

Te, Sb and W mineralization at the Black Pine mine, Montana

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The Black Pine mine is located 14.5 km NW of Philipsburg, Granite Co., Montana, USA (46°26'52"N, 113°21'56"W), and has been spartically mined since the 1880s for Au, Ag and W. The ore zone is also enriched in Te, Sb, As and P, resulting in a large suite of secondary minerals - approximately 50 species have been reported to date. The Black Pine mine is also the type locality for one new mineral, phillipsburgite. Our current investigation is centered on the mineralogy of the secondary Te minerals and the crystal chemistry of Sb and W substitution in arsenates.

So far several tellurates have been identified including dugganite and a new mineral, the P-analogue of dugganite [Pb₃Zn₃Te⁶⁺O₆(PO₄)(OH)₃]. This new mineral occurs in various shades of purple, as barrel-shaped or flatted crystals up to about 0.5 mm across. The barrel-shaped crystals can be colour zoned, with purple, greyish purple and colourless most prominent. Single crystal studies show this new mineral to be P321 with *a* = 8.392(5) and *c* = 5.204(3) Å. Its crystal structure comprises of heteropolyhedral sheets of edge-sharing TeO₆ octahedra and PbO₈ disphenoids oriented parallel to (001). The sheets are cross-linked by PO₄ and ZnO₄ tetrahedra, which share corners to form an interlinked, two- and three-connected two-dimensional net parallel to (001). This new mineral appears to be different from the previously described tellurate kuskite, Pb₃Zn₃Te⁶⁺O₆(PO₄)₂, described as orthorhombic *Cmmm*, *C222*, *Cm2m* or *Cmm2*. Several other tellurates are under investigation and may also prove to be new.

The extent of Sb and W substitution in oxysalt minerals is not well understood. At the Black Pine Mine, Sb occurs in large quantities in several Pb arsenates, namely carminite and segnitite-beudantite, whilst W is elevated in segnitite-beudantite specimens. A systematic crystallographic study is underway to track the amount of Sb and W substitution in the crystal structures of these minerals. EMPA data show that there is potential for at least a partial substitution between carminite and a theoretical new end-member, with a composition of PbSb₂(AsO₄)₂(OH)₂.

Effects of pH on the release of Cr(VI) from sparingly soluble Cr(OH)₃(s) by MnO₂(s) under circumneutral conditions

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Contamination of soil and groundwater by hexavalent chromium, Cr(VI), is a worldwide concern mainly due to the wide range of industrial applications of chromium. The deleterious effects of Cr are attributed to Cr(VI) because of its toxicity and carcinogenicity. Since Cr(VI) exists as oxyanion in aquatic systems, it is highly mobile in the subsurface. Moreover, chromate, the dominant species of Cr(VI), has weak tendency to adsorb to oxides and clay minerals under neutral to alkaline conditions. Reportedly, Cr(VI)-contaminated soil and groundwater have been successfully remediated by reducing it to less toxic Cr(III) using various reductants. Previous studies have shown that the reduction product, Cr(III), can easily be reoxidized to Cr(VI) by manganese oxide minerals under acidic conditions but may be stable under circumneutral conditions because it readily precipitates on the surface of manganese solid phases as Cr(OH)₃(s), which is suggested to hinder the heterogeneous oxidation. Our results, however, show that substantial amounts of Cr(VI) are released from Cr(OH)₃(s) in the presence of MnO₂(s) at pH > 6.

We examined the reactions occurring in the mixed suspensions of Cr(OH)₃(s) and MnO₂(s) at pH 6, 7, and 8. The suspensions were prepared with 1 g/L each of Cr(OH)₃(s) and/or MnO₂(s) in 0.01 M NaNO₃. The values of pH were maintained using 10 mM HEPES or TRIS buffers. Dissolved Cr or Mn was not detected even at pH 6 when either solid phase presents alone. In the mixed suspensions, however, dissolved Cr(VI) concentrations increased with time at pH 7 and 8 and the rate of Cr(VI) release was higher at pH 8 by a factor of 1.7 than at pH 7. Dissolved Cr(VI) concentration reached up to 17.7 μM in 550 h at pH 8, whereas it was only 0.55 μM at pH 6 in the corresponding reaction period. By contrast, dissolved Mn concentrations increased substantially (up to 71.4 μM) at pH 6 but was not detected at higher pH's during the reaction periods. The opposite pH dependence of the Cr(III) oxidation by MnO₂(s) was predicted because the corresponding redox reactions consume protons. The apparent pH dependence is attributable to the different sorption behaviors of the reaction products, Cr(VI) and Mn(II).