Thallium and Mercury in Minerals from the Mežica Ore Deposit

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This paper presents the results of a study on the contents of thallium and other microelements in galena, sphalerite and other minerals from the Mežica mine. The work is a part of a study on the contents of thallium in Pb-Zn paragenesis in Yugoslavia. As this was the first determination of thallium in sulphides by the method of atomic absorption spectrophotometry in Yugoslavia, a brief description of the method should be presented.

The Mežica deposit of lead and zinc is situated in the Karavanke area, in the eastern region of Alps. It shows a great similarity by its origin and mineral paragenesis with the alpine deposits Bleiberg and Raibl.

The mineralization in Mežica is found in the Middle Triassic limestones and dolomites intercalated by shale. The Paleozoic shale makes their base. The ore bodies are mainly bound to the Wetterstein limestone and breccia. The ore occurs in fissures and in unregular shaped tubes. There are very sharp limits between richer ore bodies and the barren wall rock.

The ore bodies consist mainly of galena. In their peripheral parts the quantity of sphalerite is rapidly increasing. Almost in all parts of the mine, the concentrations of galena are situated near the shale, but farther from this rock, the quantity of galena is decreasing faster then that of sphalerite.

The genesis of the deposit is complicated, althoug the mineral content is very simple. For example, B. Granigg and J. H. Kortischoner (1914) assume that the mineralization is of epigenetic origin, connected with rocks at the greater depth. According to A. Cissarz (1951) the origin of the deposit in Mežica is not enough explained; the appearance of the Mo shows that the deposit is connected with the Tertiary effusive volcanism. In his parallel studies of alpine deposits of lead and zinc, L. H. Jicha (1951) considers that the Mežica ore deposit is of epithermal type, and that the mineralization has taken place in three phases, which may have been continuous. J. Duhovnik (1954), A. Zorc (1955), S. Grafenauer (1962, 1965, 1969), B. Berce (1960), I. Štrucl (1965) and others have studied the Mežica deposits too.

According to the literature, the following minerals occur at Mežica: galena, sphalerite, greenockite, pyrite, arsenopyrite, marcasite, melnicovite, chalcocite, wulfenite, descloizite, hydrozincite, ilsemannite, gypsum, barite, anglesite, smithsonite, cerussite, calcite, dolomite, calamine, fluorite, quartz, limonite, sulphur.

In galena, sphalerite, wulfenite, smithsonite and hydrozincite the following elements are found: Tl, Hg, As, Bi, Co, Cr, Cu, Mn, and Ni. As pointed out before, the contents of these elements were determined by the method of atomic absorption spectrophotometry from the solution, except mercury, as well as by the semiquantitative spectrochemical analysis. The specimens have been taken from the Barbara, Igrče and Srce levels of the Mežica mine.

Procedure

The specimens investigated belong partly to the collection of the Faculty of Mining and Geology, Beograd University, but the greater part was collected at Mežica in 1958. The minerals were classified according to the grain size of galena and the colour of sphalerite. To assure the maximum purity of the minerals, the X-ray control has also been applied. The chosen material has been pulverized and homogenized by a micromill during 10 to 15 minutes. Depending on the concentration of the elements (especially Tl) a quantity of 0,2—2,0 grams was taken for the analysis.

The minerals were dissolved with corresponding acides (HNO_3, H_2SO_4, HCl, and $HClO_4$ conc.) in a vacuum system. A part of the callibrated glassware with the substance to be dissolved was put into water at a constant temperature of 80° C to avoid the separation of sulphur in the shape of round and lenticular grains, which partly absorbed the thallium from the solution. The partial absorption of thallium from the solution has also been noted with samples dissolved in open glassware.

For the determination of thallium in dissolved samples by the atomic absorption spectrophotometry the Perkin-Elmer model 303 instrument was used with permanent control by standard solution. The concentrations of thallium and other elements were determined by standard curves. As source of light emission tubes with hollow cathodes (single-element and multi-element lamps) were used, the fibres emitting ions of the corresponding element, with an operating current of 20 mA. The tubes are filled with neon. The front part of the tube, permitting the light beam to pass, is made of quartz glass. The thallium content readings were made on the wave length of 2768 Å with the slit opened towards the monochromator of 20 Å. To read the samples in water solution, a burner of stainless steel 10 cm long with three slots, and for samples extracted with organic reagents a burner of the same length with only one slot was used. The water solution was aspirated into a burner at the rate of 3 ml/minute. A mixture of acetilene and air having a constant pressure of 9 lb/inch^2 yielded the oxidation flame of 160—2300° C for reading. The samples in the water solutin, as well as those with the organic reagents, were read at the flame low temperatures. The standard conditions of sensitivity were 0,8 to 1 ppm for 1 % of absorption. The average error is ± 10 %. The influence of other elements on thallium also has been studied. The solutions of thallium were prepared with various proportions of following elements: As, Cr, Cu, Fe, Mn, Pb, Sb, and Zn, as already W. A. Venendaal and H. L. Polak (1966) had practicized but without adding of the puffers. Then Tl concentrations were read. On this occasion any influence of given elements on the concentration of thallium in the solutions was not observed.

The primary standard solution (concentration 1000 μg/ml of Tl) was prepared by dissolving 0,1303 g of $TlNO_3$ salt in 1 ml conc. nitric acid in Pyrex callibrated glassware and dilluted up to 100 ml with deionized water. The acidity of the standard solution was adapted to that of the samples, which means that was brought to the same pH. The samples treated with organic reagents: APDC — amonium pyrrolidine dithiocarbamate (C. E. Mulford, 1966), MIBK — methyl isobutyl ketone, and NDDC — sodium diethyl dithiocarbamate — were formerly dilluted and adjusted to pH 6,0 to 7,5 (E. Berman, 1967) and from 3 to 10 pH (C. E. Mulford, 1966). To obtain more accurate results, the J. E. Allan (1961) method was used, worked out by J. Story (1964), and later by E. Berman (1967) who adapted it for reading elements (Cd, Tl, and Hg) in biological materials.

Results

The contents of thallium and other elements in minerals are shown in Table 1.

The coarse and fine granular galena samples from the Barbara and Igrče levels were analysed. The contents of thallium in them are very low or none. It is observed that galena from Igrče, which contains thallium, shows higher concentrations of As and Hg than that from Barbara which does not contain it. The difference in contents of other elements, Bi, Cu, and Ni in galena in both levels (Table 1) has also been observed. It is

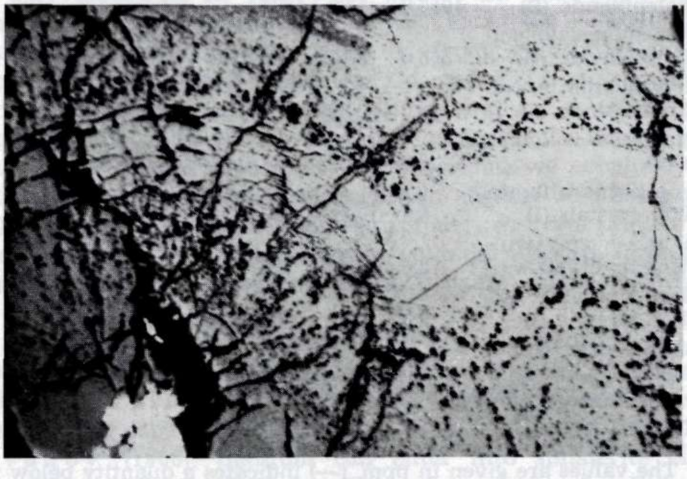

Fig. 1. The zones of sphalerite (light grey and grey) with galena (white), 60 ×, nicols //

interesting to see that galena, which contains thallium, has more Bi (approximately 8 : 1) in comparison with that from Barbara.

The sphalerite samples from the Srce level were selected after their colour, varying from dark brown to light green. The width of some zones of sphalerite is varying from 1 to 2 mm (Fig. 1). The content of thallium in them is increasing from light green up to dark brown zones and varies from 6,5 to 1057 ppm. The change of the thallium contents in some zones of sphalerite indicates the different physical-chemical conditions during their formation. There is a correlation between Tl and As. The last one increases from 4 to 1375 ppm from light to dark sphalerites. As for other elements, such tendency is shown also by Mn, whose contents vary from 24 to 144 ppm. From this it appears that the abundance of these elements is growing with the increasing Fe contents in sphalerites. This can be explained by the mode of formation of sphalerites at lower temperatures than those of the galena, as it can be clearly seen by the relation of galena and colloidal sphalerite under the microscope (Grafenauer et al. 1968).

Table 1. **The contents of elements in minerals from Mežica**

Sample	Tl	Hg	As	Bi	Co	Cr	Cu	Mn	Ni
Coarse granular galena (B)	—	0,18	16	4	—	6,0	6	4	—
Coarse granular galena (I)	2,5	0,25	188	32	—	—	14	—	2,5
Fine granular galena (B)	—	0,20	7	—	—	—	3	—	—
Fine granular galena (I)	3,0	0,29	290	30	—	—	5	—	2,5
Fine granular galena with little sphalerite (S)	3,5	0,90	240	36	6,0	—	8	3	2,5
Fine granular galena with little sphalerite and dolomite (S)	2,5	0,60	12	6	—	—	4	—	—
Dark brown sphalerite, colloidal, schalenblende (S)	1057,0	1,00	1375	—	2,5	1,6	10	144	4,6
Light brown sphalerite, colloidal, schalenblende (S)	555,0	0,17	200	—	—	—	6	95	—
Light yellow sphalerite, colloidal, schalenblende (S)	26,0	0,02	4	—	5,0	—	15	48	12,5
Pale to light green, colloidal, sphalerite (S)	6,5	0,20	—	—	4,0	—	3	24	6,0
Orange to reddish wulfenite, tabular platy crystals (I)	5,0	0,12	96	3	2,0	—	40	52	2,0
Yellowish to ash grey wulfenite, prismatic crystals (I)	12,0	0,23	120	4	3,0	—	60	96	4,0
Light yellow wulfenite, extremely thin crystals (I)	3,0	0,17	80	—	2,0	—	15	15	—
Greyish smithsonite (I), botryoidal masses	2,5	0,03	40	—	—	—	3	30	3,0
White hydrozincite (I), botryoidal coating	2,5	0,04	15	—	—	—	4	6	6,0

Remark: The values are given in ppm. (—) indicates a quantity below the limit of sensibility determined by atomic absorption spectrophotometry.

(B) = Barbara, (I) = Igrče, (S) = Srce.

By the method of atomic absorption the thallium contents were determined in sphalerite samples from 24 localities in Yugoslavia. It varies from 2,5 to 160 ppm (Table 2).

Table 2. **The thallium content in sphalerite samples**

Locality	Tl in ppm	Locality	Tl in ppm
Ajdučko Osoje	—	Lece	25
Ajvalija	80	Litica-Ljubija	3
Belo Brdo	—	Novo Brdo	—
Blagodat	—	Organdžali-Valandovo	27
Borov Dol-Inovo	—	Prečica-Avala	160
Crnac-Rogozna	2,5	Rujen-Osogovo	—
Crveni Breg-Avala	2,5	Sase	—
Janjevo	—	Srebrenica	—
Jezero-Rudnik	48	Stari Trg	12
Kižnica	—	Veliki Majdan	—
Krnja Jela-Šuplja Stijena	4	Veovača-Vareš	2,5
Kučajna	—	Zletovo	2,5

It was found by parallel analysis that the sphalerite from Mežica contains the biggest quantities of thallium, and that they vary in large limits. Very similar results were obtained by E. Schroll (1953, 1955), showing thallium and other elements in lead and zinc deposits of eastern Alps. He especially underlines the high variation in content of thallium in Bleiberg, from 3 to 3000 ppm, and he considers that its concentrations are chiefly connected with the low temperature sphalerites. R. E. Stoiber (1940) has found that the content of thallium in sphalerites is varying from 100 to 1000 ppm. The conclusion about the dependence of the element traces on the temperature of the formation of minerals was stated by I. Oftedal (1940), H. N. Warren and R. M. Thompson (1945). According to C. Harańczyk's (V. V. Ivanov, 1966) data, the sphalerites from Upper Silesia, deposited from slightly acid solutions, contain more Tl, As, and Ge, and less Cd and Ag, than sphalerites deposited from slightly alkaline solutions. Having in mind his diagram illustrating the dependence between the content of element traces in sphalerites and the conditions of their formation, we conclude that the sphalerites from Mežica were deposited from slightly acid solutions.

The higher content of thallium in sphalerites from Mežica can be explained by the origin of sphalerites of colloidal texture, formed at low temperatures. This is a very important fact for the concentration of thallium in sulphides.

It is already known that in sphalerites high contents of Pb, Cu, Ag, and Tl can be found. N. T. Voskresenskaja, I. S. Karpova (1958); E. A. Dunin-Barkovskaja (1961) assume that none of these elements is capable to substitute Zn in sphalerites. According to V. V. Ivanov (1966), thallium can enter into sphalerite either by isomorphism (the scheme $Zn^{2+} A + Tl^{+}$, where A can be Ag^{+} or Cu^{+}) or by absorption.

Thallium occurs as a characteristic element in semimetallic deposits of the mesothermal and epithermal types, connected with alpine metallogenetic epoch. It is met here in paragenesis with Sb, Pb, Zn, and Fe.

Wulfenites occur in the oxidation zone. Well formed crystals are often found in the cavities of Wetterstein limestones. They occur on the galena corroded with cerussite.

Wulfenites were selected on the basis of colour and crystal shape. Three samples of coarse platy to slaty crystals were chosen. The contents of thallium in wulfenites are pretty low, from 5 to 12 ppm, and its highest content occurs in the ash grey variety. Also As, Cu, and Mn show a somewhat higher content in the ash grey wulfenite than in the other two samples. There is some correlation between Tl, Hg, Cu, and Mn, though the contents of these elements are rather low.

The analysed smithsonite occurs in the form of cavernous or botryoidal masses and rarely as incrustations on limestone or galena. Hydrozincite, usually associated with smithsonite, appears as white botryoidal coating. Both minerals show small quantities of thallium, about 2,5 ppm. These low quantities of thallium in minerals of the oxidation zone can be explained by the hypothesis that it was washed out by the water.

Conclusions

Thallium is present in galena in traces (2,5—3 ppm), or not at all. Galena with thallium contains more As (188—290 ppm) and Bi than that without it.

The contents of thallium in sphalerites from Mežica are increasing from the light green up to the dark brown varieties (6,5—1057 ppm). There exists some correlation between Tl and As. The latter ranges from 4 to 1375 ppm. According to the results of investigations of the sphalerites from twenty four localities in Yugoslavia, the thallium content is the highest in sphalerites from Mežica. The high content of thallium in sphalerites from Mežica can be explained by their origin at low temperature.

The contents of mercury in all investigated minerals vary from traces to about 1 ppm.

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SUMMARY

The contents of thallium and mercury in galena, sphalerite, wulfenite, smithsonite and hydrozincite have been investigated and discussed. Beside Tl and Hg the contents of As, Sb, Cu, Ni, Co and Bi have been determined by atomic absorption spectrophotometry and semiquantitative spectrochemical analysis. The specimens have been taken from the sections Barbara, Igrče, and Srce of the Mežica mine.

The samples of galena were selected according to the grain size, and those of sphalerite after their colour. Only thallium traces are present in galena; in sphalerite its content varies from traces to 1057 ppm. According to the results of investigations of the sphalerite specimens from twenty-four other localities in Yugoslavia, thallium concentration is the highest in the Mežica sphalerite. It is known that in galena thallium content is generally increasing with As and Bi content. In galena from Mežica As and Bi are present only in very small quantities and accordingly the content of thallium is small or negligible.

The content of mercury was determined by a transistorized mercury detector. The contents of this element in same samples vary from traces to about 1000 ppb.

Higher concentrations of thallium in sphalerite from Mežica could be explained by occurrence of sphalerite with colloidal texture (Schalenblende) formed at low temperature, which is of the greatest importance for the concentration of thallium. It is possible that thallium is concentrated by isomorphism or by absorption.

DISCUSSION

Štrucl: Die meisten geochemischen und auch mikroskopischen Studien über Mežica wurden bisher an nicht gerade systematisch gesammelten Handstücken gemacht. Das führt gewiß zu manchen Fehlschlüssen. Es ist nämlich viel wichtiger den Erztypus als die Lokalität (Revier, Horizont o. ä.) der Probe für die geochemische Analyse anzugeben. So bestehen auch in der Lagerstätte Mežica verschiedene Vererzungstypen, die sich nicht nur nach der Form und Lage (schichtgebunden, Kluftausfüllungen, Vererzungen entlang posttriassischer Störungen usw.), sondern auch nach der geochemischen Zusammensetzung wesentlich unterscheiden. Es seien nur einige Beispiele erwähnt.

Molybdän ist als Wulfenit fast ausschließlich an posttriassische Störungen (an das sogenannte Unionsystem) gebunden, und auch der durchschnittliche Molybdängehalt ist in den Vererzungen des Unionsystems etwa zehnmal höher als in den schichtgebundenen Vererzungen.

Fluor ist mikroskopisch nachweisbar nur in schichtgebundenen Vererzungen und meistens nur dort, wo synsedimentäre und syndiagenetische Erze vorhanden sind.

Germanium findet man in der lagunären Dolomitserie des Grabenreviers, bis 300 g/t im Zinkblendekonzentrat. Die Zinkblende in anderen Vererzungen ist entweder germaniumarm oder es fehlt an diesem im ganzen.

Ähnliche Unterschiede finden wir auch in Bezug auf das **Eisen-** und **Cadmiumgehalt** der Zinkblende verschiedener Vererzungstypen.

Es scheint mir, daß auch die vorliegende höhere Thalliumgehalte an schichtgebundene Vererzungen gebunden sind.

Auf keinen Fall kann aber ein Durchschnittsgehalt von zufällig gesammelten Proben eine Lagerstätte repräsentieren.

Terzić: Die Idee war festzustellen, an welche Mineralien Tl und As gebunden sind. Das könnte ein Parameter für weitere Untersuchungen der syngenetischen und epigenetischen Vererzungen sein.

Stolfa: I suppose the sensitivity you report for Tl refers to aqueous solution. Did you find any sensitivity enhancement in the analysis of Tl in the organic phase?

Terzić: Yes, but hardly noticeable.

Stolfa: I think it is important to control the total solids concentration of solutions in order to keep as low as possible the background noise and light scattering errors especially in low level trace element analysis. In relation to this: how did you offset these inconveniences? After dissolving samples, to which volume did you bring your solutions?

Terzić: The readings were done with readout, that stifled background noise and enabled sensitivity enhancement (for thallium 0,02 μg/ml). Directly after dissolving the samples the reading was done in the volume of 25 ml.

Stolfa: I find it quite critical and troublesome working at 2—3 ppm Tl levels with a sensitivity of about 1 ppm per 1 % absorption. What about precision and accuracy?

Terzić: The content at 2—3 ppm of thallium is whole quantity in 25 ml volume.

Stolfa: Did you use the deuterium lamp backgroung corrector in the As determination?

Terzić: Yes, I did.

Glaçon: Are you sure that in schalenblende, containing much thallium and arsenic, there are no microinclusions of other minerals?

Terzić: I examined the microinclusions in sphalerite with X-rays, but on the diagrams their lines were not detectable.

Glaçon: Did you use the electron microprobe?

Terzić: Yes, I used it for the examination of Tl contents in galena. The determination did not give reliable results, because the corresponding wave lengths ($Tl_{M\alpha}$ 2 067; $Tl_{M\beta}$ 1 987 Å, and $Pb_{M\alpha}$ 2 000; $Pb_{M\beta}$ 1 921 Å) are very close one another. As a consequence, the wave length of Tl is masked by the wave length of Pb.

Schroll: Die Parallelität von Thallium und Arsen in den Schalenblenden ist ein sehr interessantes Problem, man müßte dabei aber auch das Verhalten anderer Elemente, wie z. B. As, Pb, Sb, Ge, mitverfolgen. Ich habe schwankende Elementverhältnisse gefunden. Es könnte sich hier um das spurenweise Auftreten von Mineralgläsern handeln, die man erzmikroskopisch und sonst schwer diagnostizieren kann. Mikrominerale mit As und Tl, wie Hutchinsonit, sind gleichfalls nicht auszuschließen. In allen Schalenblenden dieser Lagerstätten findet man variable Gehalte. Auch wenn man den analytischen Fehler in Betracht zieht, so deutet doch vieles auf die Bindung an Fremdminerale. Ich glaube nicht, daß größere Mengen von Tl und As in das Gitter eingebaut werden.

Terzić: Ich teile Ihre Meinung, daß Tl und As wahrscheinlich nicht in das Gitter der Schalenblende eingebaut sind.