Incorporation mechanism of tungsten in W-Fe-Cr-V-bearing rutile

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**ABSTRACT**

Rutile is a common mineral in many types of ore deposits and can carry chemical or isotopic information about the ore formation. For closer understanding of this information, the mechanisms of incorporation of minor elements should be known. In this work, we have investigated natural rutile crystals with elevated concentrations of WO3 (up to 17.7 wt%), Cr2O3 (7.5), V2O5 (4.1), FeO (7.3), and other metals. X-ray absorption spectroscopy (XAS) of rutile at the Fe K, Cr K, V K, and W K edges shows that all cations are coordinated octahedrally. The average oxidation state of V is +3.8, and that of Cr is near +4. Shell-by-shell fitting of the W L3 EXAFS data shows that W resides in the rutile structure. Raman spectroscopy excludes the possibility of hydrogen as a charge-compensating species. High-resolution TEM and electron diffraction confirm this conclusion as the entire inspected area consists of rutile single crystal with variable amounts of metals other than Ti. Our results show that rutile or its precursors can be efficient vehicles for tungsten in sedimentary rocks, leading to their enrichment in W and possibly later fertility with respect to igneous ore deposits. Leucoxene, a nanocrystalline mixture of Ti and Fe oxides, is an especially suitable candidate for such a vehicle.

**Keywords:** Rutile, tungsten, incorporation, X-ray absorption spectroscopy, transmission electron microscopy, ore deposits

**INTRODUCTION**

Rutile and cassiterite are common minerals in many types of ore deposits, for example, greisen-type deposits (e.g., Moscati and Neymark 2020). Their trace element and isotopic composition carry much information about the ore-forming processes, and, therefore, cassiterite has been called the “zircon of hydrothermal systems” (Blevin and Norman 2010), although this term could be equally well applied to rutile. The degree to which we can understand this information depends not only on detailed studies of selected ore deposits but also on the knowledge of how these elements are associated with the host mineral, what is their chemical and oxidation state, and how do they partition between coexisting minerals. The mode of association could bring additional insights into the processes that form ore deposits.

An element that is increasingly reported in elevated concentrations in rutile or cassiterite is tungsten (e.g., Kwak 1983; Rice et al. 1998; Clark and Williams-Jones 2004; Müller and Halls 2005; Novák et al. 2008; Mozola et al. 2017; Reznisky et al. 2017; Moscati and Neymark 2020; Bennett et al. 2020). The ore deposits of tungsten are commonly linked to acidic or intermediate igneous complexes but not all such complexes, no matter how evolved, develop an ore deposit, a camp of ore deposits, or even small ore occurrences (cf. Fig. 2 in Romer and Kroner 2016). For tungsten, the source magmatic rocks have been commonly assigned to reduced S-type granitic magmas of crustal origin (e.g., Yuan et al. 2018) but, as pointed out by Lecumberri-Sanchez et al. (2017), such magmatism alone is insufficient to generate Sn-W deposits. These rocks must be fertile, with pre-magmatic, elevated concentrations of W, Sn, and other elements (Romer and Kroner 2014, 2016). Fortuitous enrichment of the protolith by metals—for example by weathering of older ore deposits—could be an explanation in a few cases but would not apply to the majority of the magmatic complexes. Furthermore, it would not answer the question of the metal enrichment in the protolith but only shift it to geologically older formations.

In this work, we investigated the incorporation mechanisms of tungsten and associated elements in rutile. Using electron microprobe analyses, X-ray absorption and Raman spectroscopy, and transmission electron microscopy, the association of tungsten and other elements with the host structure was determined on the scale of micro- to nanometers. This information is then

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