.440(1),  $b$  11.154(2),  $c$  10.333(2) Å,  $V$  627.0(3) Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 4.76(1)$  g/cm<sup>3</sup> (based on the empirical formula). Diagnostic lines of the X-ray powder-diffraction pattern [ $d$  in Å( $I$ )( $hkl$ )] are: 5.31(30)(010), 4.69(40)(110), 3.70(30)(012), 3.03(60)(310), 2.82(10)(113), 2.62(100)(312),

2.39(40)(022,221), 1.67(20)(324,405). Electron-microprobe analyses yielded: CuO 69.03 (67.68–70.16), Fe<sub>2</sub>O<sub>3</sub> 0.17 (0–0.87), As<sub>2</sub>O<sub>5</sub> 15.50 (13.13–20.23), V<sub>2</sub>O<sub>5</sub> 7.72 (4.06–9.24), SO<sub>3</sub> 0.57 (0.20–0.99), Cl 8.47 (8.17–8.75), subtotal 101.46, O = Cl<sub>2</sub> –1.91 (1.84–1.97), total 99.55 (98.09–101.55) wt%. The empirical formula, normalized to O + Cl = 7 *apfu*, is Cu<sub>3.89</sub>Fe<sub>0.01</sub>O<sub>1.93</sub>[(As<sub>0.60</sub>V<sub>0.38</sub>S<sub>0.03</sub>)O<sub>4</sub>]Cl<sub>1.07</sub>, close to the ideal Cu<sub>4</sub>O<sub>2</sub>((As,V)O<sub>4</sub>)Cl confirmed by crystal-structure analysis. The mineral is named for its chemical composition: cop(per) + ars(enic).

*Keywords:* coparsite, new mineral species, arsenate–vanadate, Tolbachik volcano, Kamchatka Peninsula, Russia.

STEREOACTIVE LONE-PAIR BEHAVIOR OF Pb IN THE CRYSTAL STRUCTURE OF BIDEAUXITE:  $\text{Pb}^{2+}_2 \text{Ag}^+ \text{Cl}_3 \text{F} (\text{OH})$

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ABSTRACT

The crystal structure of bideauxite,  $\text{Pb}^{2+}_2 \text{Ag}^+ \text{Cl}_3 \text{F} (\text{OH})$ , cubic,  $a$  14.1273(6) Å,  $V$  2819.2(4) Å<sup>3</sup>,  $Fd\bar{3}m$ ,  $Z = 16$ ,  $D_{\text{calc}} = 6.26 \text{ g.cm}^{-3}$ , has been solved by direct methods and refined to an  $R$  index of 2.8% for 324 observed ( $5\sigma$ ) reflections measured with  $\text{MoK}\alpha$  X-radiation. There is one unique Ag site surrounded by an octahedral array of Cl anions, and one Pb site surrounded by nine anions with a very asymmetrical distribution of bonds and bond-lengths characteristic of stereoactive lone-pair behavior of  $\text{Pb}^{2+}$ . Four  $(\text{AgCl}_6)$  octahedra link by sharing corners to form an  $[\text{Ag}_4\text{Cl}_{18}]$  cluster, and these clusters link by sharing corners to form a three-dimensional chequerboard arrangement, with  $[\text{Pb}_4 (\text{OH})_2 \text{F}_2 \text{Cl}_{18}]$  clusters filling the interstices. The structure of bideauxite is not related to those of the paragenetically related minerals boléite and pseudoboléite.

*Keywords:* bideauxite, crystal-structure refinement, hydroxy-chloride.

## CRYSTAL-STRUCTURE DETERMINATION OF TWINNED KETTNERITE

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## ABSTRACT

The crystal structure of kettnerite,  $\text{CaBi}(\text{CO}_3)\text{OF}$ ,  $a$  3.7976(5),  $b$  3.7976(5),  $c$  13.569(4) Å,  $V$  195.71(8) Å<sup>3</sup>, space group  $Pm\bar{m}n$ ,  $Z = 2$ , has been refined to an  $R$  index of 0.016 on the basis of 265 unique, observed reflections. Although the cell and the distribution of diffraction intensities obey tetragonal symmetry, kettnerite is optically biaxial, and attempts to solve the structure with tetragonal symmetry led to stereochemical nonsense. Introduction of a twin plane *via* reflection on {110} for orthorhombic symmetry simulates tetragonal diffraction-intensity distribution for the merohedral twin, and gives a structure with sensible stereochemistry. Both large cations, Ca and Bi, have [8]-coordination, and  $\text{Bi}^{3+}$  shows stereoactive lone-pair behavior. The kettnerite structure is layered with a Ca–F layer, a Bi–O layer, and a  $\text{CO}_3$  layer with the plane of the ( $\text{CO}_3$ ) group orthogonal to the plane of the layer. Oxy-carbonate minerals are rare relative to hydroxy- and hydrated-carbonate minerals. The only cations that can satisfy the bond-valence requirements for a non-carbonate oxygen atom are those for which there is an electronic driving mechanism to produce a marked asymmetrical distribution of bond valences, such as for the uranyl group,  $(\text{UO}_2)^{2+}$ , and for large cations with stereoactive lone-pairs of electrons, *e.g.*,  $\text{Bi}^{3+}$ ,  $\text{Pb}^{2+}$ . In this regard, all oxy-carbonate minerals contain such cations.

*Keywords:* kettnerite, crystal structure, merohedral twin, stereoactive lone-pair of electrons.

## REFINEMENT OF THE CRYSTAL STRUCTURE OF RUTHERFORDINE

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## ABSTRACT

Rutherfordine,  $\text{UO}_2\text{CO}_3$ , is orthorhombic,  $a$  4.840(1),  $b$  9.273(2),  $c$  4.298(1) Å,  $V$  192.90(7) Å<sup>3</sup>, space group  $Imm2$ ,  $Z = 2$ . The structure was refined to an  $R$  index of 2.2% on the basis of 306 unique data [ $|F_o|/ss(F_o) > 5$ ] measured with  $\text{MoK}\alpha$  X-radiation on a single-crystal diffractometer. The structure consists of neutral sheets of edge- and corner-sharing ( $\text{UO}_8$ ) hexagonal bipyramids and ( $\text{CO}_3$ ) triangles, as originally proposed by Christ *et al.* (1955); our refinement, however, shows that ( $\text{CO}_3$ ) groups in alternate layers have the same orientation, not opposite orientations as originally reported. The refined value of the  $U\text{--}O(\text{uranyl})$  distance is strongly affected by the details of the absorption correction, ranging from 1.71 to 1.80 Å as a function of the plate-glancing angle used in an empirical psi-scan absorption correction and as a function of the type of weighting scheme used in the refinement. The Gaussian-quadrature method of integration also shows similar problems, but they are less extreme. The preferred value for the  $U\text{--}O(\text{uranyl})$  distance in rutherfordine is  $\sim 1.745$  Å; as rutherfordine contains no H atoms, the  $O(\text{uranyl})$  atom is [1]-coordinated, and should have the shortest  $U\text{--}O(\text{uranyl})$  distance stereochemically possible. The current work suggests that  $U\text{--}O(\text{uranyl})$  values less than 1.745 Å reported in other studies are adversely affected by less-than-optimum absorption corrections.

*Keywords:* rutherfordine, crystal structure, uranyl carbonate, uranium mineral.

## THE CRYSTAL STRUCTURE OF LUDWIGITE

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## ABSTRACT

We have refined the structure of ludwigite with a crystal taken from the Crestmore quarry, California; it is close to the end member in composition, ideally  $\text{Mg}_2\text{FeBO}_5$ . The sample has a formula  $\text{Mg}_{1.76}\text{Fe}_{1.22}\text{Al}_{0.02}\text{BO}_5$  and unit-cell dimensions  $a$  9.2411(6),  $b$  12.2948(9),  $c$  3.0213(3) Å,  $V$  342.27 Å<sup>3</sup>. The structure was refined in space group *Pbam*, to a final  $R_w = 0.023$  for 948 observed unique reflections. The very low Al content allows the refinement of the distribution of magnesium and iron in the structure without assumptions as to the location of aluminum.

*Keywords:* ludwigite, vonsenite, pinakiolite group, crystal structure, Crestmore quarry, California.

GORCEIXITE, A SINGULAR PRODUCT OF REPLACEMENT IN FOSSIL BONES FROM THE BAURU BASIN, BRAZIL

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ABSTRACT

Gorceixite, ideally  $\text{BaAl}_3(\text{PO}_4)(\text{PO}_3\text{OH})(\text{OH})_6$ , formed by the alteration of apatite in fossil bones found in Cretaceous sandstone in the Bauru Basin, southern Brazil. The original fine structure of the bone is preserved. The presence of gorceixite was established using X-ray powder diffraction, electron-microprobe analyses and optical microscopy. No convincing evidence was found to indicate a source of Ba and Sr required for the replacement of Ca in the bone phosphate.

*Keywords:* gorceixite, fossil bone, structure, optics, chemical composition, replacement, mineralogy, Bauru Basin, Brazil.



# DISCLINATIONS IN UNUSUAL GRAPHITE CRYSTALS FROM ANORTHOSITES OF UKRAINE

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## ABSTRACT

We describe unusual forms of graphite crystals in anorthosites from the Korsun–Novomirgorod pluton in Ukraine. A complete series of crystal morphologies exists, from tabular, to columnar, to pseudodipyramidal and pseudodipyramidal-prismatic, to nearly spherical. On the basis of our morphological observations, we present a possible mechanism of growth based on spiral-layer and polycentric growth in the presence of negative wedge disclinations.

*Keywords:* graphite, morphology, crystal growth, hypomorphism, disclinations, anorthosite, Korsun–Novomirgorod pluton, Ukrainian Shield.

OCCURRENCE OF *LREE*- AND Y-ARSENATES FROM A Fe–Mn DEPOSIT, LIGURIAN BRIANÇONNAIS DOMAIN, MARITIME ALPS, ITALY

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ABSTRACT

We report the occurrence of some rare and unknown *LREE*- and Y-arsenates. They are present within the Ponte dei Gorrazzi Fe–Mn deposit, associated with quartz arenites and subordinately with marbles of the Corsaglia Valley sequence, in the Ligurian Briançonnais Domain, Maritime Alps, Italy. These minerals mainly occur within microveins and microcavities as microcrystalline aggregates or small isolated prismatic crystals (up to 10  $\mu\text{m}$  in length). Three different groups have been distinguished on the basis of electron-microprobe data. 1) Group A is characterized by Y-rich grains with low *LREE* contents whose composition is consistent with the formula of chernovite ( $\text{YAsO}_4$ ). 2) Group B is characterized by *LREE*-rich grains (mainly La), with very low Y contents; their chemical composition does not correspond to any known natural phase, but it is consistent with that of the synthetic compound  $\text{LaAsO}_4$ . 3) Group-C grains are characterized by intermediate contents of Y and the *LREE*. Although they could be related to micrometer-scale intergrowths of Group A and B minerals, they are characterized by significant enrichments in Gd, Th and Ca, thus suggesting the possibility of a distinct mineral species.

*Keywords:* arsenates, chernovite, mineral chemistry, Fe–Mn deposit, Maritime Alps, Italy.

# TWO-XRD-LINE FERRIHYDRITE AND Fe–Si–Mn OXYHYDROXIDE MINERALIZATION FROM FRANKLIN SEAMOUNT, WESTERN WOODLARK BASIN, PAPUA NEW GUINEA

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## ABSTRACT

Large deposits of Fe–Si–Mn oxyhydroxide, intimately associated with active warm springs, cover the flanks and caldera of Franklin Seamount in the western Woodlark Basin, Papua New Guinea. The deposits are dominated by poorly crystalline Fe oxyhydroxide, so-called two-XRD-line ferrihydrite. Data on hydrothermal samples of ferrihydrite from Franklin Seamount provide new insights into the atomic structure and chemical composition of this mineral. Electron microscopy supported by X-ray and selected-area electron-diffraction (XRD, SAED) analysis shows that the Franklin Seamount ferrihydrite consists of soft friable agglomerates of randomly stacked colloidal platelets or crystallites, 20–90 Å in diameter, which possess short-range atomic order in two dimensions and highly variable specific surface-areas. Differential thermal analysis indicates that the ferrihydrite is very stable, not transforming to hematite until 570°C. Semiquantitative energy-dispersion spectroscopy (EDS) analysis with a spatial resolution of 35 Å indicates that agglomerates of pure ferrihydrite contain important amounts of Si (on average, 7.5 wt.% Si) and a constant Si:Fe ratio (on average, 0.45, atomic proportions) plus minor but variable amounts of sorbed P, S and As. Individual crystallites exhibit very little beam-induced damage during the EDS analysis. We suggest that Si is capable of being incorporated within the structure of the ferrihydrite. This suggestion is supported by XRD patterns showing a significant shift in the 11 (*hk*) hump to higher values of *d*, compared to Si-free ferrihydrite, and by the thermal stability of the mineral. EDS results and results of bulk analyses demonstrate the wide range of compositions of two-XRD-line ferrihydrite; nevertheless, an average composition of  ${}^{\text{VI}}(\text{Fe})_{2.9}{}^{\text{IV}}(\text{Si, Fe, Al})_{1.3}(\text{O, OH, H}_2\text{O})_{12}$  is proposed for the samples from Franklin Seamount.

*Keywords:* ferrihydrite, crystal structure, sorption, iron, silicon, X-ray powder diffraction, transmission electron microscopy, thermal analysis, Franklin Seamount, Papua New Guinea.

MÖSSBAUER SPECTRA OF PRIDERITE AND SYNTHETIC IRON-BEARING  
HOLLANDITE

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ABSTRACT

Mössbauer spectra for synthetic iron-bearing hollandites with nominal compositions of  $K_2Fe_2Ti_6O_{16}$  and  $BaFe_2Ti_6O_{16}$  and one natural sample of priderite were recorded at room temperature. All iron in the phases was found to occur as octahedral  $Fe^{3+}$  with no evidence for  $Fe^{2+}$ . Quadrupole splitting values show a trend consistent with increasing bond-length deviation of the octahedral sites.

*Keywords:* priderite, hollandite, Mössbauer spectrometry.

THE STRUCTURAL FORMULA OF TALC FROM THE TRIMOUNS DEPOSIT, PYRENEES,  
FRANCE

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#### ABSTRACT

A sample of talc (T111) from the Trimouns deposit, in the Pyrénées, France, was studied by various spectroscopic methods (FTIR, NMR, EPR and Mössbauer), as well as HRTEM and X-ray diffraction, in order to investigate the extent of minor substitutions in the tetrahedral and octahedral sites. Substitutions cause a deficiency in tetrahedral charge, compensated by an excess in octahedral charge, ensuring an electroneutrality of the structure. The charge deficiency on the layer of tetrahedra explains the active interaction between talc (used as filler) and polymer.

*Keywords:* talc, tetrahedral site, octahedral site, substitutions, spectroscopy, charge deficiency, polymer, Trimouns, Pyrénées.

## TOURMALINE COMPOSITIONS FROM THE SALIKVAN PORPHYRY Cu–Mo DEPOSIT AND VICINITY, NORTHEASTERN TURKEY

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### ABSTRACT

Tourmaline-bearing rocks occur in the Pontide volcanic island arc of northeastern Turkey, which hosts numerous small- to medium-sized Cu–Pb–Zn and Cu–Mo deposits. Weakly developed porphyry-style Cu–Mo mineralization accompanies the calc-alkaline volcano-plutonic rocks of Salikvan, in southeastern Artvin. Various types of tourmaline have been analyzed chemically, of which three main environments of formation are identified: (1) quartz–tourmaline veins, (2) tonalite porphyry and, to a lesser extent, in coarse granodiorite, and (3) tourmaline-rich rocks at the contacts of coarse granodiorite and basic volcanic rocks. Electron-microprobe data indicate that the tourmaline is relatively ferrous and calcic, and show a general trend from dravite to uvite end-members; the tourmaline at Salikvan formed by the reaction of Fe-rich hydrothermal fluids with Ca-rich amphibole and plagioclase in tonalite porphyry and granodiorite. The dominant variability in composition seems controlled by the exchange vector  $\text{CaMg}(\text{OH})_{-1}\text{Al}_{-1}$ . Tourmaline in quartz–tourmaline veins has moderate Fe/(Fe + Mg) values (0.37–0.51; mean 0.43), whereas that in tonalite porphyry is rich in iron, with a Fe/(Fe + Mg) of 0.45–0.53 (mean 0.48). Tourmaline in tourmaline-rich rocks is relatively rich in magnesium, with a Fe/(Fe + Mg) of 0.30–0.46 (mean 0.39). Trace-element contents of the tourmalines are low relative to those in tourmaline from massive sulfide deposits. Tourmaline has a

tendency to scavenge trace elements during crystallization, yielding correlations among Ag – (Au, Li, Mo, P, Pb, Sb, V, W), Au – (P, Pb, Sb, V, W), Li – (P, Pb, Sb, V, W), Mo – (Pb, Sb, V), P – (Sb, V, W), Sb – (V, W), Co – (Cr, Mn), Pb – (Sb, V), Ba–Sr, Zn–Cu, V–W, and Cr–Mn. Chondrite-normalized patterns of the rare-earth elements point out the possible contribution of hydrothermal processes to tourmaline formation. Boron isotope analyses of tourmaline from quartz–tourmaline veins and tourmaline from tourmaline-rich rocks have  $\delta^{11}\text{B}$  values of  $-9.4$  and  $-9.0\%$ , respectively, consistent with late-magmatic hydrothermal fluids.

*Keywords:* tourmaline, porphyry Cu–Mo deposit, electron-microprobe data, trace elements, rare-earth elements, boron isotope, Pontide belt, Turkey.

UPPER THERMAL STABILITY OF TOURMALINE + QUARTZ IN THE SYSTEM  
 $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3\text{-H}_2\text{O}$  AND  $\text{Na}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3\text{-H}_2\text{O-HCl}$  IN  
 HYDROTHERMAL SOLUTIONS AND SILICEOUS MELTS

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ABSTRACT

The upper thermal stability of Mg–Al tourmaline (Na-bearing and Na-free) in the presence of  $\text{H}_2\text{O}$ ,  $\text{SiO}_2$ ,  $\text{H}_3\text{BO}_3$  and HCl has been investigated experimentally at 200 MPa total pressure between 680° and 850°C as a function of the boron content of the fluid, using conventional hydrothermal cold-seal vessels and an internally heated gas apparatus, with a mixture of synthetic and natural minerals and an HCl-bearing hydrous fluid as starting material. In the Na-free system, breakdown of tourmaline + quartz occurs according to the reaction  $\text{tur} + \text{qtz} = \text{crd} + \text{sil} + \text{B-bearing fluid}$  at  $T \geq 750^\circ\text{C}$ , at  $\text{B}_2\text{O}_3$  contents in the fluid between ~0.5 and ~9 wt%. In the Na-bearing system, the reaction  $\text{tur} + \text{qtz} = \text{crd} + \text{melt}$  occurs at  $T \geq 730^\circ\text{C}$ , at  $\text{B}_2\text{O}_3$  concentrations of ~5 to ~8 wt%. The melt contains ~2 wt%  $\text{B}_2\text{O}_3$ . At lower  $\text{B}_2\text{O}_3$  concentrations in the hydrous fluid, decomposition according to reaction  $\text{tur} + \text{qtz} = \text{crd} + \text{ab} + \text{B-bearing fluid}$  was observed at ~700°C. The composition of tourmaline changes systematically as temperature increases. In the Na-bearing system, an increasing proportion of vacancies on the X-site of tourmaline was found as a result of the substitution  $\text{Na}_{-1}\text{Mg}_{-1}\text{GAl}$ , in addition to a certain amount of Al-incorporation by  $\text{Mg}_{-1}\text{H}_{-1}\text{Al}$ . In the Na-free system, the latter substitution leads to Al-enriched tourmaline.

*Keywords:* tourmaline + quartz, upper thermal stability, granite system, cordierite, hydrothermal experiments.