

Contemporary precipitation of tungsten-bearing ferrihydrite from drainage waters in the Grantcharitsa tungsten deposit, Bulgaria

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Contemporary drainage and ochreous products of its discharge from the closed abandoned old gallery at the Grantcharitsa scheelite deposit (Bulgaria) were studied by field and laboratory methods (ICP-OES, ICP-MS, SEM, EPMA, XRD). The drain is inherently diluted (EC=100-140 μ S/cm) with S (6-12 mg/L), Si (6-22 mg/L), Na (6-10 mg/L), Fe (0.2-3.3 mg/L), Mg (1.5-2 mg/L), Al (0.03-0.26 mg/L), W (0.19-3.5 μ g/L) and pH 4.4-6.0. The dissolved iron is presented by Fe²⁺ (~95%) and FeSO₄(aq) (~5%). The concentration of Fe and W and the pH of the water are variable and reach their maximum values during the dry (autumn) season. It has been established that the formation of ochreous sediments takes place with the participation of iron-oxidizing bacteria such as *Gallionella ferruginea*. The XRD pattern of the ochreous sediment corresponds to the patterns of nanocrystalline 6-lines ferrihydrite and to the structural model of ferrihydrite by Michel et al. [1] and PDF 47-1775. Besides Fe₂O₃ (55.5-64.0 wt.%), the ferrihydrite sediment contains SiO₂ (12.0-16.4 wt.%), SO₃ (1.3-2.4 wt.%), Al₂O₃ (3.1-6.8 wt.%). The most important minor element in the ferrihydrite is tungsten with a content 700-1000 ppm. There is no clear relationship between the content of tungsten in ferrihydrite sediments and in drainage waters, but the highest content of W in sediments was found in the material in contact with water with the highest content of W found by us (3.5 mg/L) at pH ~ 6. Coprecipitation with Fe³⁺ and adsorption by ferrihydrite appear to be the mechanisms for W incorporation into the ferrihydrite sediment. Fe/W ratios in water and sediments suggest almost complete extraction of W from water by ferrihydrite. It is assumed that the source of the ferrous iron and tungsten in the drainage water are melanterite and secondary W minerals described for the oxidation zone of the deposit.

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References:

[1] Michel et al. The structure of ferrihydrite, a nanocrystalline material. *Science*. 2007, 316, 1726-1729; PDF 76-2921