



# Laser ablation ICPMS study of trace element chemistry in molybdenite coupled with scanning electron microscopy (SEM) – An important tool for identification of different types of mineralization



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## ABSTRACT

Using the example of four different types of associations from the Bohemian Massif (greisen-, gold-, base metal-, and “barren granite”-related) and of one porphyry–Cu–Mo(Au) deposit from Uzbekistan, it is shown that molybdenite from a specific type of mineralization possesses a distinct trace-element geochemical composition, which is locally influenced by the presence of relevant mineral phases occurring in the form of sub-nano-, nano- to micron-scale impurities/inclusions. It is documented that, besides typically lattice-bound elements (Re, and W) and isostructural concentrations of Se and Te (substituting for S), molybdenite can concentrate other metals (e.g., Ag, As, Au, Bi, Cu, Nb, Pb, Zn, Zr) which mostly form inclusions or impurities. Typical lattice-bound elements (W, Se, Te) can locally occur as impurities or micro-inclusions. The distribution of Re in molybdenite indicates crustal sources for the group of greisen-, base-metal-, and a few of the granite-related deposits, compared to a mixed mantle/crustal source for the Au-related and majority of granite-related deposits. Greisen-related molybdenites show the highest mean values of As (40 ppm), Cu (58 ppm), and Zn (45 ppm), but the lowest mean Re value (0.4 ppm). They contain abundant inclusions of native bismuth, which are accompanied, depending on the individual deposit, by variable quantities of Bi(Se)-, Bi(Pb)-, Pb(Bi)- and Pb–Bi–Cu-bearing phases and also bismuthinite (Bi<sub>2</sub>S<sub>3</sub>), wolframite and scheelite. Gold-related molybdenite typically has the highest mean values of Ag (464 ppm), Au (24 ppm), Bi (1188 ppm), Sb (39 ppm), and Te (112 ppm) and also the highest median values of these elements. Gold mostly occurs as inclusions of native Au or in association with Bi (maldonite) and/or as Bi–Au–Te phases whereas silver is commonly present in the form of Au(Ag), and less commonly as Bi–Te–Ag, Ag–Se and Ag–Te phases. Selenium and Te are either isomorphously bound in the molybdenite structure (similarly to Re and W) and/or form micro-inclusions of different tellurides and selenides. Molybdenite from base metal associations is characterized by the highest mean Pb (3223 ppm) and the highest median Ag (12 ppm). These metals are present in the form of abundant micro-inclusions of galena locally accompanied by an Ag–S phase and anglesite [PbSO<sub>4</sub>] with indications of other chalcophile element sub-micro-inclusions. “Barren granite”-related molybdenites, dispersed in the rock matrix, in quartz and/or pegmatite veins and/or located in fractures, have the highest mean and median Ni values (16 ppm). These molybdenites are either inclusion-free or contain micro-inclusions and also indications of sub-nano-impurities depending on the locality and a type of mineralization processes reported from the region. For example, inclusions of native bismuth, galena and anglesite occur in molybdenite from Harrachov and Bohutín where base-metal mineralization was exploited in the past. Molybdenite from the Kalmakyr porphyry–Cu–Mo(Au) deposit in Uzbekistan is characterized by the highest mean Re value (236 ppm). Rhenium, Se and W have a homogeneous distribution in molybdenite from this deposit. Only galena and anglesite inclusions were identified visually in molybdenite from this type of deposit, while the presence of most likely sub-nano impurities of Cu, Zn and Ag is indicated by LA-ICPMS time-resolved depth profiles.

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## 1. Introduction

Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICPMS) spot analysis and mapping have been successfully used to document

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and interpret trends of trace element distribution in sulfides such as pyrite, arsenopyrite or sphalerite (e.g., Cook et al., 2009, 2013; Large et al., 2009, 2014; Sung et al., 2009; Lin et al., 2011; Pašava et al., 2013; Thomas et al., 2011; Winderbaum et al., 2012 and others). Blevin and Jackson (1998) used LA-ICPMS to measure a number of elements in molybdenite containing both Bi-mineral inclusions and gold. They recorded the presence of elevated Pb, Bi, Te and other elements and suggested for the first time that variation in their abundance could be a valuable petrogenetic tool. This outcome was supported by Norman et al. (2004) who highlighted the importance of molybdenite trace element data, notably Bi, for fingerprinting mineralization in granitic settings. Recently, Ciobanu et al. (2013) confirmed the usefulness of this kind of study for identification of discrete events in young magmatic–hydrothermal systems using two Au and Au–Cu–(Mo) porphyry-style deposits. Voudouris et al. (2013) described extremely Re-rich molybdenite from porphyry Cu–Mo–Au deposits (Greece) and showed its importance for gold exploration.

As an important carrier of Re, molybdenite ( $\text{MoS}_2$ ) is a useful mineral in Re–Os geochronology (Stein et al., 2001). The method offers determination of mineralization age and it has been suggested to be robust with respect to subsequent overprinting (e.g., Stein et al., 2003; Selby and Creaser, 2004) except when subjected to supergene alteration (McCandless et al., 1993). However, several studies described complex heterogeneity of molybdenite single grains which can potentially alter Re–Os ages. For example, Košler et al. (2003) have documented heterogeneity within single grains of molybdenite, caused most likely by decoupling of Re and Os, which could in turn affect the accuracy of Re–Os ages. They suggested the need for homogenization of quantities of molybdenite to capture the bulk Os/Re of the sample. Additionally, Aleinikoff et al. (2012) documented inhomogeneous elemental distributions within single grains of molybdenite which resulted in distinct core and rim Re–Os ages and trace element distribution. They suggested that it was related to a process of molybdenite dissolution/re-precipitation associated with peak high-grade regional metamorphism. Different Re–Os ages reported by Requía et al. (2003) from co-existing molybdenite grains from the Salobo iron oxide copper–gold (IOCG) deposit (Brazil) were interpreted as temporally separated pulses of molybdenite deposition. A similar scenario was suggested by Wilson et al. (2007) for molybdenite from the Cadia porphyry system, New South Wales, Australia. Golden et al. (2013) suggested that Re variations in molybdenite reflect progressive oxidation of Earth's near-surface environment.

The Bohemian Massif is known for numerous Au, Sn–W, U and base-metal deposits located in different geotectonic units and settings. These deposits are in places accompanied by molybdenite, which is widespread especially in granite-related ore deposits (Drábek et al., 1993). A pioneering study on the distributions of Re and Se in molybdenite from the Bohemian Massif was carried out by Kvaček and Trdlička (1970) and followed by Kvaček et al. (1983), and Drábek et al. (1989, 1993). Košler et al. (2003) reported inhomogeneously distributed Re in molybdenite from several gold deposits in the Bohemian Massif.

In this paper, new LA-ICPMS trace element and mineralogical data document the behavior of a wide range of trace elements in both Re-rich and also Re-poor molybdenites attributed to different types of mineralization from both the Bohemian Massif and a porphyry Cu–Mo(Au) deposit from Uzbekistan. We demonstrate heterogeneity of the single-grain molybdenites at micro- to nano-scales and how different mineralization processes are fingerprinted in the geochemical and mineralogical composition of molybdenite.

## 2. Types of deposit/mineralization sampled

Molybdenites from four different deposit/mineralization types are briefly summarized in Table 1 and their position is shown on Fig. 1. Based on X-ray diffraction data, all sampled molybdenites are of 2H polytype (Drábek et al., 1993).

### 2.1. Molybdenite from Sn–W-bearing greisenized granite and related quartz veins

Molybdenite is a widespread mineral accompanying Sn–W deposits at Cínovec, Krupka, Krásno-Hubř and Sadisdorf, located in the Krušné Hory Mts/Erzgebirge metallogenetic province related to Variscan granite-greisen rocks (Seltmann and Štemprok, 1995) in the Saxothuringian Unit of the Bohemian Massif. The post-orogenic granitoids in this area are divided into three groups: (1) older intrusive complex (OIC) classified as calc-alkaline granites, (2) younger intrusive complex (YIC) corresponding to syenogranite or alkali-feldspar granite showing “authometamorphism” as a result of enrichment in fluid components and (3) transitional (Fiala, 1968) granites filling in the compositional gap between the two types (Breiter and Frýda, 1995).

The Krupka deposit is located within the historical Krupka ore district (Sejkora and Breiter, 1999), northwest of the town of Teplice in the Krušné hory Mts (northern Bohemia, Czech Republic; Fig. 1), with documented exploitation of cassiterite from alluvial deposits in the first half of the 12th century. The Sn–W mineralization accompanied by Cu and Bi sulfides is hosted by greisens in granite, porphyries, and granite porphyries and in surrounding gneiss and/or occurs in discrete quartz veins in these rocks. The main ore minerals are cassiterite, wolframite, arsenopyrite, molybdenite, Bi-minerals including native bismuth, bismuthinite [ $\text{Bi}_2\text{S}_3$ ], emplectite [ $\text{CuBiS}_2$ ], krupkaite [ $\text{PbCuBi}_3\text{S}_6$ ], phases of tetradymite group (in the sense of Cook et al., 2007), galena, chalcocopyrite, clausthalite, anglesite, scheelite, wulfenite, ferrimolybdate [ $\text{Fe}_2(\text{MoO}_4)_3 \cdot 8\text{H}_2\text{O}$ ], kamiokite [ $\text{Fe}_2\text{Mo}_3\text{O}_8$ ], fluorite, topaz, zircon and many other minerals (Sejkora and Breiter, 1999). Remaining resources of Sn and W were estimated by Eisenreich and Breiter (1993) at 6.7 mil. t of ore averaging at 0.13% W and 0.05% Sn in greisenized granite, 438,000 t of ore with a grade of 0.42% Sn in exo-greisens, 549,000 t of ore with a grade of 0.21% Sn and 0.1% W in vein-type mineralization, and 58,000 t of ore in quartz veins with a grade of 0.48% Mo.

The Cínovec deposit (Fig. 1) has undergone extensive mining since the 14th century. Tin and tungsten mineralization is spatially associated with a cupola of lithium-albite granite (S-type), separated from the enclosing Teplice rhyolite by a continuous pegmatite rim (Stockscheider) at the contact. The ore has similar mineralogy to the Krupka deposit. On the Czech side, the calculated reserves in greisens are  $\sim 550 \times 10^6$  t of ore at 0.18% Rb, 0.26% Li and 0.01% Cs in zinnwaldite (Li-mica). From this total,  $\sim 55$  mil. t of ore contain 0.2% Sn and 0.045% W as cassiterite, wolframite and scheelite. Apart from this, the Cínovec deposit also has significant contents of Nb, Ta and especially Sc, and hence differs distinctly from the greisen ores in the western part of the Krušné hory Mts (Štemprok et al., 1995).

The Sadisdorf Sn–Cu–(W,Mo,Bi) deposit (Fig. 1) was mined intermittently from 1500 until 1954. At first, Sn and W were exploited followed later by W, Mo and Bi. The deposit is related to a structurally-complicated cataclastite which was succeeded by sub-volcanic intrusives. The centre of the deposit is related to a multiple intrusion of Sn-bearing UG3 granite into a large fluid-explosive breccia (Seltmann, 1995). Disseminated copper mineralization dominates in the upper part of the UG3 granite, whereas Mo mineralization prevails in the deeper part. The mineralogy of the deposit is similar to other greisen-type Sn–W deposits (Kolitsch et al., 1997).

The Krásno-Hubř deposit, located in the Slavkovský les Mts, yielded about 10 to 12,000 t of metallic Sn during its 600 year history until it was abandoned in 1987. The Sn–W–Li ores are within quartz veins and stocks, in greisen bodies, and the main ore minerals include zinnwaldite, muscovite, topaz, cassiterite, wolframite, chalcocopyrite, sphalerite, arsenopyrite accompanied by less common molybdenite, stannite, bornite and covellite. The ore grade decreased from 1.5–1.7% Sn close to the surface, in 1540, to 0.2–0.4% Sn at depth in the 18th century. It is a typical greisen type deposit, spatially connected to the younger intrusive complex of S-type acidic intrusions and especially with their Li–F rich members. The age of mineralization was determined

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