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Spherulites of native arsenic from the Sedefche deposit, Eastern Rhodopes

Thomas Kerestedjian, Vassilka Mladenova

Abstract. Native arsenic spherulites, formed of platy individuals (Akadani type aggregates) were found in the Sedefche deposit.

The described spherulites are about 1 mm in size. On breaking they reveal a typical onion like foliation. Enlarged SEM images of the spherulite surfaces show a number of perfectly shaped pseudohexagonal platy crystals about 20 μm in size, almost parallel to each other and with their *c* axes parallel to the spherulite radius. The observed in SEM foliation is expressed in the polished section as concentric zone boundaries. Under crossed polars an almost perfect Maltian cross is observed.

Oxidation is a typical feature of the observed material. It starts being noticeable as early as one day after polishing. SEM observations of the tarnished surface show numerous, small (3 μm mean size) perfectly shaped As_2O_3 crystals.

In the Sedefche locality the native As is deposited at the very end of the mineralization process. Its deposition from hydrothermal solutions is only possible under 150°C. In this case very low S activity is required for the native As formation instead of sulphoarsenides. This requirement looks to be fulfilled in our case, because the whole quantity of S available is already deposited in earlier deposition stages.

Key words: arsenic, spherulite, Eastern Rhodopes
Address: T. Kerestedjian - Geological Institute, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria
V. Mladenova - Sofia University, Dept. Mineral., Petrol. and Econ. Geol., 1000 Sofia, Bulgaria

Керестеджиян Т., В. Младенова, 1998. Сферолити от самороден арсен от находище Седефче, Източни Родопи. - *Геохим., минерал. и петрол.*, **34**, 27-34

Сферолити от самороден арсен, състоящи се от плоски кристални индивиди (агрегати тип Акадани) бяха установени в находище Седефче.

Размерът на сферолитите е около 1 мм. При разчупване те показват характерно луковично разлистване. Наблюдението в SEM разкрива множество добре оформени псевдо-хексагонални плоски кристали, разположени почти успоредно един спрямо друг и с осите *c* паралелни на радиуса на сферолита. Наблюдаваното луковично разлистване се проявява като концентрична зоналност в полираните шлифи. При кръстосани николи се наблюдава добре изразен Малтийски кръст.

Окисляването е характерно свойство на изследвания материал. То започва да става видимо дори 1 ден след полирането. Наблюдението в SEM разкрива множество малки (3 μm средно), добре оформени кристалчета от As_2O_3.

В находище Седефче минералът е отложен в самият край на хидротермалния процес. Неговото отлагане от разтвора е възможно само при температури под 150°C. При това положение е необхо-

димо активността на S да е изключително ниска, за да не се образуват сулфоарсениди. Това условие изглежда изпълнено в нашия случай, тъй като цялото количество S е било вече отложено в края на процеса.

Ключови думи: арсен, сферолит, Източни Родопи
Адрес: Т. Керестеджиян - Геологически институт, Българска академия на науките, 1113 София
В. Младенова - Софийски университет, кат. Минерал., петрол. и пол. изк., 1000 София

Introduction

Even known long ago native arsenic is a relatively scarce mineral. This applies especially for the spherulitic morphology. Well developed spherulites, consisting of tiny individuals regularly spread in all directions are extremely rare (Gediegen Arsen, 1983). This sort of aggregates, revealing fine rhombohedral or flat prismatic crystal terminations on the surface is known as Akadani type aggregates (after the Akadani mine, Japan, where they were described for the first time).

In Bulgaria native arsenic is described twice: Vassilev (1958) in Velikovez, Bourgas region and Mankov (1973) in Osogovo ore district. Both descriptions refer to irregular, kidney-like, or belt-shaped aggregates.

Regional geological setting

The Sedefche deposit is of Miocene age and is situated in the south-east periphery of the Zvezdel-Pcheloyad ore field, located at the border of the East Rhodope Paleogene depression. The location of the ore field is determined by the intersection of two deep-reaching faults with submeridional and subequatorial direction (Gergelchev, 1971). The region comprises Pre-Tertiary basement metamorphic rocks of the Rhodope massif and Tertiary volcano-sedimentary cover.

The metamorphic series appear only in the eastern part of the region, consisting of biotite- and two-micas-gneiss, amphibolites, marble and kyanite-garnet-biotite schists. The rest of the ore field is entirely composed of the Tertiary cover. They overlie unconformably and transgressively the basement and include sedimentary, volcano-sedimentary, volcanic and plutonic rocks (Atanasov, 1965). The ore field itself is dominated by products of an intense Oligocene magmatism consisting of intermediate to acid volcanic-subvolcanic rocks and post-intrusive dikes of dacites and rhyolites, which are located in the southern part of the region and intersect all the above lithologic types.

All the magmatic rocks exhibit intense and extensive hydrothermal alteration assemblages, which refer to a series of hydrothermal alterations including propylitization (Atanasov, 1965; Radonova, 1973). The different varieties of propylitization are due to the composition of the adjacent wall-rock.

The Sedefche deposit comprises a submeridional area 2.5 km long and about 1.5 km wide. It consists of three mineralized areas: Sedefche-South, Sedefche-North and Ralitza. The most perspective one, Sedefche-North, has a strike length of more than 400 m. Ralitza is located in the greatest occurrence of metamorphic rocks in the region and the most important concentrations are established in the silicified marbles.

The Sedefche deposit is considered to be of hydrothermal-metasomatic origin hosted by metamorphic, volcanic and sediment rocks.

Paragenetic sequence

Five distinct parageneses can be distinguished on the basis of the textural relations of the various minerals (Mladenova, 1997). The mineralogy of the gangue is largely dominated by SiO_2: chalcedony and quartz.

Paragenesis I includes pyrrhotite, arsenopyrite and chalcedony. The pyrrhotite is almost completely transformed into pyrite and/or marcasite. Their grains are very porous, lamellar, with narrow gaps. Arsenopyrite occurs as isolated rhombohedral

crystals or as microaggregates formed after the primary pyrrhotite.

Paragenesis II comprises pyrite, marcasite, sphalerite, galena, chalcopyrite, fahlore, chalcopyrite and quartz, the two first formed partly at the expense of the preceding pyrrhotite.

Paragenesis III is characterized by Ag-Pb sulphoantimonides (freieslebenite, fizeliite, andorite, diaphorite, polybasite, owyheeite and two undetermined species) followed by Ag sulphoantimonides (miargyrite, pyrargyrite) and arsenopyrite as isolated crystals.

Paragenesis IV represents the precipitation of abundant stibnite and scarce native arsenic grains.

Paragenesis V is composed of baryte formed separately, at the very end of the process.

Materials and methods

Investigated samples are collected at the locality surface, from highly silicified hydrothermaly altered rocks. The silicification is developed over a breccia or volcanic breccia with probable andesitic composition. The rock-forming minerals currently composing the samples are mainly quartz, some pumpellyite and very few clay minerals. This composition is to classify the rock as secondary quartzite.

Polished samples were prepared from single spherulites included in plastic pills. Because of the low hardness of the material polishing was performed manually on very soft cloth with Al_2O_3 down to 0.05 μm. Machine polishing was skipped to avoid heating of the sample, that invokes rapid oxidation. Bulk ore polished sections were also prepared to reveal the assemblage.

Microprobe investigations were performed on JEOL JSM 35 CF, at 25 kV using Tracor Northern EDS analyzer.

TEM studies were made on TESLA BS613.

Diffractometric investigations were performed on TUR M62 using CoKα and step 0.025°Θ.

Debye-Scherrer photographs were taken using CoKα and 22 h exposure.

Description of As aggregates

Hundreds of spherulites 0.5-1 mm in diameter could be observed in the 10 cm large hand specimen taken out of an exploration shaft, about 10 m deep. They are steel gray, with strong metallic luster and brittle. Their hardness is considerably lower then that of a steel needle well matching the

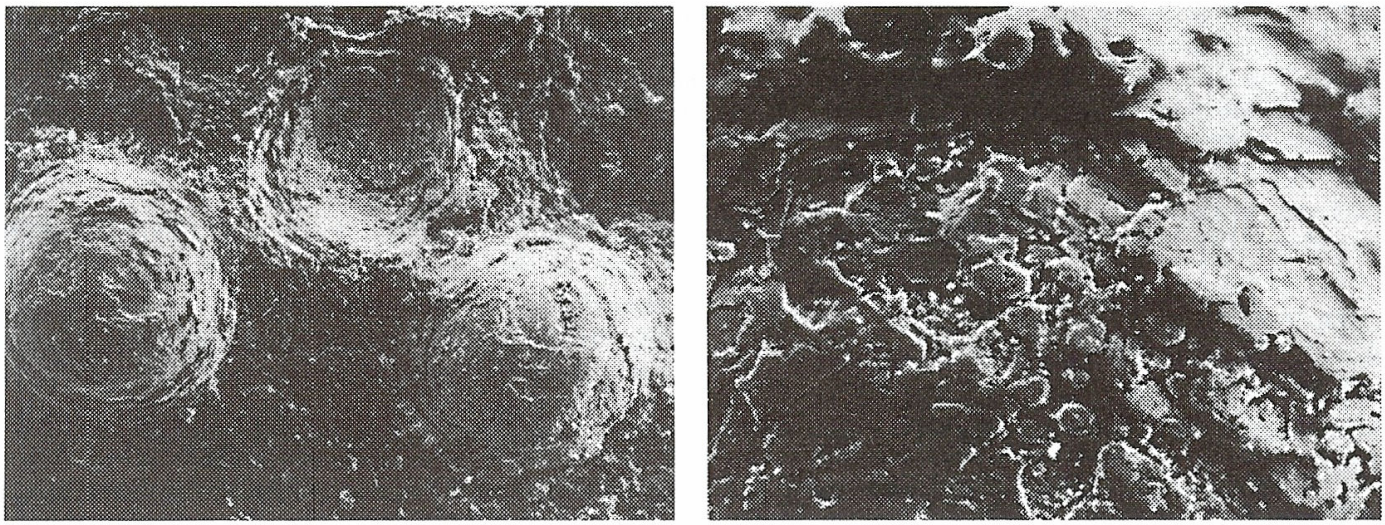

Fig. 1. Native As spherulites with onion like structure in highly quartzitized andesitic rock (left, SEM, x 60). Perfectly shaped pseudohexagonal platy As crystals revealed in an interslice surface, on breaking the spherulite (right, SEM, x 440)

Фиг. 1. Сферолити от самороден арсен с луковична структура в силно окварцен андезит (ляво, SEM, x 60). Добре оформени псевдохексагонални плочести кристали от самороден арсен се разкриват по междуслоевите граници при счупване на сферолита (дясно, SEM, x 440)

theoretical 3.5.

On breaking the spherulites reveal a typical onion like foliation well visible on Fig. 1(left). Enlarged SEM images of the spherulite surfaces show a number of perfectly shaped pseudohexagonal platy crystals about 20 μm in size (Fig.1, right) almost parallel to each other and with their *c* axes parallel to the spherulite radius.

Polished sections

Spherulitic aggregates are white and strongly reflecting, without bireflectance effects. They are almost uniform, excluding some small imperfection in respect to the equality of the direction spread.

Oxidation is a typical feature of the observed material. It starts being noticeable as early as one day after polishing. The photograph on Fig. 3 (left) has been taken 2 days later. It reveals clear separation of oxidizing and nonoxidizing areas in the polished section.

SEM observations 4 days later (Fig.3, right) show that tarnished surface consists of numerous, small (3 mm mean size) perfectly shaped As_2O_3 crystals. They cover the whole surface almost uniformly, however, the areas corresponding to white

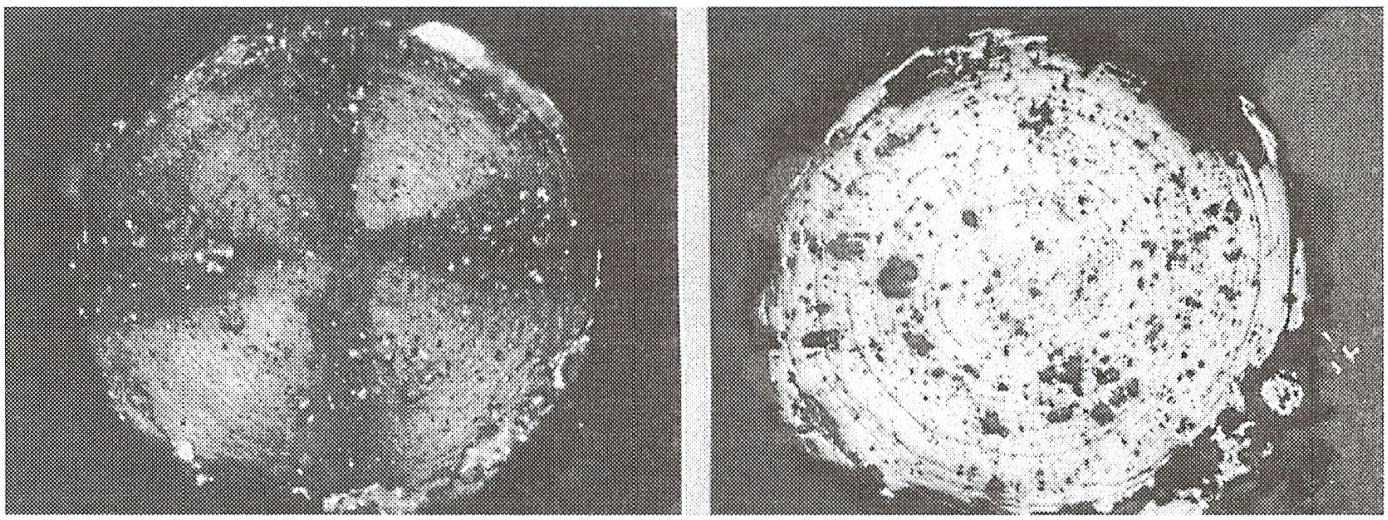

Fig. 2. Polished section across the spherulite center, revealing zonal structure and solid inclusions grabbed from the andesitic matrix during the growth (right, parallel polars, x 120). Maltian cross, revealing the typical spherulitic structure (left, crossed polars, x 120)

Фиг. 2. Полиран през през центъра на сферолит, разкриващ зонален строеж и твърди включения, заграбени от андезитовата матрица по време на растеж (дясно, успоредни николи, x 120). Малтийски кръст, разкриващ типична сферолитова структура (ляво, кръстосани николи, x 120)

the small grains of quartz and silicates grabbed from the basaltic matrix (Fig.2, left). The observed in SEM foliation is expressed in the polished section as concentric zone boundaries.

In polarized light (crossed polars) an almost perfect Maltian cross is observed (Fig.2, right). This typical for spherulitic aggregates pattern proves the availability of subindividuals equally spread in all directions so that there are always enough of them oriented in the respective directions of light fading. The cross remains on its place on rotating, however some distortion can be noticed. The last feature proves ones on Fig. 3 (right) are considerably less populated. On the plain polished section surface the crystals are irregularly oriented, however in the interslice boundaries, where the population is very high (because of the better vapor circulation) they are parallel to each other and laterally plated.

Chemical composition

Microprobe analyses showed almost pure As, with Sb contents varying from 0.5 to 2 wt.%. Numerous analyses were performed to check the aggregate homogeneity with

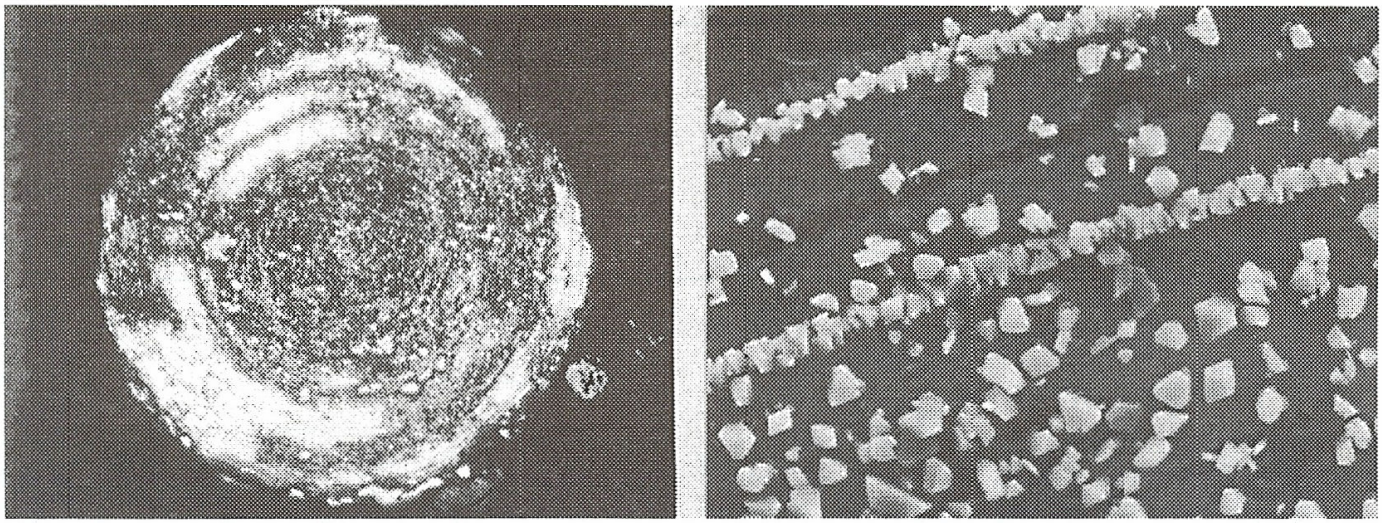

Fig. 3. Tarnishing of the section surface 48 h after the polishing. The different amount of oxidation appears related to interslice boundaries and areas with more inclusions or other defects (left, parallel polars, x 120). Arsenolite crystals on the surface and in interslice boundaries where they are closely packed and laterally flattened (right, SEM, x 1100)
Фиг. 3. Окисление на повърхността на шлифа 48 часа след полирането. Различната оксидация изглежда е свързана с междуслоеви граници и области с повече включения или дефекти (ляво, успоредни николи, х 120). Арсенолитови кристали на повърхността и в междуслоеви пространства където кристалите са плътно подредени и странично сплеснати (дясно, SEM, х 1100)

regard to the possible zonal distribution of impurities, causing different tarnishing effects. The results didn't prove this possibility. The Sb content in the mentioned limits was uniformly spread, without any dependence to the zoning.

X-ray studies

The heterogeneous tarnishing is described by Ramdohr (1975) as characteristic for the orthorhombic As variety - arsenolamprite gave us the reason to test the possibility by X-ray methods.

The Debye-Scherrer photograph taken from a single growth band (table 1) showed at least one peak (5.30 Å) corresponding within the limits of accuracy to the strongest arsenolamprite line 5.44 Å and unavailable both in native As and arsenolite diagrams. All the other peaks that could be attributed to arsenolamprite (unavailable in native As) could also be treated as arsenolite lines.

In the diffractometric sample (Fig. 4), prepared by grinding of several spherulites the 5.30 Å peak was not observed.

This leaves us still in the position to accept the possibility for minor amount of arsenolamprite in some spherulites, that we have been lucky to have in the Debye-Scherrer sample and happened to be too small in the diffractometric case.

Anyway, we are uncertain to prove the existence of arsenolamprite in our samples based on the available data. The very similar X-ray patterns of the two As minerals, together with the close coincidence between arsenolamprite lines and those of the always available there arsenolite is the reason for the long way to the recognition of arsenolamprite by the IMA new minerals commission after its characterization by Johan (1959). Our situation is similar to that in Copiapo, where Hintze (1886) introduced the arsenolamprite mineral name for the first time, but both Jung (1926) and Padera and Fishera (1956) found only rhombohedral As and arsenolite in their X-ray patterns from samples collected at the same locality. The situation was very doubtful until arsenolamprite was confirmed by Clark (1970). In our case we even have data for the existence and nonexistence of arsenolamprite from one and the same hand specimen.

In respect to the oxidation product formed on the polished section surface we also had two structural possibilities arsenolite and claudetite. As far as no single species sample could be prepared from

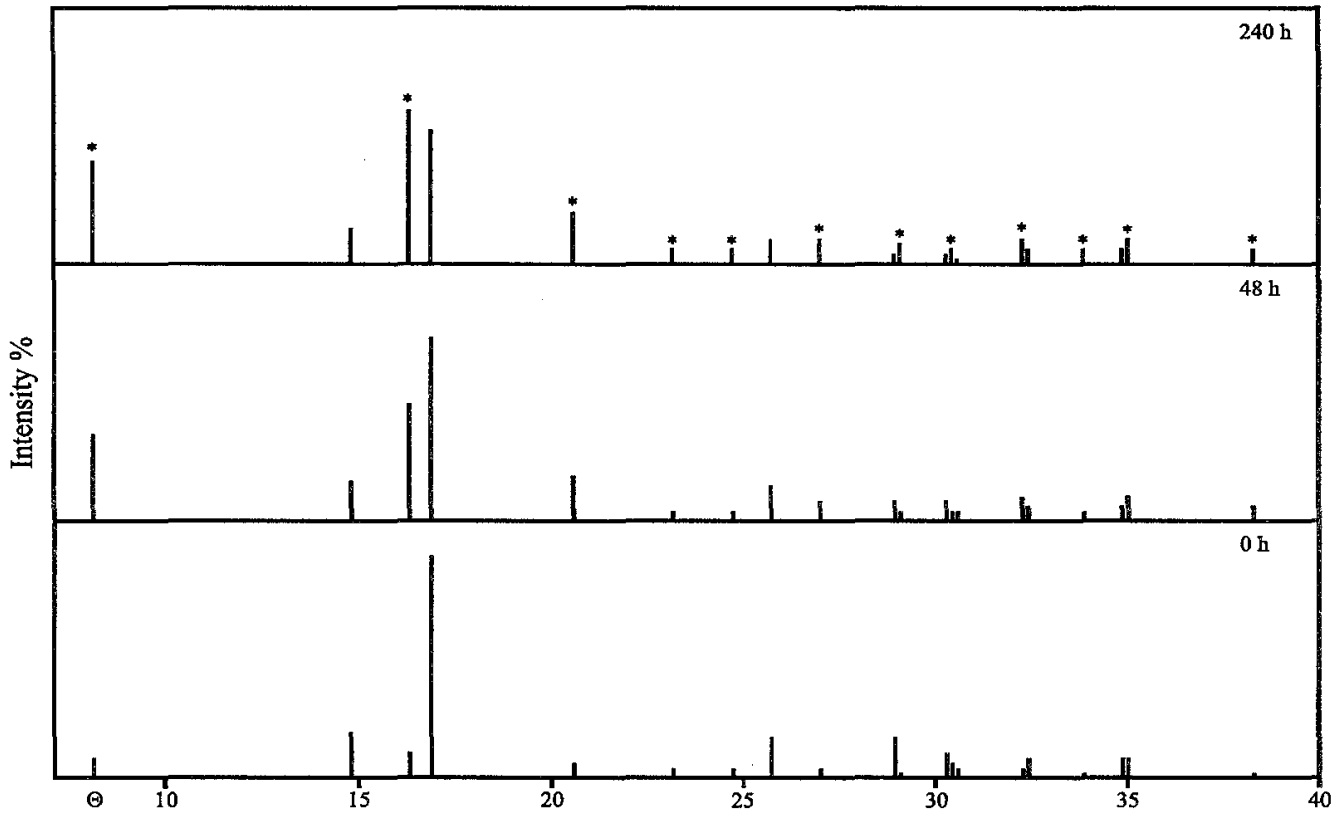

Fig. 4. X-ray diffraction patterns of the As spherulites: 0, 48 and 240 h after grinding respectively. Arsenolite peaks denoted by asterisk

Фиг. 4. Рентгенова дифракционна картина на арсеновите сферолити - съответно 0, 48 и 240 часа след стриване. Пиковете на арсенолита са означени със звездичка

these ultra fine crystals (Fig.3, right) the diffractometric patterns of arsenic spherulites were taken just after grinding and after 48 and 240 hours respectively. This provided the possibility to trace the intensity changes of characteristic peaks due to the progressive alteration of As into As_2O_3 (Fig. 4). The observed extra lines in the As pattern could all be indexed as arsenolite lines and no evidence for claudetite existence could be found there.

Microdiffraction

An unsuccessful attempt for microdiffractometric investigation was made using 100 kV transmission electron microscope. The As (arsenolamprite?) particles got melted as soon as the beam was targeted on them because of the very high absorption of the As.

Syngle crystal X-ray studies

Buerger's precession photograph was tried for elucidating the fine aggregate texture, but samples gave almost no X-ray patterns. The possible explanation of this phenomenon is probably the same as in the case of microdiffraction. If not complete melting, the X-ray probably causes isomorphization of the material when exposed for the longer time necessary for this method. The duration of the Debye-Scherrer experiment looks to be the upper time limit (at the given intensity) for X-ray exposure before loosing structure.

Genetic considerations

In Sedefche As is represented as a major constituent or trace element in a number of minerals (Mladenova, 1997). As a native element it is deposited at the very end of the deposition process. According to Sergeeva and Chodakhovski (1969) native As can be deposited from hydrothermal solutions under 150°C. In this case very low S activity is required for the native As formation instead of sulphoarsenides. This

Table 1
X-ray powder diffraction data of the investigated sample (Debye-Scherrer method), compared to related reference data
Таблица 1
Междуплоскостни разстояния на изследвания образец (Дебай-Шерер) съпоставени със справочни данни

Arsenic PDF 5-0632			This study		Arsenolamprite PDF 29-0142		
dÅ	I	hkl	dÅ	I	dÅ	I	hkl
			5.300	20	5.440	100	002
3.520	26	003	3.480	60	3.480	60	012
3.112	6	011	3.130	30			
2.771	100	102	2.770	100			
					2.740	80	004
					2.720	100	111
			2.260	20	2.235	60	020
2.050	24	014	2.040	80			
			1.960	10			
1.879	26	110	1.875	90	1.877	60	121
					1.836	20	006
					1.815	60	200
1.768	10	105	1.779	5			
1.757	7	006	1.760	10	1.731	80	115
1.658	6	113	1.656	30	1.697	40	016
					1.622	20	?
1.556	11	022	1.559	40	1.548	20	?
					1.520	60	204
					1.444	20	125
			1.420	10	1.419	20	026
1.386	6	204	1.390	30	1.380	20	?
1.367	4	017			1.362	60	131
1.289	5	025					
1.284	5	116	1.283	60	1.261	60	206
1.222	1	121	1.224	20			
1.199	7	212	1.202	70	1.209	60	127
1.172	1	009	1.172	20	1.197	40	301
					1.155	40	036
1.116	4	124	1.120	60	1.115	100	119
1.106	2	207	1.106	30			
1.086	3	300	1.086	50			
1.063	3	215	1.064	50			
1.037	2	303	1.037	20			
			1.029	30			
0.995	2	119	0.997	10			
0.953	2	127	0.970	20			
0.940	1	220					
0.920	3	1.0.11					
0.900	1	218					
0.890	2	132					

requirement looks to be fulfilled in our case, because the whole quantity of S available is already deposited in earlier deposition stages. Additional argument for the solution exhausting is the low Sb content in described As samples (very common as an impurity in native arsenic in other cases), regardless of the availability of Sb minerals earlier in the paragenesis.

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