

O31-05

Nano-scale phase intergrowths in crystals of a 'new' tungstate mineral from Pittong, Victoria, Australia.

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Strongly oxidised W-Mo-Bi deposits are ideal environments for the formation of a wide range of rare, unusual and potentially new species of tungstates and molybdates. For example, recent discoveries at localities in eastern Australia have yielded assemblages containing koechlinite, betpakdalite, russellite and the new species elsmoreite. In this paper we report on a synchrotron-TEM investigation of a secondary tungstate found at an abandoned W-Bi-Au mine at Pittong, about 35 km west of Ballarat, in Victoria. The mineral occurs as glistening yellow encrustations of platy crystals on etched wolframite (manganese ferberite) enclosed in reef quartz. SEM examination revealed that crystals are curved plates only about 1 μm thick forming open aggregates up to 0.2 mm across. Chemical analysis (EPMA and CHN) showed major W, Fe, Na and H_2O , giving an approximate formula $\text{NaFe}^{+3}[(\text{WO}_3\text{OH})_4]\text{H}_2\text{O}$. Powder X-ray diffraction (PXRD) obtained using synchrotron radiation gave a pattern which could not be matched and which showed a mixture of sharp and broad peaks. The positions and intensities of the sharp peaks are similar to those in the PXRD patterns for synthetic Bi-Fe niobate phases. Our recent structure determinations for these latter phases show that they can be described in terms of unit-cell-scale intergrowths of slabs of pyrochlore-type with hexagonal tungsten bronze (HTB)-type structures.

Single crystal diffraction patterns showed that the crystals have hexagonal symmetry, with $a = 7.31 \text{ \AA}$ and with c approximately 19.5 \AA . However the spacings of the diffraction spots along c^* are not commensurate, consistent with disorder in the stacking along the c axis. The nature of this disorder was studied using high resolution transmission electron microscopy (TEM) images. These show that individual crystallites consist of a core of pyrochlore/HTB intergrowth phase, surrounded by a thin ($\sim 30 \text{ \AA}$) rim of pure HTB type. The ultra-thin rims of the HTB phase give the broad peaks in the PXRD patterns. Furthermore, the TEM images of the core show variations in the widths of the pyrochlore and HTB blocks, and it is this variation that gives the incommensurate character to the diffraction patterns. The special difficulties associated with preparing mineral-naming proposals for these types of disordered intergrowth minerals will be discussed.

O31-06

Menezesite from Cajati, São Paulo, Brazil: The first heteropoly niobate mineral

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The new mineral menezesite, $\text{Ba}_2\text{MgZr}_4(\text{BaNb}_1\text{O}_4)_2\text{.12H}_2\text{O}$, cubic, has been found in the last years of the decade of 1970 by Luiz Alberto Dias Menezes Filho, but its study has begun only in May 2003. The mineral was named in honor of Menezes (born 1950), mining engineer, mineral collector and merchant. He studied the minerals from Cajati. The menezesite IMA number is 2005-023. It occurs in the contact zone between dolomite-carbonatite and "Jacupirangite" (= a pyroxenite) at the Jacupiranga mine, in Cajati county, São Paulo state, Brazil. This is also the type locality for quintinite-2H. The associated minerals are dolomite, calcite, magnetite, clinohumite, phlogopite, aenylite, strontianite and tochilinite. Menezesite was formed as a vug mineral. The mineral forms aggregates of rhombododecahedra up to 1 mm. The color is reddish brown, the streak white and the luster vitreous. It is transparent. Menezesite is the first natural heteropoly niobate. The first synthetic heteropoly niobates were obtained in 2002. Heteropolyaniobates are negatively charged clusters of corner- and edge-sharing early transition-metal MO_6 octahedra and the heteronion is usually located in the interior of the cluster. The geometry, composition, and charge of these clusters are varied through synthesis parameters, and cluster properties are highly tunable as a function of these characteristics. Heteropolyaniobates have been employed in a range of applications that include virus-binding inorganic drugs (including AIDS virus), homogeneous and heterogeneous catalysts, electro-optic and electrochromic materials, metal and protein binding, and as building blocks for nanostructuring of materials. The heteropolyaniobates of W, Mo, and V, which have found numerous applications, are formed simply by acidification of solutions of their oxoanions. Unlike other heteropolyaniobates, heteropoly niobates are basic rather than acidic, which means they can survive longer in the generally basic or neutral environments of radioactive wastes and blood, respectively. Once such compounds bind with a virus, it is no longer capable of entering a cell to damage it. Heteropolyaniobates may also bind with radionuclides (actinides), which remove them from the mixture by phase separation for easier and safer storage. The complete menezesite description is in preparation. Financial support by FAPESP.

O31-07

Kintoreite-Corkite solid solution mineral from Japan

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Kintoreite is Pb-Fe-P-dominant member of the alunite-beudantite-crandallite group (Pring et al., 1995). This mineral is a member of segnitite (Pb-Fe-As-dominant) and plumbojarosite (Pb-Fe-S-dominant) series and is P-dominant. The chemical formula of the alunite-beudantite-crandallite group minerals is $\text{AB}_2\text{X}_2(\text{OH})_6$, where A=Ph, K, Na, Ca, ...; B=Fe, Al, ...; $\text{X}_2=(\text{PO}_4)_2$, $(\text{AsO}_4)_2$, $(\text{SO}_4)_2$, $(\text{PO}_3)_2(\text{SO}_4)$. In the system of Pb-Fe series, corkite and beudantite are defined as $\text{P:S}=1:1$ and $\text{As:S}=1:1$ minerals, respectively. Kintoreite-corkite ss mineral was found with faustite from Kawazu mine, Shizuoka Prefecture, Japan (Matsuyama et al., 1996). This mineral occurs as brown crust and is accompanied with goethite and other Fe-oxides. EDS analysis was performed. The sample is zoned in the back-scattered-electron image. Since each zone is thin compared with electron beam diameter, chemical analysis was difficult. Cell parameters were obtained with XRD analysis and the mineral was identified as kintoreite-corkite ss mineral. The strongest lines of X-ray powder-diffraction pattern [d in angstrom (1)(hkl)] are: 5.92 (80)(101), 3.65 (39)(110), 3.06 (100) (113), 2.955 (26) (202), 2.811 (24)(006), 2.527 (27) (024), 2.251 (37) (107), 1.970 (27) (303), 1.820 (19) (220) and 1.487 (17)(0,1,11). The X-ray data were indexed on a hexagonal unit cell, giving $a=7.2863 \text{ \AA}$, $c=16.865 \text{ \AA}$. The chemical composition obtained with preliminary analysis was that of around the boundary of kintoreite and corkite. The typical composition is as follows: PbO 33.78, Al_2O_3 3.33, Fe_2O_3 32.5, P_2O_5 16.46, SO_3 6.35 and total 92.42.

Detailed data will be shown and we will discuss on the kintoreite-corkite ss.

O31-08

Cs analogue of polyliothionite from rare-element granitic rocks in China

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Known examples of Cs-bearing micas to date include nanopingite ($\text{Cs}_2\text{O} = 25.29 \text{ wt\%}$, Yang et al., 1988), cesian biotite ($\text{Cs}_2\text{O} = 5.97 \text{ wt\%}$, Ginsburg et al., 1972) and rubidian cesian phlogopite ($\text{Cs}_2\text{O} = 6.60 \text{ wt\%}$, Hawthorne et al., 1999). Polyliothionite with extreme Cs enrichment has been found in the Yichun lepidolite-topaz granite (Jiangxi, E China) and in the Koktokay #3 pegmatite (Xinjiang, NW China).

Two types of occurrence of the cesian polyliothionite are described in the Yichun granite, one consists of inclusions of Cs-rich polyliothionite within rock-forming minerals, the other represents a replacement rim around the primary polyliothionite flakes. Electron-microprobe analyses show dominant Cs_2O contents up to 25.8 wt%, or 0.9 apfu (based on 11O). Li_2O contents calculated according to Tindle-Webb's equation varies around 4.0 wt%. The estimated ^{31}Al varies mostly in the range of 0.09 and 0.40 apfu, and the $\text{Cs}/(\text{K}+\text{Cs})$ ratio exceeds 0.50, even up to 0.96. These parameters plot the Cs-rich micas from the Yichun granites, in the diagram of ^{31}Al versus $\text{Cs}/(\text{K}+\text{Cs})$, in the area of Cs-analogue of polyliothionite.

In the Koktokay #3 pegmatite, four types of occurrence of the Cs-dominant polyliothionite are characterized: (1) Cs-dominant polyliothionite as outer zone on compositionally conventional polyliothionite core; (2) Cs-dominant polyliothionite as fine-flaked overgrowth on muscovite veinlet; (3) Cs-dominant polyliothionite as veinlets in main polyliothionite; and (4) Cs-dominant polyliothionite veinlets in elbaite. Electron microprobe analyses revealed clearly extreme Cs enrichment in polyliothionite (also up to 26 wt% Cs_2O). F contents are determined in the range of 4-5.5 wt%. Calculated Li_2O contents oscillate about 4 wt%. The estimated ^{31}Al varies in the range of 0.11 and 0.37, and $\text{Cs}/(\text{K}+\text{Cs})$ ratio ranges from 0.61 to 0.92. Therefore, Cs-rich micas are classified into Cs-dominant analogue of polyliothionite in the ^{31}Al versus $\text{Cs}/(\text{K}+\text{Cs})$ diagram.

Micro-X-ray diffraction patterns of the polyliothionite with conventional composition (1.86 wt% Cs_2O) and high Cs contents (25.26 wt% Cs_2O) are characterized by several strong peaks [d in \AA (1)(hkl): 2.983(48)(025), 2.593(38)(200), 1.506(100)(-3.32), 1.014(45)(446)], and are thus consistent, in the low-angle region, with the standard patterns for polyliothionite found in the JCPDS catalog.

Micro-Raman spectra show several characteristic peaks for mica, such as 1140-1150 and 708-711 cm^{-1} , thus revealing that Cs-dominant polyliothionite is structurally similar to that of the Cs-poor polyliothionite.

To summarize up, Cs-rich micas both from the Yichun granite and from the Koktokay pegmatite are in fact the Cs-dominant analogue of polyliothionite, which can be proposed as a new species in the mica group.