

## O IZVORU MOLIBDENA V SVINČEVEM IN CINKOVEM RUDIŠČU MEŽICA

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S 3 fotografijami

Obširna literatura (Schroll, 1949) obravnava vprašanje nastanka vulfenita v svinčevih in cinkovih rudiščih Koroške (Mežica, Rute—Bleiberg in druga), pri čemer prihajajo avtorji do zaključka, da je mogel vulfenit nastati s koncentracijo v skrilavcih prvotnega molibdena ali pa neposredno iz hidrotermalnih raztopin, ki so pozneje z obogatitvijo z drugimi prviniami povzročile nastanek teh rudišč.

Vulfenit teh rudišč je značilen oksidacijski mineral, nikjer ga namreč ne najdemo pod spodnjo mejo oksidacije, ki se z napredkom rudarskih del premika vedno globlje. Vendar nam prav zato nastopanje vulfenita ne poda nobenega dokaza niti za eno niti za drugo teorijo o izvoru prvotnega molibdena.

Kristalne oblike vulfenita so v mežiškem rudniku izredno pestre, vendar siromašne s kristalnimi ploskvami, ki so razen tega še nepopolno razvite. Glavna razlika med temi kristali, ki so po navadi ploščičasti po pinakoidu (001), je v tem, da nastopajo na višjih obzorjih kristali, ki so debelejši, tako da moremo opaziti tudi jasne piramide, visoke do 8 mm. Na spodnjih obzorjih najdemo samo kristale, ki so izredno tanki po ploskvah istega pinakoida (15. obzorje), drugih likov ne najdemo. Debelina takih ploščic znaša samo 0.1 mm. Kristali se ločijo med seboj tudi po barvi, ki pa ni odvisna od debeline ploščic. Kristali vulfenita z višjih obzorij so rjavkastordeči — oranžni, kristali s spodnjih obzorij so pa medenorumeni.

Po vseh teh podatkih bi si mogli predstavljati, da je nastanek vulfenita povezan predvsem z napredkom rudarskih del, za kar govori manjša debelina ploščic s povečanjem globine. Kristali so nepravilno razviti ter imajo le redko jasne kristalne ploskve. Tudi to govori za hitro rast, ki si jo moremo predstavljati pod pogoji oksidacije, povezane z napredkom rudarskih del. Podobno hitro rast oksidacije v odkopani rudi podaja za Rute Jelenc (1953).

Podrobna mikroskopska preiskovanja ing. Petra Graška (1952) so pokazala, da nastopa v rudišču tudi molibdenit, ki so ga delno po pomoti označevali za jordizit. Poznejša preiskovanja na rudniku samem, posebno s kemičnimi analizami, kakor tudi mikroskopska preiskovanja

v našem inštitutu, so pokazala, da so podatki, ki jih je navedel, pravilni in da je tudi jordizit v glavnem molibdenit. Redki so primeri, ko jordizita nismo mogli prištevati molibdenitu, ker v obruskih nismo opazovali refleksijskega pleohroizma, značilnega za molibdenit.

Kemična analiza vzorca, v katerem je bil prvič v mežiškem rudišču določen molibdenit, daje sledeče podatke:

Vzorec je analiziral prof. dr ing. Lad. Guzelj, za kar se mu najlepše zahvaljujem.

|                  |       |         |                  |         |    |       |               |
|------------------|-------|---------|------------------|---------|----|-------|---------------|
| Pb               | 50.36 | 50.12 % | PbS              | 58.11 % | Pb | 50.36 | 76.16         |
| Mo               | 9.38  | 9.01    | MoS <sub>2</sub> | 15.67   | Mo | 9.38  | — 60.85       |
| Fe               | 1.11  | nd.     | FeS <sub>2</sub> | 2.38    | Fe | 1.11  | 15.31 S 15.86 |
| CaO              | 6.49  | 5.35    |                  |         |    |       |               |
| MgO              | 0.84  | 0.30    |                  |         |    |       |               |
| S                | 15.86 | 17.15   |                  |         |    |       |               |
| CO <sub>2</sub>  | 2.64  | nd.     |                  |         |    |       |               |
| SiO <sub>2</sub> | 0.30  | nd.     |                  |         |    |       |               |
| H <sub>2</sub> O | 2.99  | nd.     |                  |         |    |       |               |

Vsota: 89.97

Analiza ni popolna, kar kaže vsota vseh oksidov, vendar nas zadovolji, ker jasno kaže molibden, ki smo ga v obliki molibdenita našli pod mikroskopom. Razlika za S je verjetno dopolnjena s sadro, ki se razvija v obrusku. Po vsem tem moremo sklepati, da je mineral, ki sta ga Matija Drovenik in Peter Grašek označila po optičnih lastnostih za molibdenit, res **molibdenit** ter da ta mineral istočasno predstavlja prvotno obliko nastopanja molibdena v mežiškem rudišču. Vulfenit je mogel nastati iz molibdenita šele po oksidaciji, ki je v mežiškem rudišču zaradi močnih tektonskih porušitev izredno močna. Te tektonske porušitve so nastale delno pred, delno pa po orudenjenju z molibdenitom in drugimi minerali.

Po nastopanju molibdenita in njegovem odnosu do galenita moremo sklepati, da je molibdenit starejši od galenita ter da je verjetno nastal v isti mineralizacijski fazi, seveda pri višji temperaturi. Posebno jasno dokazuje to nastopanje galenita (sl. 1, 2, 3) v razpokah v molibdenitu, ki so mlajše od molibdenita in starejše od galenita.

To razlago podpira tudi dejstvo, da so našli sorazmerno majhne količine molibdenita (Germovšek, 1954) tudi v pirometasomatskih magnetitnih rudiščih na zahodnem Pohorju skupno s pirotinom, halkopiritom, sfaleritom in galenitom na področju Male Kope. Pirotina in halkopirita do sedaj še niso našli v mežiški rudi, našli pa so arzenopirit (Jicha, 1951), ki prav tako predstavlja visokotemperaturni mineral.

Na področju Male Kope ni usedlin, ki bi bile prvotno najbolj bogate z molibdenom (Schroll, 1949) in v katerih naj bi prišlo do nastopanja molibdenita po obogatenju. Rudišča so na kontaktu med dacitom in marmorom. Vsi dosedanji preiskovalci, ki zagovarjajo sedimentarni izvor molibdena, navajajo najvišje koncentracije v glinastih in laporastih

plasteh. Tudi v tem rudišču nastopa molibden v sulfidni obliki kot v Mežici.

Drugo dejstvo, ki govori za drugo teorijo in razlago, je majhna debelina rabeljskih karditskih skrilavcev. Če bi nastopal prvotni molibden v teh skrilavcih v tako majhnih količinah, kot jih navaja Schroll, bi bila količina molibdena premajhna za ves vulfenit, ki so ga že do sedaj nakopali v mežiškem rudišču (ca. 30.000 t koncentrata po podatkih, ki jih je zbral ing. Lojze Zorc).

Po teh dokazih je za nastanek molibdenita in vulfenita v mežiškem rudišču in verjetno tudi v ostalih koroških rudiščih mogoča samo druga teorija, po kateri si predstavljamo izvor molibdena v hidrotermalnih raztopinah, ki so pozneje z izpremembo sestava povzročile nastanek celotnih svinčevo-cinkovih rudišč. Petrascheck (Schroll, 1949) in ostali avtorji zastopajo isto teorijo, ki je bila dokazana že z nastopanjem molibdenita v Bleibergu.

Sprejel uredniški odbor dne 16. junija 1954.

## ON THE ORIGIN OF MOLYBDENUM IN THE LEAD-ZINC ORE-DEPOSIT OF MEŽICA

Numerous authors have yet discussed the question of origin of molybdenum in the lead-zinc ore-deposits in Koroška (Carinthia) (Mežica, Rute, Bleiberg and others). Some of them concluded, the wulfenite has been formed out off primary molybdenum in shales by its concentration. The others have found the origin of molybdenum in the hydrothermal solutions forming later on the lead- and zinc deposits, when enriched by latter elements.

The wulfenite is significant for the oxidation-zone of the deposit. It has not been found yet bellow the boundary of oxidation zone. This gets deeper and deeper because of the progress of mining works. Thus the occurrence of wulfenite does not prove any of theories mentioned above.

The crystals of wulfenite are very badly formed and they are poor in crystal faces. They differ between themselves in a great degree. The main difference between the crystals, which are usually tabular on pinacoid (001), is their thickness. On upper horizons we can find well developed pyramidal forms of crystals up to 8 mm in height. On the lower horizons we find thin crystals representing just pinacoids without any other form. They are only 0,1 mm thick. The crystals differ also in colour. Those from the upper horizons are brownish red to orange and those of the lower horizons honey-yellow.

According to all these data we can suppose, the forming of the wulfenite crystals was in connection with the progress of the mining works. The decrement of the thickness with the increasing depth of the deposit developed is the best proof of that. The crystals are very irregular with

very rare well developed crystal faces (on upper horizons). That proves the fast crystal growth under the oxidation conditions caused by the progress of mining works. Similar fast oxidation of the mined ore has been found by Jelenc (1953).

Detailed microscopic examinations of the Mežica-ores by P. Grašek have shown, the molybdenite occurs in the deposit also. It was partly falsely determined as jordizite. Later examinations at the mine itself, especially by means of the chemical analysis as well as the microscopic examinations in our institute have proved, all the data for molybdenite are correct as well as that the jordizite belongs mainly to molybdenite. In exceptional cases only we were not able to observe the reflexion pleochroism characteristic for molybdenite on the polished surfaces.

The chemical analysis of the sample, in which the molybdenite in the Mežica lead-zinc ore-deposit was stated first, is as follows:

The author wishes to thank Prof. L. Guzelj, Technical High School in Ljubljana for the chemical analysis.

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| H <sub>2</sub> O | 2.99  | n. d.   |                  |         |       |       |               |
| <hr/>            |       |         |                  |         |       |       |               |
| 89.97            |       |         |                  |         |       |       |               |

The analysis data are not complete but they serve us very well, as they show the molybdenum, which we have found in the form of molybdenite in polished surfaces. The difference in S is most probably caused by the occurrence of gypsum determined on weathered polished surface.

According to all these data we can conclude, the mineral determined by M. Drovenik and P. Grašek as molybdenite, according to the optical properties, is molybdenite indeed. It represents at the same time the primary source of molybdenum in the Mežica-deposit. The wulfenite has been formed out of molybdenite by the process of oxidation. The oxidation was very strong due to heavy tectonic processes taking place partly before and partly after the mineralisation by molybdenite and other minerals.

On the base of occurrence of molybdenite and its relation to the galena we can conclude, the molybdenite is older than galena. It has crystallised most probably during the same mineralisation phase at the higher temperature only. A fair proof of that is the occurrence of galena in fractures in the molybdenite. The fractures are thus younger than molybdenite and older than galena.

This explanation is supported by the fact, relatively small quantities of molybdenite have been found (Germovšek, 1954) in the pyrometasomatic magnetite ore-bodies in the Western Pohorje Mountains together with the pyrrhotite, chalcopyrite, sphalerite and galena in the Mala Kopa-area. Pyrrhotite and chalcopyrite have not been found yet in the Mežica-ore, but arsenopyrite has been determined in one specimen (Jicha), representing the high temperature minerals in this deposit.

In the Mala Kopa-area there are no sediments in which molybdenite could be formed by the enrichment of the primary molybdenum in the sediments themselves. The deposits are limited to the contacts between the dacite and marble. All the authors, advocating the sedimentary origin of molybdenum indicate the shales and clays as the rocks richest in molybdenum. Such rocks do not occur in the vicinity of the ore-deposits. The molybdenum in the Mala Kopa region occur in the form of molybdenite. The form is the same as in Mežica, where the greater part of it has been oxidized to wulfenite.

The second point proving the hydrothermal origin of the molybdenum is the thickness of the Rabelj (Raibl) Cardita Shales. Their quantity is too small, that wulfenite, mined up to time only, could originate in them (ca. 30.000 ts of Mo-concentrate according to data compiled by Ing. Lojze Zorc). The percent of molybdenum in the shales is too low to form so large a quantity of wulfenite.

On the base of all these data we can conclude, the origin of molybdenite and wulfenite in the Mežica lead-zinc ore-deposit as well as in other deposits of the same type in Koroška (Carinthia) are the hydrothermal solutions, which later on formed the entire lead-zinc ore-deposits occurring in this region. Petraschek (Schroll, 1949) and other authors represent the same theory, proved first by the occurrence of molybdenite in Bleiberg.

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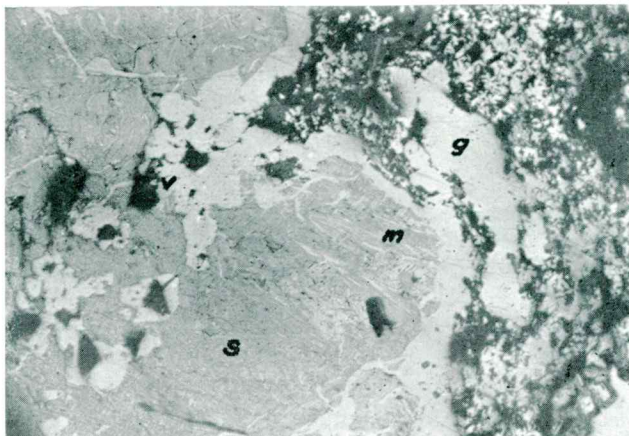
# O izvoru molibdena v svinčevem in cinkovem rudišču Mežica On the Origin of Molybdenum in the Lead-Zinc Ore-Deposit of Mežica

1. slika

Galenit z molibdenitom v skrilavcu, Mežica. Severni del 3h rudišča — obzorje Barbara: pol., 150 ×, galenit (g), molibden (m), skrilavec (s), luknjice (v).

Fig. 1.

Galena with molybdenite in the Cardita-Shale, Mežica. The northern part of the 3h ore-deposit — the Barbara-horizon: pol., 150 ×, (s), Vugs (v).

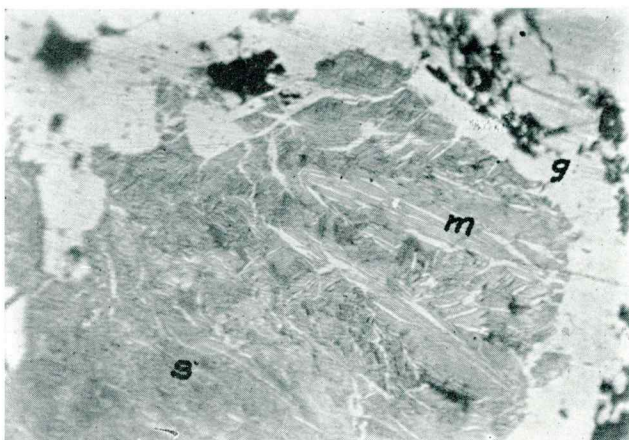


2. slika

Galenit z molibdenitom v skrilavcu, Mežica. Severni del 3h rudišča — obzorje Barbara: pol. 0°, 300 ×, galenit (g), molibdenit (m), skrilavec (s), luknjice (v).

Fig. 2.

Galena with molybdenite in the Cardita-Shale, Mežica. The northern part of the 3h ore-deposit — the Barbara-horizon: pol. 0°, 300 ×, Galena (g), Molybdenite (m), Shale (s), Vugs (v).



3. slika

Galenit z molibdenitom v skrilavcu, Mežica. Severni del 3h rudišča — obzorje Barbara: pol. 90°, 300 ×, galenit (g), molibdenit (m), skrilavec (s), luknjice (v).

Fig. 3.

Galena with molybdenite in the Cardita-Shale, Mežica. The northern part of the 3h ore-deposit — the Barbara-horizon: pol. 90°, 300 ×, Galena (g), Molybdenite (m), Shale (s), Vugs (v).

