

Molybdenite as a Rhenium Carrier: First Results of a Spectroscopic Approach Using Synchrotron Radiation

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ABSTRACT

The chemical and physical properties of rhenium render it a highly demanded metal for advanced applications in important industrial fields. This very scarce element occurs mainly in ores of porphyry copper-molybdenum deposits associated with the mineral molybdenite, MoS₂, but it has also been found in granite pegmatites and quartz veins as well as in volcanic gases. Molybdenite is a typical polytype mineral which crystal structure is based on the stacking of [S-Mo-S] with molybdenum in prismatic coordination by sulphide anions; however, it is not yet clearly established if rhenium ions replace Mo⁴⁺ cations in a disordered way or else, if such replacement gives rise to dispersed nanodomains of a rhenium-rich phase. As a contribution to clarify this question, an X-ray absorption spectroscopy (XANES) study using synchrotron radiation was performed at the Re L₃-edge of rhenium-containing molybdenite samples. Obtained results are described and discussed supporting the generally accepted structural perspective that rhenium is mainly carried by molybdenite through the isomorphous replacement of Mo, rather than by the formation of dispersed Re-specific nanophase(s).

Keywords: Molybdenite Polytypes; Rhenium; Re L₃ Absorption Edge; XANES

1. Introduction

Rhenium (Re) was the last naturally occurring element to be discovered, with a mean concentration in the earth's crust of the order of 1 ppb [1]. This very scarce element has been found in granite pegmatites and quartz veins (e.g. in Japan [2]) as well as in volcanic gases, namely from the Kudryavy Volcano, Kurile Islands [3], but it occurs mainly in ores of porphyry copper-molybdenum deposits [4-9] associated to molybdenite, MoS₂, generally recognized as the main Re-carrier in nature [10,11]. Indeed, specific rhenium minerals are so far confined to very few sulphides among which rheniite, ReS₂ [12]—expected to be structurally identical to synthetic rhenium disulphide [13] despite its crystal structure has not yet been fully determined [14], and tarkianite (Cu, Fe) (Re, Mo)₄S₈ [15], a lacunar kenotetrahedral [16] thiospinel.

The unique combination of physical and chemical properties of rhenium and its alloys makes this element extremely attractive, particularly as a coating (being highly refractory and resistant to corrosion), thus highly de-

manded in a great diversity of industrial fields, from the production of high-temperature super-alloys for aircraft engines to catalysts in the production of lead-free high-octane gasolines [17]. Rhenium has been extracted mainly as a by-product of the copper mining industry, once the metal is oxidized to the molecular compound dirhenium heptaoxide in the course of roasting molybdenum sulphide ores [18], being subsequently recovered from the flue dusts under the form of ammonium perrhenate [19]. The largest world rhenium producer is currently Chile, followed by the United States, Peru and Poland [20].

The hypothesis that rhenium-content of molybdenite could be enhanced in the rhombohedral polytype was raised by the study of molybdenite polytypism addressed in detail forty years ago [21-24]. Nevertheless, the way rhenium is incorporated is not yet clearly established—that is, if Re-ions just replace Mo-ions in a disordered way and in real dependence from the polytype or else, if rhenium forms specific nanophase(s) and occurs concentrated in nanodomains. With the purpose of contributing

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