

A Tale of Tungsten/Wolfram, Ore Formation, and Apatite-Fluorite Gangue

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First extracted from scheelite (which was initially named tungsten) and later wolframite, tungsten/wolfram (both names were accepted by IUPAC until 2005) is a critical metal by virtue of its extraordinarily high tensile strength and a supply that is dominated by a single country. Tungsten is concentrated hydrothermally to form ore deposits and, until recently, was thought to be mobilised dominantly as HWO_4^- . Our experimental study of tungsten speciation in fluoride-enriched hydrothermal fluids, however, has shown that tungsten also dissolves as $\text{H}_3\text{WO}_4\text{F}_2^-$. Moreover, at the pH typical of tungsten ore-forming systems ($< \sim 5$), $\text{H}_3\text{WO}_4\text{F}_2^-$ is the dominant species in solution for NaF concentrations as low as 0.05m. This is important because the hydrothermal fluids forming tungsten deposits have been estimated to contain elevated concentrations of fluorine, and fluorite and topaz (and also apatite) are common gangue minerals. A feature of some of the richest tungsten deposits is that the ores are the products of the remobilisation of sub-economic mineralisation, commonly in the form of scheelite that has been replaced by fluorite and/or apatite. Here, we present results of an experimental study of the solubility of scheelite. They show that phosphate and fluoride sequester calcium from scheelite to form apatite and/or fluorite, releasing hundreds of ppm of tungsten to the fluid, especially at near neutral pH. This provides a compelling explanation for why magmatic hydrothermal fluids exsolved from later, more evolved phosphorus- and fluorine-rich magmas are able to remobilise earlier subeconomic scheelite mineralisation to form large and even giant high-grade tungsten deposits. Thus, although fluoride- and possibly phosphate-bearing tungstate species play an essential role in tungsten transport, fluoride and phosphate are arguably more important in their roles as the agents that enable some magmatic-hydrothermal systems (notably those that undergo multiple stages of evolution) to produce the giant deposits required to meet the global demand for this critical metal.