

INSTABILITY OF PEROVSKITE IN A CO₂-RICH ENVIRONMENT: EXAMPLES FROM CARBONATITE AND KIMBERLITE

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ABSTRACT

Intricate multiphase pseudomorphs after perovskite (Nb-, *LREE*-poor) from calcite carbonatite (Sebljavr complex, Kola Peninsula, Russia) and serpentine calcite kimberlite (Iron Mountain, Wyoming) are described. In the kimberlite, the major products of perovskite replacement are (in order of crystallization): kassite, anatase and titanite plus calcite, ilmenite, *LREE*-Ti oxide [? lucasite-(Ce)]. In the carbonatite, perovskite is initially replaced by anatase plus calcite and, subsequently, ilmenite and ancylite-(Ce). In both instances, the development of calcite and Ti-bearing phases after perovskite involved initial progressive leaching of Ca²⁺ from the structure followed by crystallization of ilmenite and *LREE* minerals in the final stages, after the precipitation of groundmass calcite. The formation of kassite and titanite in the pseudomorphs in kimberlite was controlled by a lower Ca leach-rate and higher activity of SiO₂ in this system, compared with the carbonatite. The similarity between the two types of pseudomorphs results from the instability of Nb-*LREE*-poor perovskite in a CO₂-rich fluid at low temperatures. Perovskite is considered an unsuitable host for radioactive ⁹⁰Sr and *REE* isotopes due to the low resistance of CaTiO₃ to leaching and incompatibility of Sr and the rare earths with the products of perovskite replacement.

Keywords: perovskite, anatase, ilmenite, kassite, ancylite-(Ce), lucasite-(Ce), carbonatite, kimberlite, Sebljavr complex, Kola Peninsula, Russia, Iron Mountain, Wyoming.

COMPOSITIONAL VARIATION OF PEROVSKITE-GROUP MINERALS FROM THE
Khibina Complex, Kola Peninsula

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ABSTRACT

Perovskite-group minerals from the Khibina alkaline complex, Kola Peninsula of Russia, are primarily members of the lueshite – perovskite – loparite-(Ce) solid solution series. The widest compositional range is exhibited by perovskite-group minerals from the foidolite series, poikilitic nepheline syenite (rischorrite) and associated pegmatites. The trend of compositional evolution of perovskite-group minerals is from perovskite *sensu stricto* through cerian and cerian niobian perovskite to calcian niobian, niobian calcian and niobian loparite-(Ce), and then to isolueshite, a Na–Nb-dominant member of the perovskite family. This trend corresponds well with the trend established for loparite from the Lovozero stratified intrusion. Loparite in metasomatic rocks of the Khibina complex may represent either a relict assemblage or a late-stage phase crystallized from metasomatic fluids.

Keywords: perovskite, loparite, isolueshite, ultramafite, foidolite, nepheline syenite, albitite, Khibina alkaline complex, Kola Peninsula, Russia.

A NEW TYPE OF SCANDIUM MINERALIZATION IN PHOSCORITES AND CARBONATITES OF THE KOVDOR MASSIF, RUSSIA

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ABSTRACT

Scandium mineralization of a new genetic type has been discovered in the Kovdor alkaline-ultrabasic massif, Kola Peninsula, Russia. It is represented by a new mineral, juonniite, simplified formula $\text{CaMgSc}(\text{PO}_4)_2(\text{OH})\cdot 4\text{H}_2\text{O}$, occurring in low-temperature hydrothermal assemblages in the phoscorite – carbonatite complex of the Kovdor massif. The mineral forms spherulites up to 0.8 mm in diameter and is associated with late carbonates and hydrous phosphates. Juonniite occurrences are confined to a linear reactivated fault, which intersects phoscorites and carbonatites. Metasomatism of phoscorites caused almost a two-fold enrichment in Sc in clinohumite-bearing units. Late hydrothermal solutions affected cataclastic clinohumite-bearing phoscorites along the fault zone; the subsequent dissolution of sulfides and Sc-bearing minerals (*e.g.*, forsterite, baddeleyite, pyrochlore-group minerals, *etc.*) was accompanied by mobilization of traces of Sc, most likely in the form of carbonate and sulfate. Fluorapatite-bearing carbonatites with abundant cavities provided the necessary conditions for the precipitation of scandium in the form of a hydrous phosphate, juonniite.

Keywords: scandium, carbonatites, phoscorites, clinohumite, cataclasis, mineralization, juonniite, hydrothermal alteration, Kovdor massif, Kola Peninsula, Russia.

APATITE AS A MONITOR OF FRACTIONATION, DEGASSING, AND METAMORPHISM IN THE SUDBURY IGNEOUS COMPLEX, ONTARIO

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ABSTRACT

Apatite occurs as an accessory phase throughout the Sudbury Igneous Complex (SIC), Ontario, a layered igneous complex consisting dominantly of norite, quartz gabbro, and granophyre. Apatite also is present in the overlying tuffaceous rocks of the Onaping Formation. Representative samples from three traverses (NW, NE, SW) across the complex have been studied in detail; the NW suite is the most pristine. Apatite is found primarily as a post-cumulus (or intergranular) phase, but becomes a cumulus mineral in the quartz gabbro. Despite textural signs of rapid growth, the apatite is homogeneous. It is F-rich; Cl and OH contents decrease from the base of the complex upward, as in several other layered intrusions. In the SIC, Cl and OH probably decreased relative to F upon vapor saturation of the evolving melt. The concentrations of *LREE*, up to 2 wt% La₂O₃ + Ce₂O₃ + Nd₂O₃, are highest in apatite near the base of the complex. The chondrite-normalized *REE* patterns and ⁸⁷Sr/⁸⁶Sr values (0.707–0.708) are similar in apatite from each rock type of the SIC. The complex evolved normally by fractional crystallization of a single batch of highly contaminated basic magma. The high initial ⁸⁷Sr/⁸⁶Sr values in apatite indicate that the relatively silica-rich basic magma had a substantial crustal component, or possibly consisted entirely of remelted crust. The apatite from the norite and that from the granophyre had a common magmatic source. Apatite from metamorphosed parts of the complex has significantly lower levels of Cl and *LREE*, compared to primary apatite from the NW section; furthermore, its ⁸⁷Sr/⁸⁶Sr value has been reset (up to 0.739) by exchange of strontium with adjacent K-rich minerals during recrystallization.

Keywords: apatite, Sudbury Igneous Complex, crystal chemistry, cumulates, contamination, trace elements, metamorphic recrystallization, Ontario.

CHEMICAL CONTROLS ON THE SOLUBILITY OF Zr-BEARING PHASES IN
SIMPLIFIED PERALKALINE MELTS AND APPLICATION TO THE STRANGE LAKE
INTRUSION, QUEBEC – LABRADOR

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ABSTRACT

The solubility of Zr-bearing minerals was measured in H₂O-saturated, peralkaline haplobasaltic, haplosyenitic and haplogranitic melts \pm Cl \pm F at 800°C and 1 kbar. In halogen-free and F-bearing melts, the solubility of Zr-bearing phases reached a maximum of 4 and 3.5 wt.% ZrO₂, respectively, in melts with 57 to 60 wt.% silica. No such maximum was observed for Cl-bearing compositions, which became saturated in a Zr-bearing phase at ZrO₂^{melt} concentrations of 2 to 2.2 wt.%. A silica concentration of 57 to 60 wt.% represents a threshold above which zircon is the saturating Zr-bearing phase for all compositions. For compositions with SiO₂ content below this range, wadeite (K₂ZrSi₃O₉) crystallizes in the halogen-free experiments, whereas ZrO₂ is the saturating phase in the F- and Cl-bearing experiments. The positive slope of the wadeite saturation curve on X(ZrO₂) – X(SiO₂) plots suggests that increasing activity of silica increases the solubility of wadeite. Since this behavior of wadeite is not expected based on a simple dissolution mechanism, a more complex equilibrium involving different structural units is proposed. Observations that zircon is scarce, whereas elpidite (Na₂ZrSi₆O₁₅•3H₂O) and other alkali and alkaline-earth zirconosilicates are abundant in the Strange Lake peralkaline intrusive complex in northern Quebec – Labrador, indicate that the parent magma did not saturate with a Zr-bearing mineral until it cooled to a low temperature, probably less than 600°C.

Keywords: zircon, wadeite, solubility, peralkaline magmas, Strange Lake granite, Quebec – Labrador.

MORPHOLOGY OF CHIOLITE TWINS FROM THE MOREFIELD MINE, AMELIA COUNTY, VIRGINIA

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ABSTRACT

Well-formed twinned crystals of chiolite to 3 mm long have recently been found in replacement bodies in pegmatitic granite at the Morefield mine, Amelia County, Virginia. Crystals are composed primarily of the forms {011} and {017}(?), and are invariably twinned on {011}. The twins range from subequant to elongate, and from relatively simple contact twins to complex penetration twins with hourglass- or S- or L-shaped cross-sections. Untwinned crystals have not been seen.

Keywords: chiolite, twin, growth dynamics, Morefield mine, Virginia.

TRICLINIC MUSCOVITE: X-RAY DIFFRACTION, NEUTRON DIFFRACTION AND PHOTO-ACOUSTIC FTIR SPECTROSCOPY

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ABSTRACT

Details of the H site in muscovite were determined using single-crystal neutron-diffraction data collected at room temperature and powder neutron-diffraction data collected at 12 K. Single-crystal neutron-diffraction data, collected at room temperature by Rothbauer (1971), were re-examined using a split-site model for H in the space group $C2/c$. Low-temperature neutron-diffraction data were used to evaluate the thermal-vibrational effect on the distribution of nuclear density at the H sites. The separation of the two sites is wider (0.78 \AA) at 12 K, but separate nuclear-density maxima were not observed. At least two unique OH stretching bands are revealed by FTIR PAS (Fourier-Transform InfraRed PhotoAcoustic Spectroscopy) experiments. The intensity ratio of the component bands changes as the mirror speed varies, allowing detection of individual stretching bands in severely overlapped spectra. This result confirms that there are two distinct OH groups in the structure of the muscovite examined here. Collectively, these results indicate that there are two distinct H-atom positions in the structure of this muscovite, either disordered with long-range $C2/c$ symmetry or ordered with lower symmetry. Long-exposure precession photos recorded at room temperature show weak $h0l$ (l odd) reflections that violate c -glide symmetry, assumed to exist in muscovite designated as the polytype $2M_1$. Single-crystal peak-profiling also revealed similar well-defined reflections that are confirmed to be Bragg reflections, and not due to double diffraction. Combined with previous second-harmonic generation data on muscovite, these results indicate $C\bar{1}$ symmetry for this sample of muscovite. The driving force for the symmetry lowering from $C2/c$ to $C\bar{1}$ in muscovite involves cooperative ordering of H atoms over two distinct positions in the structure.

Keywords: muscovite, triclinic symmetry, H-atom positions, neutron diffraction, Rietveld structure refinement, Fourier-transform infrared photo-acoustic spectroscopy.

X-RAY AND NEUTRON SINGLE-CRYSTAL STUDY OF $P4/n$ VESUVIANITEALESSANDRO PAVESE¹*Dipartimento di Scienze della Terra, Università di Milano, Via Botticelli 23, I-20133, Milano, Italy*MAURO PRENCIPE¹ AND MARIO TRIBAUDINO¹*Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, Via Valperga Caluso 35, I-10125, Torino, Italy*STEEN SØRENSEN AAGAARD¹*Risø National Laboratory, DK-4000, Roskilde, Denmark*

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ABSTRACT

Single-crystal X-ray- and neutron-diffraction refinements ($R = 3.9\%$ and 6.6% , respectively) were performed on a sample of $4/n$ vesuvianite [a 15.532(1), c 11.821(1) Å, V 2851.7(5) Å³] from a rodingite in Val d'Ala, Piemonte, Italy. The results demonstrate an ordered distribution of Ca over Ca(4) a,b and of Fe over $M(3)a,b$ sites, whereas no preference is shown by Al, Fe and Mg atoms at $M(2)a,b$ sites. Moreover, the neutron refinement located five hydrogen positions [H(10) a,b,c and H(11) a,b], statistically occupied. H(11) a,b atoms are bonded to O(11) a and b , whereas H(10) a,b,c atoms are located along the 4-fold axis, and form hydroxyl groups with O(10) a and b . The presence of hydrogen gives rise to several possible local configurations, leading to complex schemes of order–disorder.

Keywords: vesuvianite, X-ray diffraction, neutron diffraction, cation distribution, H-bearing sites, order–disorder.

THE CRYSTAL STRUCTURE OF $\text{Na}_2\text{MgGd}_2(\text{Si}_4\text{O}_{12})\text{F}_2$ AND ITS RELATIONSHIP WITH LEUCOPHANITE

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ABSTRACT

The structure of a newly synthesized rare-earth fluorosilicate, $\text{Na}_2\text{MgGd}_2(\text{Si}_4\text{O}_{12})\text{F}_2$, was determined using single-crystal X-ray diffraction. It crystallizes in the monoclinic system, $P2_1/c$, with unit-cell parameters a 5.178(3), b 7.510(2), c 14.381(4) Å, β 90.22(2)°, V 559.1(2) Å³ and $Z = 2$. The structure consists of SiO_4 tetrahedra in [010] zigzag chains connected by MgO_4F_2 octahedra. The stacking of the resulting $\text{Mg}(\text{Si}_4\text{O}_{12})\text{F}_2$ sheets defines voids in which Gd^{3+} and Na^+ are found. Similar silicate chains, connected by BeO_3F tetrahedra, exist in leucophanite and result in $\text{Be}_2(\text{Si}_4\text{O}_{12})\text{F}_2$ sheets.

Keywords: fluoride, silicate, rare earth, new synthetic species, structure.

SYNTHESIS AND RIETVELD REFINEMENT OF NEW PHOSPHATE AND ARSENATE ANALOGUES OF PARACELSIAN

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ABSTRACT

Two new arsenates with the general formula $A^{2+}(\text{ZnAsO}_4)_2$ ($A = \text{Sr}, \text{Ba}$) were synthesized by solid-state reaction. Furthermore, $\text{Ba}(\text{ZnPO}_4)_2$ was obtained under hydrothermal conditions. X-ray diffractograms of these compounds were indexed with a monoclinic unit-cell, and their structures were refined by the Rietveld method using reported atomic coordinates for paracelsian $\text{Ba}(\text{AlSiO}_4)_2$. Comparison of these structures with those of aluminosilicate and gallogermanate isomorphs illustrates a strong deviation to the pseudo-orthorhombic symmetry that may be explained by the very different charges and ionic radii of the tetrahedrally coordinated cations. Distortion of the tetrahedral sites as well as of the network of tetrahedra are found. The paracelsian form of $\text{Ba}(\text{ZnPO}_4)_2$ may only be obtained under hydrothermal conditions and at a temperature ($T = 500^\circ\text{C}$, $P = 2 \text{ kbar}$); it undergoes an irreversible transition at $T = 800^\circ\text{C}$ and ambient pressure to a hexagonal form with space group $P3m1$.

Keywords: paracelsian, monoarsenate, monophosphate, Rietveld analysis, polymorphism.

RIGID-BODY CHARACTER OF THE SO₄ GROUPS IN CELESTINE, ANGLESITE AND BARITE

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ABSTRACT

The crystal structures of natural celestine (Sr_{1.00})SO₄, anglesite (Pb_{0.99}Sr_{0.01})SO₄, and barite (Ba_{0.99}Sr_{0.01})SO₄ have been refined in space group *Pbnm* utilizing rotating anode, Mo X-ray diffraction data from single crystals. Unit-cell parameters for celestine are *a* 6.8671(7), *b* 8.3545(8), and *c* 5.3458(6) Å, for anglesite, *a* 6.9549(9), *b* 8.472(1), and *c* 5.3973(8) Å, and for barite, *a* 7.154(1), *b* 8.879(2), and *c* 5.454(1) Å. Structural data are presented for these sulfates with greatly improved precision over previous studies due to high peak to background intensity ratios and precise analytical absorption corrections. The final model *R*(*F*) values are 0.025, 0.041, and 0.019, for celestine, anglesite, and barite, respectively. The average bond-distance from divalent cation to the nearest twelve oxygen atoms is 2.827(1) Å in celestine, 2.864(5) Å in anglesite, and 2.951(2) Å in barite. The average sulfur-to-oxygen bond distance is 1.475(2) Å in celestine, 1.476(6) Å in anglesite, and 1.476(2) Å in barite. The sulfate tetrahedra in each structure show very similar distortions that are attributed to the bonding of the various oxygen atoms to the divalent cations, which is similar in each structure. Thus, the different metal cations do not seem to affect the size or shape of the sulfate tetrahedra. An analysis of the displacement parameters suggests that the SO₄ groups behave as rigid molecular units, with an apparent shortening of the S–O bonds of 0.008–0.010 Å.

Keywords: sulfates, celestine, anglesite, barite, X-ray diffraction data, rigid-body motion.

THE STRUCTURE OF COMPREIGNACITE, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$

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ABSTRACT

The structure of compreignacite, $K_2[(UO_2)_3O_2(OH)_3]_2(H_2O)_7$, $Z = 2$, orthorhombic, a 14.8591(7), b 7.1747(3), c 12.1871(5) Å, V 1299.3(2) Å³, space group $Pnmm$, has been solved by direct methods and refined by full-matrix least-squares techniques to an agreement factor (R) of 3.2% and a goodness-of-fit (S) of 1.05 using 1497 unique observed reflections ($|F_o| \geq 4\sigma_F$) collected with $MoK\alpha$ X-radiation and a CCD (charge-coupled device) area detector. The structure contains two symmetrically distinct U^{6+} cations that are part of $(UO_2)^{2+}$ uranyl ions (Ur), both of which are in turn coordinated by two O atoms and three OH groups arranged at the equatorial corners of pentagonal bipyramids. The uranyl polyhedra share equatorial edges and corners to form sheets of polyhedra that are parallel to (100) at $x \approx 1/4$ and $3/4$. The sheets are topologically identical to the sheets that occur in the structures of becquerelite, billietite, protasite, richetite, and α - U_3O_8 . There is one symmetrically distinct partially occupied K position and three symmetrically distinct H_2O groups in the interlayer at $x \approx 0$ and $1/2$. Each K cation is coordinated by four O_{Ur} atoms of the adjacent sheets of uranyl polyhedra, as well as three H_2O groups. Two of the symmetrically distinct H_2O groups in the structure are bonded to K, and the other is held in the structure only by H bonds. The K polyhedra share a face, forming a dimer with the composition $K_2O_6(H_2O)_4$. Additional linkages between the interlayer constituents and the sheets of uranyl polyhedra are provided by H bonds.

Keywords: compreignacite, uranyl mineral, uranium, structure determination, uranyl oxide hydrate.

THE STRUCTURE OF BOLTWOODITE AND IMPLICATIONS OF SOLID SOLUTION TOWARD SODIUM BOLTWOODITE

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ABSTRACT

The structure of boltwoodite, monoclinic, a 7.0772(8), b 7.0597(8), c 6.6479(7) Å, β 104.982(2)°, V 320.9(1) Å³, space group $P2_1/m$, has been refined by full-matrix least-squares techniques to an agreement factor (R) of 3.2% and a goodness-of-fit (S) of 1.13 using 760 unique observed reflections ($|F_o| \geq 4\sigma_F$) collected with MoK α X-radiation and a CCD (charge-coupled device) area detector. The structure determination provided the formula $(K_{0.56}Na_{0.42})[(UO_2)(SiO_3OH)](H_2O)_{1.5}$, $Z = 2$, which is supported by analyses done with an electron microprobe, and which differs from the previously accepted formula in the absence of a hydronium ion, the presence of an acid silicate group, and the number of H₂O. The structure contains silicate tetrahedra and uranyl pentagonal bipyramids that share edges and corners to form aaa-uranophane-type sheets that are parallel to (100) at $x \approx \frac{1}{4}$ and $\frac{3}{4}$. There are four distinct partially occupied sites in the interlayer that correspond to one Na, one K, and two H₂O groups. Local arrangements result in either Na ϕ_6 octahedra (ϕ : unspecified anion) or K ϕ_7 polyhedra. Local arrangements of the interlayer are non-centrosymmetric, although the long-range symmetry of the structure is consistent with space group $P2_1/m$. The structure of boltwoodite permits substantial variation of interlayer composition, which is significant from the perspective of mineral stability. In addition, boltwoodite may be a key phase in determining the future mobility of certain radionuclides in a geological repository containing spent nuclear fuel.

Keywords: boltwoodite, sodium boltwoodite, uranophane, spent nuclear fuel, repository, crystal structure, uranyl mineral.

BLATONITE, $\text{UO}_2\text{CO}_3\cdot\text{H}_2\text{O}$, A NEW URANYL CARBONATE MONOHYDRATE FROM SAN JUAN COUNTY, UTAH

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ABSTRACT

Blatonite, ideally $\text{UO}_2\text{CO}_3\cdot\text{H}_2\text{O}$, is a new uranyl carbonate mineral found in the Jomac mine, Brown's Rim, San Juan County, Utah. It occurs in seams of gypsum located between some bedding planes of a layer of siltstones within the Triassic Shinarump conglomerate. Associated U^{6+} minerals are boltwoodite, coconinoite, metazeunerite, and rutherfordine, together with the Cu^{2+} minerals azurite, brochantite, carbonate-cyanotrichite and malachite. Blatonite occurs as acicular crystals that are canary yellow and translucent with a silky luster and colorless streak. It strongly fluoresces in UV. $H_{\text{Mohs}} = 2-3$. $D_{\text{meas.}} = 4.05(2)$, $D_{\text{calc.}} = 4.02 \text{ g/cm}^3$ (idealized formula). Optically uniaxial (+), $\omega = 1.588(2)$, $\epsilon = 1.612(2)$. The crystals are nonpleochroic. Blatonite is hexagonal or trigonal (space group unknown): $a = 15.79(1)$, $c = 23.93(3) \text{ \AA}$, $V = 5167(9) \text{ \AA}^3$ and $Z = 36$. The strongest reflections of the X-ray powder pattern [$d(\text{in } \text{ \AA})(I)hkl$] are: 7.86(47)110, 6.91(55)103, 6.56(77)201, 4.76(40)114, 4.34(36)213 and 3.06(100)207. Electron microprobe and thermogravimetric analyses gave UO_3 81.98, CO_2 12.82, H_2O 5.38, total 100.18 wt %. The empirical formula is $0.988 \text{ UO}_2\cdot 1.004 \text{ CO}_2\cdot 1.029 \text{ H}_2\text{O}$. The name honors the Belgian crystallographer Norbert Blaton, University of Leuven, Belgium. Holotype material is deposited in the mineralogical collection of the Royal Belgian Institute of Natural Sciences, Brussels, Belgium.

Keywords: blatonite, new mineral species, uranyl carbonate monohydrate, Jomac mine, San Juan County, Utah.

GRAESERITE, Fe₄Ti₃AsO₁₃(OH), A NEW MINERAL SPECIES OF THE DERBYLITE GROUP FROM THE MONTE LEONE NAPPE, BINNTAL REGION, WESTERN ALPS, SWITZERLAND

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ABSTRACT

Graeserite, ideally Fe₄Ti₃AsO₁₃(OH), is a new mineral species of the derbylite group, which includes derbylite, tomichite, and hemloite. It is found in needle-shaped crystals, elongate along the *c* axis. Graeserite is monoclinic, space group *A2/m*, with the cell parameters *a* 7.184(2), *b* 14.289(6), *c* 5.006(2) Å, β 105.17(2)°, *V* 495.9(2) Å³, *Z* = 2, *D*_{calc.} = 4.56 g/cm³. The VHN_{25g} is 521 (Mohs hardness ~5½). The strongest five lines of the X-ray powder-diffraction pattern [*d* in Å(*I*)(*hkl*)] are: 2.681(100)(231), 2.846(80)(131), 1.583(50)(351), 3.117 (30)(220), and 2.029(30)(122). Graeserite is black and metallic, with a black streak; it displays a conchoidal fracture. Pleochroism, bireflectance and internal reflections were not observed. The measured values of reflectance in air are compared with those of other members of the derbylite group. Electron-microprobe analyses gave TiO₂ 40.89, Fe₂O₃ 33.64, FeO_{calc} 3.94, PbO 5.00, As₂O₃ 13.51, Sb₂O₃ 1.43, and H₂O_{calc} 1.30, total 99.80 wt.%. The empirical formula, based on 13 atoms of oxygen and one hydroxyl group, is (Fe³⁺_{2.91}Fe²⁺_{0.38}Ti_{0.54}Pb_{0.15})_{Σ3.98}Ti₃(As³⁺_{0.94}Sb³⁺_{0.07})_{Σ1.01}O₁₃(OH). Graeserite occurs as a hydrothermal mineral in Alpine-type fissures in gneisses of the Monte Leone nappe at the locality Lärcheltini, in the Binntal region of Switzerland, in association with other rare arsenic oxides. With the name, we honor Stephan Graeser, University of Basel, Switzerland, for his fundamental studies of arsenic-bearing minerals.

Keywords: graeserite, new mineral species, derbylite group, Binntal region, Western Alps, Switzerland.

THE RESPONSE OF LUMINESCENCE IN SYNTHETIC CALCITE TO LABORATORY HEATING

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ABSTRACT

Synthetic calcite doped with Mn and Mg has been prepared from aqueous solutions of CaCl₂ using four different methods: (1) rapid precipitation using Na₂CO₃, (2) rapid precipitation using NaHCO₃, (3) rapid precipitation using ammonium carbonate, and (4) slow precipitation from solutions in contact with ammonium carbonate vapor. Calcite prepared using methods (1) to (3) forms rhombs 1 to 4 mm across and has relatively broad XRD peaks. Calcite prepared using method (4) forms rhombs up to 1 mm across and has relatively narrow XRD peak widths. Cathodoluminescence (CL) spectra were obtained to characterize the intensity, wavelength and bandwidth of emission. Calcite prepared using methods (1) and (2) generally has lower CL intensity than compositionally similar calcite prepared using methods (3) and (4). The wavelength of emission is independent of concentration where Mn and Mg total less than approximately 0.01 atoms per formula unit, but increases at higher concentrations of these elements. The bandwidth increases with the concentrations of Mn and Mg. Calcite prepared by methods (1) to (4) was heated in CO₂ and hydrothermally in the temperature range 75 to 400°C. Calcite prepared using methods (1) to (3) usually coarsens significantly, and XRD peak widths become smaller on heating, especially in the presence of water. Little change in grain size or XRD peak widths takes place on heating calcite prepared using method (4). The intensity of CL increases as a consequence of heating. Calcite made by methods (1) and (2) shows larger relative increases in CL intensity on heating than that made by methods (3) and (4). Hydrothermal treatment promotes a greater increase in CL intensity than does heating in CO₂. The wavelength of emission increases and bandwidth decreases on heating calcite that contains more than approximately 0.01 Mn and Mg *apfu*. Where the concentration of these elements is lower, changes in wavelength and bandwidth on heating are smaller and erratic in direction. The effects of heating on CL intensity and XRD peak width are attributed to the annihilation of defects during recrystallization. Changes in the wavelength and bandwidth of CL emission on heating are attributed to local redistribution of the activator ions.

Keywords: calcite, synthesis, luminescence, recrystallization.

RARE SULFOSALTS FROM VULCANO, AEOLIAN ISLANDS, ITALY. I. Se-BEARING KIRKIITE, $Pb_{10}(Bi,As)_6(S,Se)_{19}$

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ABSTRACT

This note reports the first occurrence of a Se-bearing variety of kirkiite, a rare lead – bismuth – arsenic sulfosalt, from the deepest part of fumarole F11, La Fossa crater, island of Vulcano, Italy. Small crystals of sphalerite and aggregates of cannizzarite occur sporadically on the kirkiite crystals. Optical properties, X-ray powder-diffraction data and the results of electron-microprobe analyses are compared with those of kirkiite from type locality as well as of phase A, the synthetic analogue. An electron-microdiffraction study revealed the presence of three structural varieties of kirkiite. The Se content ranges from 0.73 to 1.16 wt%. As and Bi concentrations vary from 6.49 to 7.98 wt% and from 14.32 to 16.84 wt%, respectively. The composition field of kirkiite from Vulcano can be described by the formula $Pb_{10}(As_{6-x}Bi_x)_{\Sigma 6}(S_{19-y}Se_y)_{\Sigma 19}$, where $2.3 \leq x \leq 2.8$ and $0.3 \leq y \leq 0.5$, which is close to the ideal formula $Pb_{10}(As,Bi)_6(S,Se)_{19}$. Kirkiite and its associated minerals at Vulcano crystallized at a high fugacity of sulfur and a high temperature (470°C, direct measurements). This temperature is in agreement with that known for the synthetic analogue, stable at 400°C.

Keywords: kirkiite, cannizzarite, Pb–Bi–As sulfosalts, Pb–Bi sulfosalts, fumarolic incrustations, Vulcano Island, Italy.

CRYSTALLOGRAPHY, MINERAL CHEMISTRY AND CHEMICAL NOMENCLATURE OF GOLDFIELDITE, THE TELLURIAN MEMBER OF TETRAHEDRITE SOLID-SOLUTION SERIES

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ABSTRACT

This comprehensive review on goldfieldite, $\text{Cu}_{10}\text{Te}_4\text{S}_{13}$, and tellurian phases of the tetrahedrite solid-solution series (tetrahedrite_{ss}), contains a summary of crystallographic properties and compositional data. A new classification scheme for these minerals is proposed. Furthermore, the association of these minerals to specific ore environments is discussed. The bond angles and the optical properties of goldfieldite and tetrahedrite are very similar. The cell dimension of goldfieldite is intermediate between that of tennantite and tetrahedrite; thus it is strongly controlled by the ionic radius of Te. As expected, Cu vacancies in goldfieldite reduce the size of the unit cell. The best electron-microprobe analyses are obtained when S is standardized on tetrahedrite, bismuthinite or stibnite. The preferred procedure for calculating structural formulae of tellurian examples of the tetrahedrite_{ss} from electron-microprobe results is based on total numbers of atoms, as this distributes possible analytical errors over all elements. Owing to the occurrence of vacancies in goldfieldite, the calculation should be based on 29 atoms per formula unit (*apfu*) for minerals with 2 or less Te *apfu* [$\text{Te}/(\text{Te} + \text{As} + \text{Sb} + \text{Bi} + \text{Te}) < 0.5$]. For more Te-rich compositions, formula calculation on the basis of $29 - 4[\text{Te}/(\text{Te} + \text{As} + \text{Sb} + \text{Bi}) - 0.5]$ *apfu* is recommended. A review of available electron-microprobe data on goldfieldite and tellurian members of the tetrahedrite_{ss} supports previous observations on the substitutions. For up to 2 Te *apfu*, substitution of Te^{4+} for $(\text{As}, \text{Sb}, \text{Bi})^{3+}$ is coupled with Cu^+ for $(\text{Fe}, \text{Zn})^{2+}$ substitution, whereas higher levels of Te result in vacancies (reduced Cu contents). A nomenclature grid for goldfieldite and the other Cu-dominant examples of the tetrahedrite_{ss} is proposed on the basis of their semimetal content. The name "goldfieldite" is reserved for those compositions of the tetrahedrite_{ss} that contain more than 3 *apfu* of Te. For those minerals with 2 to 3 *apfu* of Te, modifying adjectives such as arsenoan, stiboan or bismuthoan should be used, according to the second most abundant element. The remaining tellurian minerals of the tetrahedrite_{ss} should be named according to the most abundant semimetal (tennantite for the As-rich member, tetrahedrite for the Sb-rich one) preceded by "tellurian", provided that at least 1 *apfu* of Te is present. Most of these tellurian minerals of the tetrahedrite_{ss} are found in high-sulfidation epithermal Au deposits, regardless whether they are As- or Sb-rich. A few cases have been reported from porphyry Cu

and volcanogenic massive sulfide deposits.

Keywords: goldfieldite, tetrahedrite solid-solution series, electron-microprobe data, substitutions, structural formula, nomenclature, ore deposits.

LINDSTRÖMITE FROM COBALT, ONTARIO

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ABSTRACT

The results of the characterization of a well-ordered lindströmite from the Drummond mine (also known as the Silver Miller mine), 3 km southeast of Cobalt, Ontario are reported. Chemical analyses by electron microprobe gave the composition $\text{Cu}_{2.70}\text{Pb}_{2.80}\text{Bi}_{7.18}\text{Sb}_{0.09}\text{S}_{15}$, intermediate between the ideal composition of lindströmite $\text{Cu}_3\text{Pb}_3\text{Bi}_7\text{S}_{15}$ and of krupkaite $\text{CuPbBi}_3\text{S}_6$. Least-squares refinement of the powder X-ray-diffraction pattern gave an orthorhombic cell $a = 55.99(3)$, $b = 11.549(3)$, $c = 4.010(1)$ Å, which is within error limits of the cell given for lindströmite from the type locality, Gladhammar, Sweden. The optical properties in reflected light and the indentation hardness are reported, and were found to be very similar to those of krupkaite and hammarite. It is not possible to distinguish among intermediate members of the bismuthinite – aikinite series on the basis of their optical properties or indentation hardness. Electron-diffraction patterns reveal a well-ordered $5a$ superlattice of the bismuthinite parent cell, the superlattice reflections are sharp, and there is no evidence of streaking along a^* . High-resolution images show the perfectly ordered nature of the structure. The nature of compositional ordering processes in these bismuthinite – aikinite minerals is discussed.

Keywords: lindströmite, bismuthinite – aikinite series, supercell ordering, transmission electron microscopy, Cobalt, Ontario.

AN OCCURRENCE OF TOBERMORITE IN TERTIARY BASALTS FROM PATAGONIA, CHILE

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ABSTRACT

The hydrated calcium silicate tobermorite has been found in continental alkaline basalts of Tertiary age at Puyuhuapi, in Chilean Patagonia. Tobermorite occupies the core of amygdules, accompanied by small amounts of tacharanite, a silicate similar in composition to tobermorite. Other secondary minerals identified are phillipsite (Ba-rich variety?), which commonly occurs as a rim mineral associated with tobermorite in the same amygdule, analcime, and various Ca–Na–K zeolites. The tobermorite belongs to the 11 Å variety and is akin to the “anomalous” type, as indicated by XRD and chemical data (EPMA, SEM–EDX, ICP). Conditions for its formation imply hydrothermal activity at temperatures *ca.* 150°C, involving solutions with Na, Al and a low Ca/Si value. These conditions are similar to those favoring the occurrence of tacharanite. This is the first mention of tobermorite and tacharanite in an Andean environment.

Keywords: tobermorite, tacharanite, zeolites, alkaline basalts, Tertiary, Patagonian Andes, Chile.