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# R A D O V I

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Nakoliko meseci po izlasku iz štampe knj. br. 37. usledile su intervencije pojedinih autora, koji su 1998. god, pre bombardovanja, predali svoje radove, a nisu se našli ni u knj. br. 36. niti u br. 37. Mora se naglasiti da ovaj Redakcioni odbor nije odgovoran za to, jer on niti ih je dobio, niti ih je imao na dnevnom redu svojih sednica, pa prema tome nije ni mogao da ih uzme u proceduru za štampanje. Neki od autora su u medjuvremenu doneli kopije tih radova, a Redakcioni odbor ih je uključio u redovnu proceduru za publikovanje u knj. br. 38.

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U Beogradu 2003. god.

Glavni i odgovorni urednik

Dr. Radule Popović, naučni savetnik

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# X-RAY INVESTIGATIONS OF SCHEELITE AND PYRITE FROM ALDINAC (STARA PLANINA Mt.)

(with 1 Figure and 4 Tables)

Key words: Stara Planina Mt., Aldinac, scheelite, pyrite, indiced X-ray powder diffraction pattern, unit cell dimensions, pale-blue fluorescence of scheelite.

At one representative sample there was indiced powder diffraction pattern and done qualitative-semiquantitative X-ray powder diffraction analysis.

It was established that the investigated sample contains scheelite and pyrite, nevertheless scheelite is of some greater quantity than pyrite.

There were calculated following unit cell dimensions:

scheelite:

$a_o$ = 5,243(1)Å; $c_o$ = 11,364(4)Å; and $V_o$ = 312,4(1)$Å^3$;

pyrite:

$a_o$ = 5,4151(4)Å; and $V_o$ = 158,79(3)$Å^3$;

These unit cell dimensions are in excellent agreement with the literature datas and they are only with slightly smaller values, and which indicate to minnor exchanging with ions of smaller ionic radius in the structures of these two minerals.

Investigations under the UV-light manifested that scheelite fluorescence at pale-blue colour.

In this way it was established and approved presence of the scheelite on this locality.

## INTRODUCTION AND GEOLOGICAL COMPOSITION OF THE LOCALITY

During the reconsideration of the aeromagnetic anomalies at the Stara Planina Mt., which was accomplished by "Geoinstitut" in 1997, there were discovered tungsten occurences at Aldinac village locality. At this occasion there wasn't determined any tungsten mineral, because contents of this element was relatively low, and also because there were analyzed small number of samples.

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With later investigations of this locality there were found quartz veins with sulphides, and which contain noteworthy tungsten concentrations. These veins are located in hydrothermally altered gabbro and diabase. At their direct vicinity there are penetrations of granitoid rocks, predominantly granodiorite-porphyrites, and less, dacites and quartz-latites (K o v a č e v i ć, 2002).

Gabbro is predominantly composed from plagioclases and pyroxenes, and accessory apatite, sphene and metallic minerals. Diabases are located in the vein forms in gabbro, thickness from few centimeters to 10 m, and also they are composed from plagioclases and pyroxenes. Granodiorite-porphyrites are located in the form of two big penetrations in gabbro, and also as numerous smaller vein form penetrations. Mineral composition of the granodiorite-porphyrite contains from quartz, orthoclase, plagioclases, hornblende and biotite. Quartz-latites and dacites are located only as small penetrations in gabbro. Aldinac locality distinguished with very complex tectonics at which dominate so called Repušnica Fault, with spread direction northwest-southeast.

With the oremicroscopic investigations of the samples from ore quartz veins, and which have increased tungsten concentrations, it was established presence of the scheelite in the Aldinac village locality and in the locality of Velika Žljeburina creek. At both of these localities scheelite was associated with pyrite and chalcopyrite. Non-ore minerals are, beside quartz, carbonates (K o v a č e v i ć, 2002).

For certain and reliable scheelite determination there were applied X-ray investigations and investigations under UV-lamp.

Since during the material preparation there was also concentration of pyrite together with scheelite, on this occasion we will represent likewise results of these investigations.

Scheelite from ours localities mostly prepossessed investigators attention during the 50's of the last Century (M a n d i ć, 1953; T a l i ć and V a n đ e l, 1955; A r s e n i j e v i ć, 1956a,b and 1957; and N o v a k o v i ć and V a n đ e l, 1958).

These authors mostly investigated scheelite's occurences, their colour, fluorescency, geochemical characteristics, i.e. chemical ingredients and impurities, etc.

As we can see, there is a small number of publications about scheelite, and it is characteristic that there is a lack of the X-ray - crystallographic investigations. Pyrite from ours localities is much better investigated than scheelite, but also there is considerable deficiency of the X-ray examinations.

## MATERIAL PREPARATION AND INVESTIGATION METHODS

For determination of scheelite and pyrite, it was selected one representative sample. This sample is a part of the quartz-sulphide ore vein at which was by oremicroscopic investigations, established presence of scheelite, pyrite, chalcopyrite and carbonates.

This sample was mechanically squashed and sieved, and after that separated with methylen iodide and with electromagnet. By that way it was isolated heavy diamagnetic fraction, with density over 3,32 g/cm$^3$. In this fraction it can be expected, by their electromagnetic and density properties, dominate presence of the scheelite and pyrite, because another minerals were separated in other fractions.

Separated fraction was investigated under UV-lamp, and then powdered and investigated with the X-ray powder diffraction analysis.

The sample was recorded at automatically diffractometer for powder "PHILIPS", model PW-1710. There was used long-focus (LFF), Cu-anode (U = 40 kV and I = 30 mA), with monochromated $K\alpha_1$ radiation ($\lambda$ = 1,54060Å) and Xe proportional counter. Diffraction datas were collected in angle range 2$\theta$ from 5° to 65° with keeping back with 1 second on every 0,02°. For measurement the angle positions of diffraction maximums and their belonging intensities there was used base program PW-1877.

Precision of the diffractometer was controled before and after experiment with metallic Si powder.

Identification of the present mineral phases was done with comparison of the interplanar spacings (d) and relative intensities (I) with the literature datas, that is corresponding card from JCPDS-ASTM database.

Calculation of the unit cell dimensions was accomplished with programme LSUCRI for personal computer.

## RESULTS AND DISCUSSION

### Oremicroscopic and investigations under UV-lamp

At basis of the oremicroscopic investigations there were established following ore minerals: pyrite, chalcopyrite and scheelite.

Non-ore minerals are: quartz and mineral from the carbonate group.

Pyrite and chalcopyrite are dominate ore minerals, therewith pyrite is relatively something over chalcopyrite, while scheelite is with small extensity, and only localy, with big intensity.

From non-ore minerals quartz is dominate, and carbonate is minorly represented in fibril forms which permeate the ore minerals.

Pyrite appears as xenomorphic to hypidiomorphic excrescencive grains and as individual idiomorphic crystals of the hexahedron habit. More or less it is cataclasted.

Chalcopyrite is present as xenomorphic grains which overtakes and cements pyrite and scheelite, or it produces small impregnations in quartz.

Scheelite appears as hypidiomorphic grains, size mostly about 2 mm, and rarely smaller, which are cracked along one or two directions, and that cracks are somewhere filled with carbonate and chalcopyrite.

In paper by K o v a č e v i ć et al. (2003), at Figure 4, it can be clearly seen the manner of the intergrowth and shapes of the established ore minerals, and which are present in this representative sample from Aldinac.

Investigations under UV-lamp manifested that scheelite fluorescence at pale-blue colour.

### X-ray investigations

Through X-ray investigations there was indiced X-ray powder diffraction pattern of one representative sample from the scheelite-pyrite mineralization (represented at Figure 1), in 2$\theta$ range from 5° to 65°, with observed values of the interplanar spacings ($d_{obs}$) and identified minerals:

S - scheelite, P - pyrite, and Q? - quartz?.

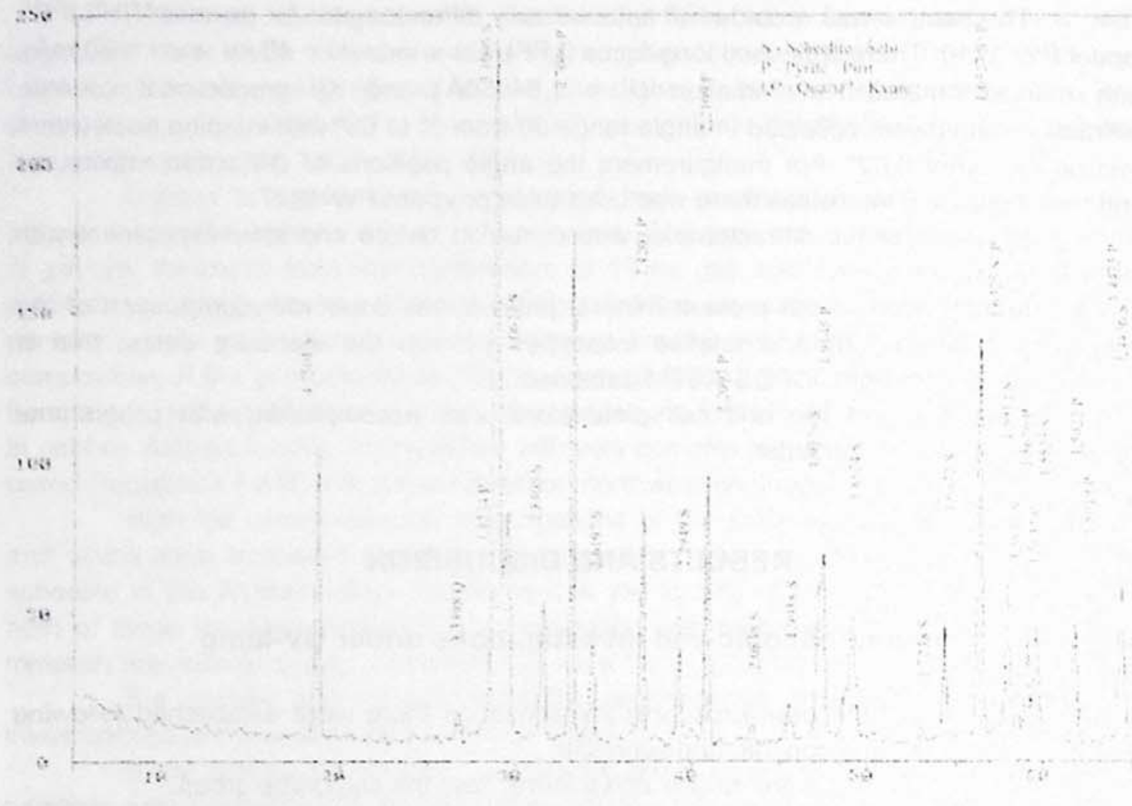


Figure 1: Indiced X-ray powder diffraction pattern.

With the X-ray qualitative-semiquantitative powder diffraction analysis it was established that, by its quantity, investigated sample contains from scheelite, pyrite and quartz?.

Although they are almost equally represented, quantity of scheelite is something over pyrite.

Presence of quartz? is uncertain, because of its minnor quantity and very small number of reflections (1). Quartz? was most probably entered accidentally, because material preparation was done at manner which prevents such cases.

## Scheelite

Values of the observed intensities ($I_{obs}$) and observed ($d_{obs}$) and calculated ($d_{calc}$) interplanar spacings of scheelite from the investigated sample, with responsable from the literature datas (B l a n c h a r d, 1989), and also with responsable Miller's indices (hkl) are represented together at Table 1.

Table 1: Powder diffraction pattern of scheelite.

| scheelite (JCPDS 41-1431) | | | scheelite (Aldinac) | | |
|---|---|---|---|---|---|
| h k l | I | d | $I_{obs}$ | $d_{obs}$ | $d_{calc}$ |
| 1 0 1 | 84 | 4,7645 | 40,55 | 4,7501 | 4,7607 |
| 1 1 2 | 100 | 3,1049 | 100,00 | 3,1006 | 3,1049 |
| 1 0 3 | 30 | 3,0714 | 22,34 | 3,0677 | 3,0705 |
| 0 0 4 | 39 | 2,8426 | 21,41 | 2,8405 | 2,8411 |
| 2 0 0 | 19 | 2,6213 | 13,55 | 2,6197 | 2,6215 |
| 2 0 2 | 1 | 2,3803 | | | |
| 2 1 1 | 18 | 2,2962 | 12,83 | 2,2949 | 2,2963 |
| 1 1 4 | 3 | 2,2562 | | | |
| 1 0 5 | 6 | 2,0865 | 2,53 | 2,0838 | 2,0854 |
| 2 1 3 | 10 | 1,9943 | 4,16 | 1,9938 | 1,9937 |
| 2 0 4 | 36 | 1,9276 | 20,95 | 1,9270 | 1,9266 |
| 2 2 0 | 15 | 1,8536 | 15,84 | 1,8524 | 1,8536 |
| 3 0 1 | 3 | 1,7271 | 2,53 | 1,7238 | 1,7273 |
| 1 1 6 | 17 | 1,6877 | 14,68 | 1,6872 | 1,6867 |
| 2 1 5$\alpha_1$ | 8 | 1,6326 | 56,44 | 1,6327 | 1,6320 |
| 2 1 5$\alpha_2$ | 8 | 1,6326 | 32,17 | 1,6325 | 1,6320 |
| 3 1 2 | 23 | 1,5921 | 21,41 | 1,5912 | 1,5916 |
| 3 0 3 | 4 | 1,5873 | 11,78 | 1,5871 | 1,5869 |
| 2 2 4 | 13 | 1,5528 | 13,92 | 1,5523 | 1,5524 |
| 3 2 1 | 5 | 1,4426 | 13,19 | 1,4436 | 1,4424 |

Through the LSUCRI programme there were calculated in space group $I4_1/a$ unit cell dimensions of scheelite with 18 reflections from investigated sample and represented together with literature datas (B l a n c h a r d, 1989) at Table 2.

Table 2: Calculated unit cell dimensions of scheelite.

| | scheelite (JCPDS 41-1431) | scheelite (Aldinac) |
|---|---|---|
| $a_o$ (Å) | 5,242 | 5,243(1) |
| $c_o$ (Å) | 11,37 | 11,364(4) |
| $V_o$ (Å$^3$) | 312,63 | 312,4(1) |

From the observed results (Tables 1 and 2) it can be seen that the d-values and unit cell dimensions of scheelite from Aldinac are slightly smaller, and that they are in excellent agreement with the literature datas (B l a n c h a r d, 1989).

## Pyrite

Values of the observed intensities ($I_{obs}$) and observed ($d_{obs}$) and calculated ($d_{calc}$) interplanar spacings of pyrite from the investigated sample, with responsable from the literature datas (N o d l a n d et al., 1989), and also with responsable Miller's indices (hkl) are represented together at Table 3.

Table 3: Powder diffraction pattern of pyrite.

| pyrite (JCPDS 42-1340) | | | pyrite (Aldinac) | | |
|---|---|---|---|---|---|
| h k l | I | d | $I_{obs}$ | $d_{obs}$ | $d_{calc}$ |
| 1 1 1 | 31 | 3,1280 | 35,64 | 3,1234 | 3,1264 |
| 2 0 0 | 100 | 2,7055 | 83,80 | 2,7066 | 2,7075 |
| 2 1 0 | 53 | 2,4209 | 37,45 | 2,4207 | 2,4217 |
| 2 1 1$\alpha_1$ | 40 | 2,2107 | 49,91 | 2,2109 | 2,2107 |
| 2 1 1$\alpha_2$ | 40 | 2,2107 | 20,05 | 2,2093 | 2,2107 |
| 2 2 0 | 36 | 1,9160 | 29,95 | 1,9145 | 1,9145 |
| 2 2 1 | 1 | 1,8061 | | | |
| 3 1 1$\alpha_1$ | 69 | 1,6333 | 56,44 | 1,6327 | 1,6327 |
| 3 1 1$\alpha_2$ | 69 | 1,6333 | 32,17 | 1,6325 | 1,6327 |
| 2 2 2$\alpha_1$ | 11 | 1,5639 | 17,46 | 1,5636 | 1,5632 |
| 2 2 2$\alpha_2$ | 11 | 1,5639 | 9,21 | 1,5633 | 1,5632 |
| 0 2 3$\alpha_1$ | 13 | 1,5023 | 18,73 | 1,5022 | 1,5019 |
| 0 2 3$\alpha_2$ | 13 | 1,5023 | 9,21 | 1,5019 | 1,5019 |
| 3 2 1 | 16 | 1,4479 | 31,61 | 1,4475 | 1,4472 |

Through the LSUCRI programme there were calculated in space group Pa3 unit cell dimensions of pyrite with 13 reflections from investigated sample and represented together with the literature datas (N o d l a n d et al., 1989) at Table 4.

Table 4: Calculated unit cell dimensions of pyrite.

| | pyrite (JCPDS 42-1340) | pyrite (Aldinac) |
|---|---|---|
| $a_o$ (Å) | 5,417 | 5,4151(4) |
| $V_o$ (Å$^3$) | 159,04 | 158,79(3) |

From the observed results (Tables 3 and 4) it can be seen that the d-values and unit cell dimensions of pyrite from Aldinac (as like at scheelite) are slightly smaller, and that they are in excellent agreement with the literature datas (N o d l a n d et al., 1989).

From the literature datas it is well known that in scheelite it is most usually present molybdenum (to 8%), and also copper may replace calcium (D a n a, 1955).

Chemical analysis, unfortunately, wasn't done, and so we will not enter deeper in this problematic, but from the unit cell dimensions of scheelite it can be presumed that some small part of this elements was exchanged, namely W with Mo and/or Ca with Cu.

## CONCLUSION

Through oremicroscopic investigations there were established from ore minerals pyrite, chalcopyrite and scheelite, and from non-ore, quartz and mineral from the carbonate group.

Pyrite and chalcopyrite are dominate ore minerals, therewith pyrite is relatively something over chalcopyrite, while scheelite is with small extensity, and only localy, with big intensity.

From non-ore minerals quartz is dominate, and carbonate is minorly represented as fibril forms which permeate ore minerals.

Investigations under UV-lamp manifested that scheelite fluorescence at pale-blue colour.

For certain determination and approving of the scheelite on this locality, there were implemented X-ray investigations. There was indiced powder diffraction pattern and done qualitative-semiquantitative X-ray powder diffraction analysis at one representative sample.

It was manifested that investigated sample contains scheelite and pyrite, nevertheless scheelite is of some greater quantity than pyrite.

There were calculated following unit cell dimensions:

**scheelite:**

$a_o$ = 5,243(1)Å; $c_o$ = 11,364(4)Å; and $V_o$ = 312,4(1)Å$^3$;

**pyrite:**

$a_o$ = 5,4151(4)Å; and $V_o$ = 158,79(3)Å$^3$;

Unit cell dimensions were well calculated because in this experimental range scheelite and pyrite have all reflections with different d-values, except $d_{\alpha 1}$ = 1,6327Å and $d_{\alpha 2}$ = 1,6325Å, and so there were no overlap of the diffraction maximums.

Unit cell dimensions of scheelite and pyrite are in excellent agreement with the literature datas. They are only with slightly smaller values, which indicate to minnor exchanging with ions of smaller ionic radius in the structures of these two minerals.

It can be presumed that in the scheelite structure some small part of elements was exchanged, namely W with Mo and/or Ca with Cu.

We hope that ours detail X-ray - crystallographicaly results of scheelite and pyrite will be a contribution to crystallography and mineralogy from ours locality, because we didn't found such results in present and available literature datas in our Country.

Recenzent,

Prof. dr. Lj. Cvetković

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