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The significance of wulfenite morphology as shown on crystals from Mezica, Slovenia

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В един музеен образец с размери 4 на 6 cm вулфенитът (от под 1 до 10 mm) се придружава само от дребнозърнест калцит и много малко лимонит и върху едната страна показва закономерно постепенно изменение на хабитуса на кристалите от тънкоплочест до бипирамидален. С микросонда не са открити примеси. Хабитусните форми са n{011} (ρ_{011} = 65°47', c/a = 2,2234), c{001} и a{010} с характерни различия в повърхностния им релеф. Наблюдавани са две ясни зони с бипирамидални и плочести кристали, разделени от зона с изометрични форми, в която има и хемиморфни кристали. Образецът е рядък пример на толкова добре изразени морфоложки изменения при вулфенита. Те се тълкуват въз основа на предишни наблюдения на автора върху лабораторната кристализация на оловния молибдат. Оловно-молибдатното отношение в разтворите контролира прехода от плочест към бипирамидален хабитус като излишъкът на молибдатни йони води до преобладаващо развитие на пинакоида. Растеж в среда с голям градиент на това отношение може да обясни и хемиморфията на минерала. Развитието на един или друг вид бипирамида се контролира по сложен начин от киселинността на средата. Подчертано е взаимодействието кристал/среда като контролиращ морфологията фактор, чието изучаване може да хвърли повече светлина върху природната кристализация.

Ключови думи: вулфенит, Межица, форми на растеж, хабитусни изменения.
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Introduction

Laboratory crystallization of wulfenite by chemical reactions in aqueous solutions under ambient conditions has revealed strong solution-chemistry effects on its growth morphology (Vesselinov, 1995; 1996). The experimental conditions reproduced fairly well the general features of wulfenite formation in an oxidation zone. The present study, part of which was reported at a poster session during IMA'94 General Meeting in Pisa, Italy (Vesselinov, 1994), attempts to demonstrate that the effects observed are capable of explaining some well-known and elusive morphological phenomena in the mineral. The argument is based on an instructive specimen, No

4865' of the Sofia Natural History Museum collection, in which wulfenite crystals exhibit drastic habit changes from thin tabular to dipyramidal over a distance of some four centimetres only. Specimen's locality is broadly given as Mezica, Slovenia.

A comprehensive review of the limestone-hosted lead-zinc deposit of Mezica with its large oxidation zone famous for the abundant wulfenite has been recently given by Strucl (1984; see also Bancroft et al., 1991, for a brief description). The ores of fine-grained galena and sphalerite either interstratify the host Triassic limestone sequence, or form discordant veinlike bodies where oxidation products and especially wulfenite are by far the most abundant. Of the other minerals in the supergene association limonite, calcite and cerussite are ubiquitous, smithsonite and hydrozincite are common, hemimorphite and descloizite are of local occurrence, and anglesite is rare. Wulfenite crystals are of millimetre size and tabular shape mostly but there are also pyramidal and dipyramidal habits. Overgrowths of one or both pinacoid faces by tiny pyramids are quite frequent. An exceptional example describes steep-pyramidal to needle-shaped wulfenite crystals occurring in highly corroded galena in close association with cerussite, and with minium, massicot and litharge found nearby. Although sought, no relationship has been found between the minor element content, especially of copper, chromium and calcium, and the shape or colour of crystals which varies widely from greenish to yellow and amber to red and dark brown. Hydrogeologically, the area, percolated by abundant water, is thought to have not changed much since the Pliocene. Present-day groundwater is of calcium-magnesium hydrocarbonate-sulphate composition and pH of *7,5* to *8,0*. Wulfenite formation is described by Strucl (1984) as a result of the reaction of ionic lead, supplied in water during galena oxidation, and soluble molybdate complexes originating from jordisite disseminated in the host limestone.

Another relevant reference is to Hurlbut (1955) whose discovery of a feeble piezoeffect in wulfenite was also made on crystals from Mezica, and who thus was the first and only one to present physical evidence in support of wulfenite tetartohedrism (point group 4) suspected from morphological observations.

Crystal characterization

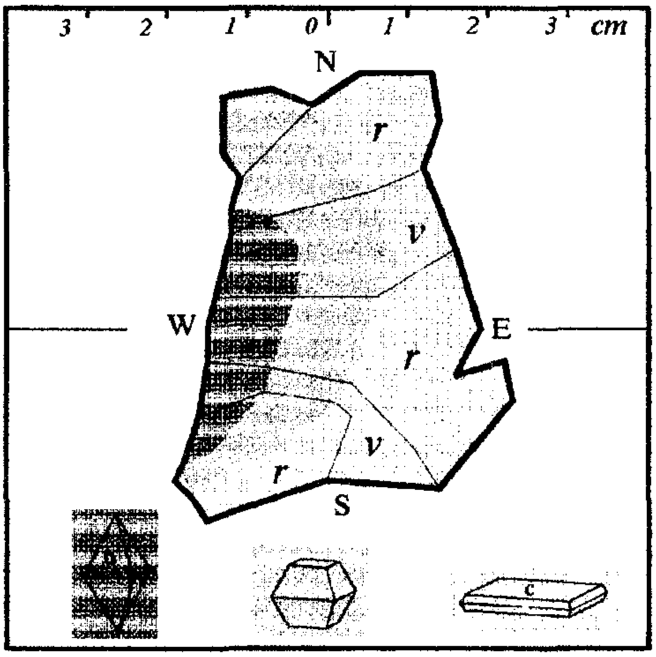
The specimen in this study (Fig. 1) is a piece of a wulfenite aggregate with some powdery calcite and occasional spots of limonite. It can be described as consisting of a "backbone" structure of densely packed wulfenite platelets which supports a "back side" of drusy wulfenite of uniform brown colour and thin-tabular habit, and a "front side" covered by dozens of crystals ranging in colour from lemon yellow to amber and red to brown, and in habit from thin tabular to dipyramidal, including a zone of hemimorphic crystals. Taking great care not to ruin the museum specimen, a piece of the "backbone" substrate and 15 crystals of inferior quality were extracted for examination.

The piece of substrate was polished across the structure, coated with carbon and analyzed on a Jeol SUPERPROBE-733 microanalyzer. Wulfenite (with interstitial calcite) did not show any detectable trace elements. The same negative result was obtained for 5 crystals, carbon-coated for scanning electron microscopy after goniometric measurements.

Measurements with a two-circle Goldschmidt-type goniometer were made on all extracted crystals grouped as follows: 4 brown thin platelets (2 to 10 mm in size)

Fig. 1. "Front" side of the Mezica specimen mapped to show the distribution of wulfenite habits, dominated by n{011} and c{001}, in W-E "ridges" (*r*) of crystals sticking up above the surface and in "valleys" (*v*) where wulfenite is associated with powdery calcite

Фиг. 1. "Предната" страна на образеца от Межица със схема на разпределението на хабитусите на вулфенита, определени от n{011} и c{001}, в "хребети" (*r*) от кристали, стърчащи над повърхността на образеца, и в "долини" (*v*), където вулфенитът асоциира с дребнозърнест калцит



from the "back" side, and 11 crystals from the "front" side including 2 brown cuboid crystals (0,5 and 2 mm), 3 yellow platelets (2 to 5 mm), 4 amber to red dipyramids with pinacoids (0,3 to 2 mm), and 2 lemon yellow dipyramids with very small pinacoids (0,2 mm). Among the forms observed, to be described below, n {011} produced by far the best signals and in most crystals all its 8 faces could be measured with fairly high accuracy. The weighted mean of its polar angle is ρ_{011} = 65°47' ± 2' which defines $c/a = 2.2234 \pm 0.0035$ for this Mezica wulfenite. Cleavage {011} surfaces of good quality were observed in 6 crystals, in 3 of which inferior {001} cleavage was also seen, and in 2 of them poor {112} cleavage was present as well. The variable crystal habit is defined by simple combinations of *c*{001}, *n*{011} and *a*{010} which show marked differences in their surface relief (Pl. I; Pl. II).

c{001} is covered by a thin oriented overgrowth of lighter colour than the substrate crystals and rarely shows flat portions (Pl. II,4). On the dipyramidal crystals the overgrowth consists of numerous tiny pyramids producing well-defined reflections corresponding to *n*{011} (Pl. II,2) and *e*{112} (Pl. II,4), the latter generally predominating. On the tabular crystals (Pl. I,5,6) the overgrowth has additionally developed rough {001} surfaces and the faces seem covered with "pits" faceted by *n*+*e*. On 4 crystals *c*{001} showed a kind of polar development with one of its faces being covered by pyramidal overgrowths whereas the other had flat portions and faceted "pits". Photographs of similar overgrowths have been shown by Strucl (1984; Pl. 11, Figs 2 and 3).

n{011} shows pronounced layer growth with steps spreading out of growth hillocks. The flat layers produce brilliant signals from which shorter or longer beams of reflected light come out along the zonal directions of the systems of subparallel growth steps. One system (Pl. I,1,2,3; Pl. II,1) consists of two sets, one shorter than the other on a given face, thus marking the absence of symmetry planes along the fourfold axis. The zonal directions of these steps are highly variable due to the changing outlines of vicinals but [131], [141] and [151] have been measured on some crystals. The respective light rays commonly extend to {hk0} areas. On the larger dipyramidal crystals, the growth hillocks abruptly increase in number and their shape becomes less regular towards the pinacoid thus indicating a sharp change in the growth

PLATE I

SEM photographs

1. An amber-coloured wulfenite crystal from the dipyramidal (W) side of the specimen shown in Fig. 1. (001) is covered with a pyramidal overgrowth, {011} shows growth layers spreading to a small {hk0} area at the base of the crystal
2. Similar to 1. but the dipyramidal crystal shows signs of hemimorphic development
3. Pronounced hemimorphism in a yellow crystal from the equant-dipyramidal zone in Fig. 1 (see also Fig.2) bounded by {001}, {011}, {010} and unequally developed hemihedra {130} and {310}. The latter two forms show growth steps coming from {011} and {010}
4. Brown platelets from the "back" side of the specimen. The pinacoid surfaces of both generations are covered with a lighter-coloured overgrowth
5. A platelet from the "back" side of the specimen showing growth layers on {011} and an oriented overgrowth on {001}
6. Detail of 5. showing the morphology of the overgrowth resembling "pits" faceted by {011} surfaces

ТАБЛИЦА I

СЕМ снимки

1. Оранжев вулфенитов кристал от бипирамидалната (W) зона на образеца, показан на фиг. 1. (001) е покрита с малки пирамидки, а {011} — със слоеве на растеж, които се простират към малката област {hk0} в основата на кристала
2. Като 1., но бипирамидалният кристал показва признаци на хемиморфно развитие
3. Подчертан хемиморфизъм в жълт кристал от зоната с изометрични форми на фиг. 1 (вж също фиг. 2), остенен от {001}, {011}, {010} и нееднакво развити хемиедри {130} и {310}. Върху последните се виждат стъпала, идващи от {011} и {010}
4. Кафяви плочки от "задната" страна на образеца. Пинакоидалните повърхности и на двете генерации са покрити с по-светъл вулфенитов слой
5. Плочка от "задната" страна на образеца със слоеве на растеж върху {011} и ориентирано нарастнал по-светъл слой върху {001}
6. Детайл от 5. Морфологията на слоя върху {001} наподобява "дупки", остенени от повърхности на {011}

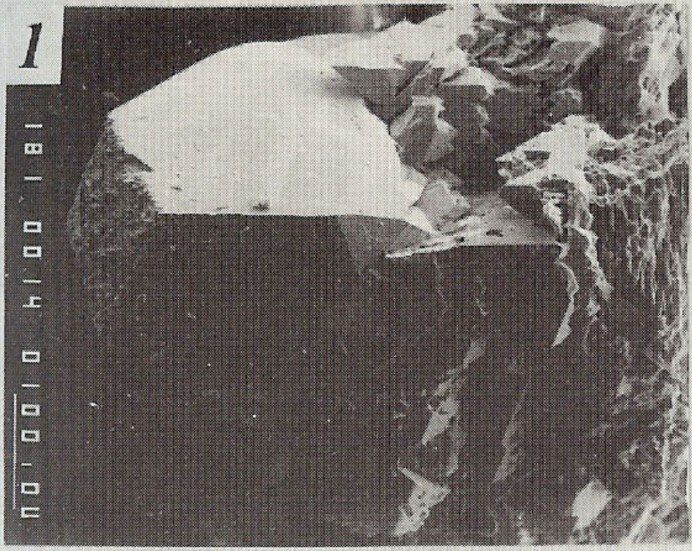
PLATE II

1. A (101) surface with growth steps roughly parallel to [151] and [141]. Wulfenite hemihedrism is also shown by one set of steps being longer than the other
2. A hemimorphic crystal from the dipyramidal (W) zone on the specimen (Fig. 1). The pyramids on (001) are oriented parallel to {011}, a face of which is shown to be covered with growth hillocks. A "suture" line parallel to [010], marking a change in the growth conditions, is seen close to the pinacoid overgrowth
3. A group of neighbouring crystals of thick-tabular to (di)pyramidal habits
4. Yellow platelets from the tabular (E) side of the specimen (Fig. 1). The pyramidal overgrowth is shown to reflect parallel to {112}
5. Two hemimorphic crystals from the equant-dipyramidal zone on the specimen (Fig. 1; see also Fig. 2). Their {011} surfaces show a sharp change in the growth relief at some distance from the pinacoid
6. Slightly barrel-shaped cuboid crystals from the S edge of the specimen (Fig. 1). The narrow {011} face, brought to reflection on the largest crystal to the left, shows growth steps

ТАБЛИЦА II

1. Повърхност на (101) със стъпала на растеж, приблизително успоредни на [151] и [141]. Едната система е и по-дълга от другата като проява на хемиедрията на вулфенита
2. Хемиморфен кристал от бипирамидалната (W) област върху образеца (фиг. 1). Пирамидките върху (001) са ориентирани успоредно на {011}, чиято стена е покрита с хълмчета на растеж. Вижда се "сутурна" линия, успоредна на [010], близо до пирамидките върху пинакоида, която бележи промяна в условията на растеж
3. Група близко разположени кристали с дебелоплочест до (би)пирамидален хабитус
4. Жълти плочки от съответната (E) област върху образеца (фиг. 1). Пирамидките върху (001) в случая отразяват успоредно на {112}
5. Два хемиморфни кристала от зоната с изометрични форми върху образеца (фиг. 1; вж и фиг. 2). Върху стените им {011} се вижда рязка промяна на релефа на известно разстояние от пинакоида
6. Кубоподобни, слабо бъчвовидни кристали от ръба S на образеца (фиг. 1). Върху тясната стена на {011}, отразяваща от най-големия кристал вляво, се виждат стъпала на растеж

1



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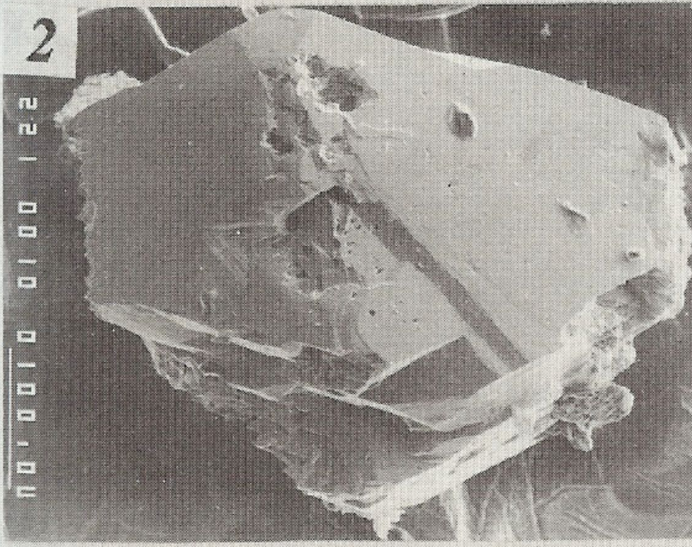

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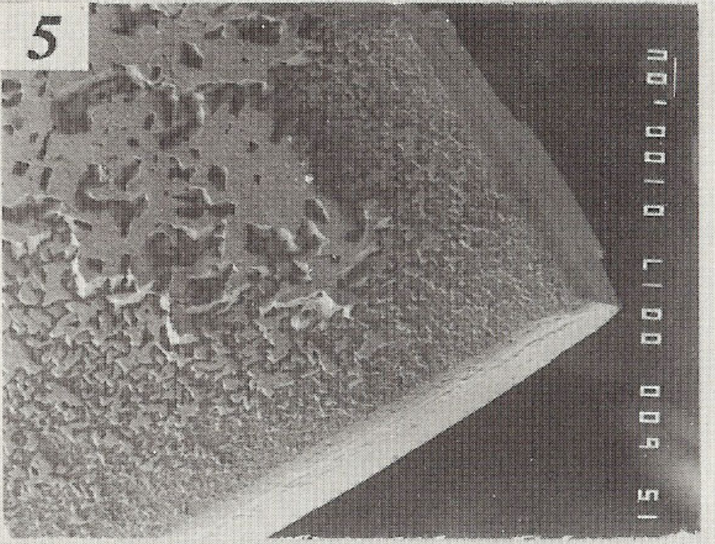

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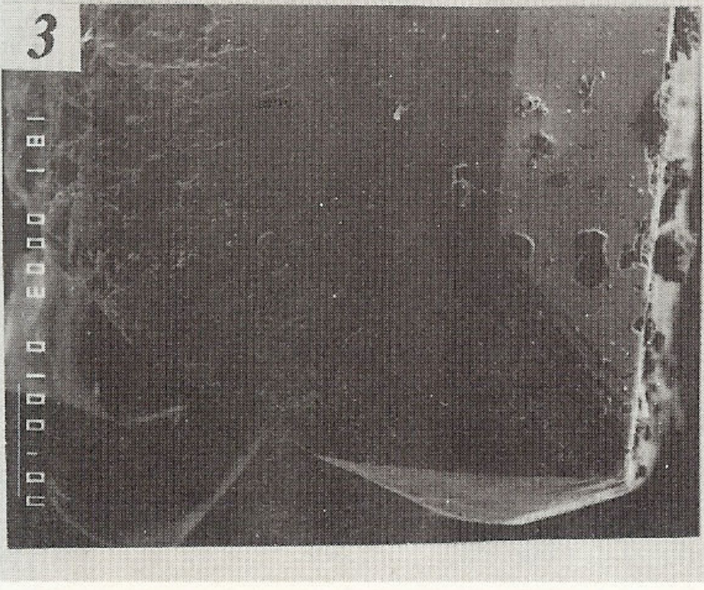

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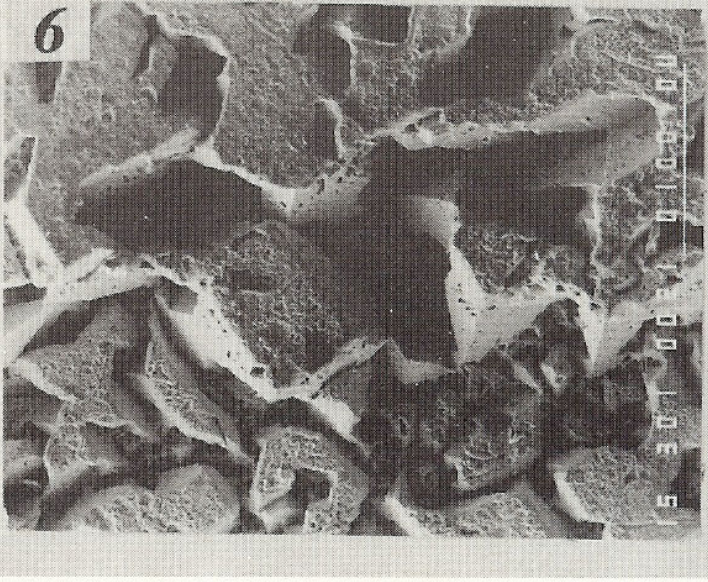
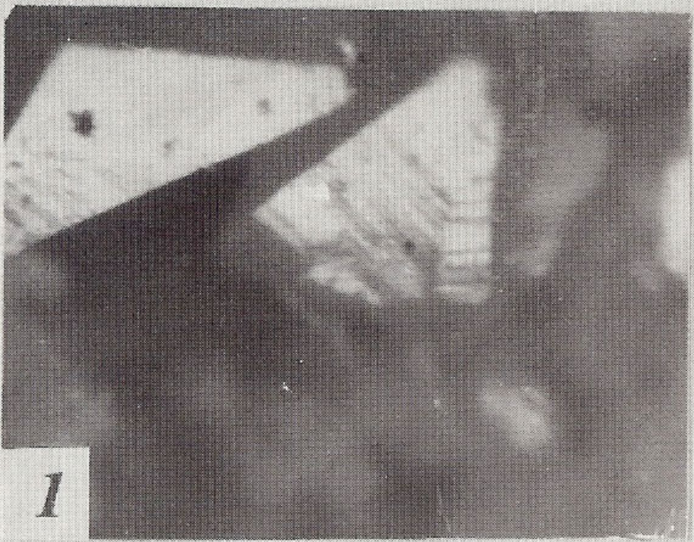


ТАБЛИЦА II **PLATE II**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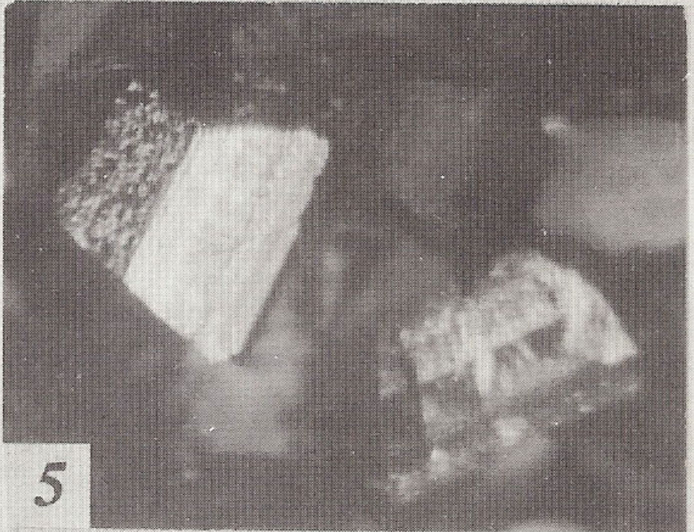
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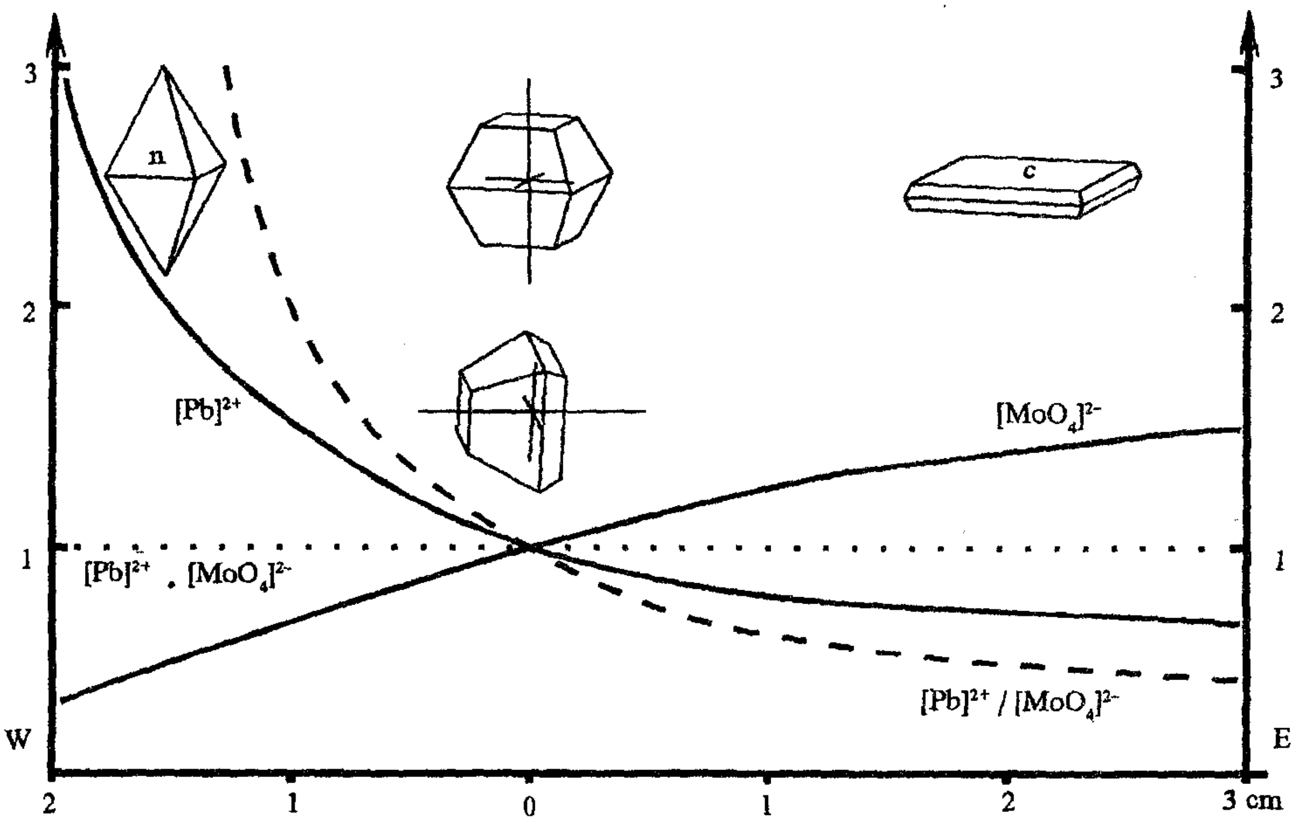

Fig. 2. Diagram of the presumed concentration distribution of wulfenite constituents, their product and ratio along the W-E line in Fig. 1 during growth. In the zone of equant shapes a crystal will grow hemimorphic if its fourfold axis lies along the direction of lead-to-molybdate ratio change

Фиг. 2. Качествена схема на предполагаемото разпределение на концентрациите на компонентите на вулфенита, на произведението и на отношението им по линията W-E на фиг. 1 по време на растежа на кристалите. Ако в зоната на изометрични форми някой кристал лежи с четворната си ос успоредно на изменението на олово-молибдатното отношение, то той ще израстне хемиморфен.

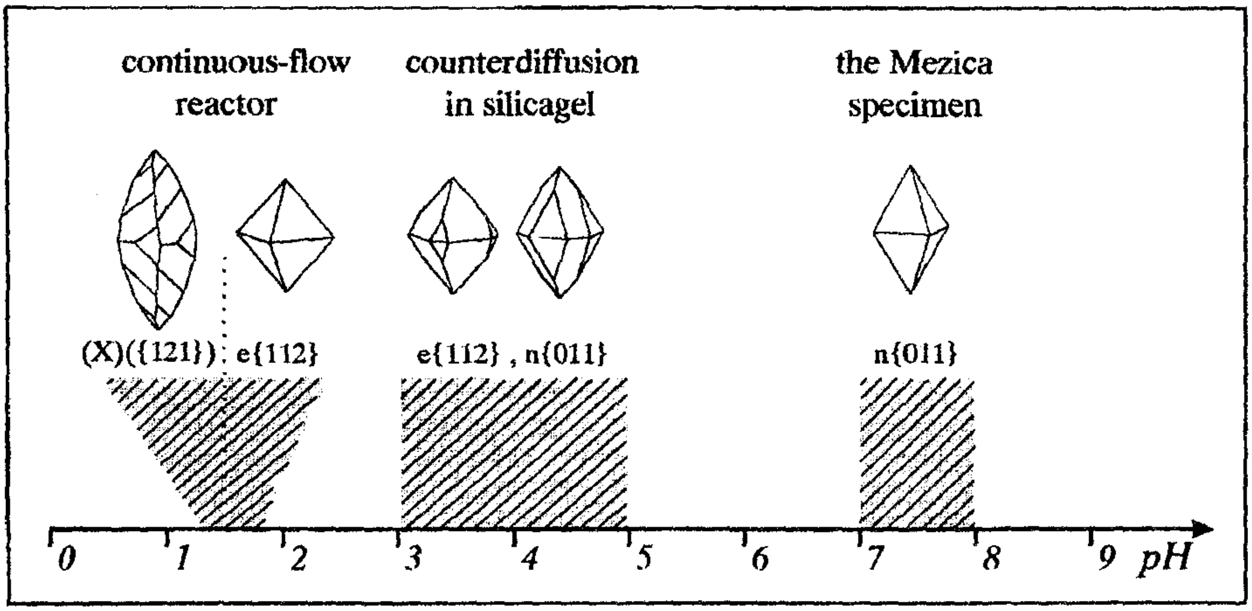

Fig. 3. Diagram of the predominant dipyramids in different pH ranges in which the results of this study are combined with laboratory observations (Vesselinov, 1995)

Фиг. 3. Схема на хабитусните бипирамиди в различни области на pH — данните от настоящото изследване са съчетани с наблюдаваното в лабораторията (Vesselinov, 1995) conditions (Pl. II,2,5). On 2 dipyramidal crystals this system was combined with well-defined [011] steps, and on 2 tabular ones with [010] steps.

a{010} and the whole [001] zone is a typical example of stepped development. On the thin platelets (Pl. I,4; Pl. II,4) *a* is fairly flat but on the thicker ones it is curved both around [001] and [010] so that the cuboid crystals are somewhat barrel-shaped (Pl. II,6). It usually decays into series of thick [001] steps which, combined with the step systems coming from the {011} faces, produce poorly defined {hk0} forms among which {510} and {310} have shown comparatively flat faces on several crystals (Pl. I,3).

Other measured forms include *s*{013}, which showed very narrow faces on 2 tabular crystals, and *e*{112} with hardly detectable faces on 2 dipyramidal crystals. The latter form, however, was always present on the {001} overgrowths.

Hemimorphic features in addition to those described for the {001} overgrowths are shown by some equant-dipyramidal crystals (Pl. I,2,3; Pl. II,2,3,5) which have one pinacoid face larger than the other very similar to the crystals studied by Hurlbut (1955).

Habit patterns and growth sequence in the specimen

On the "back" side crystallization has been markedly more voluminous than on the "front" side. It has produced (Pl. I,4,5,6) an early generation of large thin platelets (typically up to 10 mm wide and 0.2 mm thick) followed by a second generation of ten times smaller platelets preferentially deposited over the central areas of earlier ones. A final lighter-coloured overgrowth on all pinacoid surfaces sandwiches the dark-brown platelets. The changes in the rate of crystallization have had no effect on crystal morphology and all crystals are uniformly thin tabular.

The "front" side, mapped in terms of three E-to-W "ridges" separated from N to S by two "valleys" (Fig. 1), exhibits a regular habit pattern of gradual changes. The "ridges" consist of groups of crystals up to 4 mm in size which stick up above the specimen surface whereas the lower "valleys" between them contain abundant powdery calcite interspersed with tiny wulfenite crystals. The central "ridge" starts at its E end with platelets (Pl. II,4) which appear continuously from the "back" side becoming gradually thicker and more yellow in colour. Towards the centre (Pl. I,3; Pl. II,3,5) they already are brightly yellow and equant-dipyramidal. Hemimorphic shapes are frequent, the side with the smaller {001} face and larger {011} pointing generally outwards. Further towards the W end (Pl. I,1,2; Pl. II,1,2) the pinacoid surfaces become gradually smaller and disappear at the edge of the specimen, the colour turning to amber. On the larger dipyramids, the abrupt change in the hillock pattern on {011}, described in the previous section, is easily distinguished under the stereomicroscope. All pinacoid surfaces in the "ridge" are covered by lighter lemon-yellow overgrowths. The N and S "ridges" exhibit the same E—W patterns, and at the S edge of the specimen there is a small area of brown cuboid crystals (Pl. II,6) which gradually pass over the edge into the platelets on the "back" side. The same habit distribution persists in the two "valleys" but the colour is markedly lighter, lemon-yellow to almost colourless, resembling that of the overgrowth which is absent on these much smaller crystals. Similar to the "back" side, no crystals of one habit sitting on ones of another habit are seen on the entire "front" side. The amount of crystals deposited along the E—W lines is more or less uniform. The habit change from tabular $c+n+a$ to equant $n+c+a$ to dipyramidal n takes place over some 15 mm, the distinct zone of equant (including hemimorphic) crystals dividing the platelets on the E side from the dipyramids on the W side.

This evidence can be summarized as follows. Wulfenite crystallization, more voluminous on the "back" than on the "front" side, most likely was a continuous process but there are records of two events during which the rate of deposition increased abruptly. The first one provoked the formation of the second wulfenite generation on the "back" side, and perhaps it was also responsible for the much milder increase of growth rate on the "front" side indicated by the change of hillock patterns on {011}. The second one deposited the final overgrowth and probably the tiny crystals in the "valleys". Crystallization rate was more or less uniform along the E—W lines dropping crystals of uniform size. The habit pattern, identical in the "ridges" and "valleys", is not related to crystal size, or to colour (and to detectable contents of some minor element), or to pH of solutions which can be evaluated as close to neutral, comparable to that of present-day groundwater, by the uniform presence of calcite. Whatever changes may have taken place in the environment they had not disturbed the habit pattern over the small area, and in this respect the growth conditions may be regarded as stationary throughout the deposition.

Comparison with habit change models

So far the attempts to explain wulfenite morphology have generally led to three models, two of which are based on observations of natural crystals and the third one on laboratory crystallization. They lay stress on different environmental factors which could be responsible for major habit changes, and the evidence in this study provides a good basis for comparison.

In a recent diagram based on studies going as far back as the early sixties, Костов (1993) has suggested that the rise of supersaturation from low to high would produce wulfenite habit changes from (thin) tabular to equant to dipyramidal. Applied to the specimen in this study this scheme would imply an increase of the overall supersaturation from the "back" side via the E part of the "front" side to its W edge. Since the habit pattern does not change in the specimen, the scheme would also imply that the same conditions persisted during the entire period of crystallization which would have resulted in more voluminous deposition on the "front" side and not on the "back" side as observed. Furthermore, the rate-of-deposition changes observed in the specimen should have produced crystals of one habit sitting on ones of another habit, and such cases are absent from the specimen. Thus, it can be safely concluded that supersaturation has not been a major factor in the morphological control in this case.

In another model, Williams (1966) has emphasized the role of pH and Eh of solutions during oxidation under ambient conditions finding no relation between minor element content and wulfenite morphology. These two factors has been roughly defined by the associations of wulfenite with cerussite, mimetite, hemimorphite, willemite and plattnerite, the order of the assemblages marking increasing acidity (between pH *9* and *3*) and oxidation potential, starting from "mildly acid waters at a fairly low Eh" in the wulfenite-cerussite assemblage. Wulfenite habit in this paragenetic scheme changes from (thick) tabular with {hhl} and {0kl} (cerussite), to (thin) tabular with {hhl}, {0kl} and minor {hk0} (mimetite), to the same tabular habit with somewhat more important {hk0} (hemimorphite), to tabular and equant-dipyramidal with {hhl} (willemite), and to steep dipyramidal or (tabular) prismatic with dominant {hk0} (plattnerite). It can be seen immediately that this scheme is also inapplicable to the pattern observed in this study because it implies increasing acidity from the tabular to the dipyramidal zones on the "front" side. Acid environments, however, are ruled out by the uniform presence of calcite, and the crystallization of tiny dipyramids over the carbonate in the "valleys" is conclusive evidence against the proposed relationship. Mezica provides another example, mentioned at the beginning, where the scheme is not obeyed, viz. the steep-pyramidal wulfenite found with cerussite in corroded galena and associated with lead oxides.

These difficulties can be cleared up by using the diagram of wulfenite morphology derived from laboratory experiments (Vesselinov, 1995; 1996) made by mixing lead and molybdate reactants in nitric-acid aqueous and silicagel systems at room temperature and atmospheric pressure. Grown in a wide range of supersaturations and acidities (pH *1,3* to *6*), the crystals reached up to 0,5 mm in size. Although the laboratory systems did not include mildly acid to slightly alkaline hydrocarbonate solutions (as in the wulfenite-cerussite assemblage of Williams, 1966, or in Mezica), in other respects they simulated fairly well the major features of natural environments, as follows: a) crystallization from dilute aqueous solutions at ambient temperature and pressure (Williams, 1966); b) spatially separated sources of the lead and molybdate constituents (like in Mezica); c) variety of acidity and oxidation states controlled by the concentration of nitric acid which is an oxidant as well (all assemblages of Williams, 1966, except the cerussite one); and d) silica-free and silica-bearing environments (silicagel growth imitates the willemite-hemimorphite environments of Williams, 1966). The numerous experiments have revealed two very pronounced solution-chemistry effects on wulfenite growth forms, further emphasized by increasing supersaturation. These factors were the lead-to-molybdate concentration ratio in solutions and the nitric-acid concentration. They will be used below to interpret the morphological pattern in the Mezica specimen.

Habit change from tabular to dipyramidal. Wulfenite hemimorphism

The habit pattern in Fig. 1 is very similar if not identical to the experimentally observed ones illustrated in Fig. 1 and 2 and Pl. I, 1 of Vesselinov (1995). Its cause has been traced back to the chemical assymetry in systems where crystallization is preceded by reaction and the reactants are supplied to the site of mixing, reaction and crystallization from different sources. In such systems the reactant concentrations diminish in opposite directions along the space coordinate so that at one of its ends one of the reactant is in excess of the other whereas at the other end the ratio is inversed. The concentration of the reaction product, however, defined, according to the law of mass action, by the product of the reactant concentrations, could be one and the same at contrasting reactant ratios. Under such conditions, crystallization would proceed at a more or less uniform supersaturation (controlled by the uniform product of concentrations) in the entire system but in an excess of one or the other reactant in the opposite parts of it. This situation was commonly observed in the laboratory where steady supply of reactants (both in counterdiffusion systems and in a continuous-flow reactor) created stationary concentration fields of this kind and invariably produced wulfenite platelets at the excess-molybdate side and dipyramids at the excess-lead side. Fig. 2 is a modified version of Fig. 2 in Vesselinov (1995) interpreting the habit pattern in the specimen (Fig. 1) in terms of the laboratory results. The abscissa is the W—E line along the central "ridge" on the "front" side, and the ordinates are the presumed reactant concentrations in arbitrary units. The steeply sloping curve of lead concentration illustrates the idea that ionic lead, consumed quickly by reaction and crystallization, was released by closely located galena. In contrast, the molybdate constituent came from distant sources (Strucl, 1984) in the form of complexes which sustained much less variable concentration field over larger distances, their continuous disintegration feeding the reaction at the site of crystallization. Steady supply of constituents created a stationary field of uniform supersaturation (uniform product of reactant concentrations) responsible for the more or less uniform quantity of precipitated lead molybdate along the W—E line. Wulfenite habit, however, responded with a drastic change to the contrasting difference between the lead-to-molybdate ratios in solution at the W and E ends of the system. This scheme has geochemical and crystallochemical implications capable of explaining some well-known morphological phenomena in wulfenite and related minerals as in the few examples given below.

Geochemically, sufficiently high excess-lead environments under supergene conditions could be expected only very near the lead sources because of the low migration ability of lead. Accordingly, dipyramidal wulfenite is rare and in many well-documented examples it sits directly over galena (e.g. Костов, 1961; Strucl, 1984). In contrast, calcium is available in much higher concentrations and the calcium minerals of scheelite structure generally form in calcium-rich environments so that dipyramidal habits are correspondingly common (powellite) or predominant (scheelite).

Crystallochemically, this scheme has suggested an explanation of wulfenite tetartohedrism as a growth-induced phenomenon (Vesselinov, 1995) rather than a purely structural one (Kleber, 1956). It is illustrated in Fig. 2 where two crystals with their axes shown are depicted in the equant-habit zone. According to the scheme, the symmetry 4/m will be reduced to 4 if a large enough crystal is oriented with its fourfold axis parallel to the direction of chemical change so that its end growing in excess-molybdate environment will develop a larger pinacoid face. This author (Vesselinov, 1995) has proposed a mechanism in which the growth rate of {001} surfaces is retarded by selectively adsorbed MoO_6-polymers forming over them in excess-molybdate solutions. It has been shown that besides hemimorphism this mechanism may produce polar differences in stoichiometry and impurity levels along the fourfold axis which may explain the piezoelectricity effect observed by Hurlbut (1955). Thus, wulfenite hemimorphism treated as a kinetically-induced rather than a structural phenomenon may provide a way for reconciling the mineralogical evidence of polar wulfenite (e.g. Костов, 1993) with the non-mineralogical evidence of centrosymmetric lead molybdate (e.g. Блистанов и др., 1982).

Laboratory growth has given no indication of similar effects caused by lead species in solution or over the growing faces. Yet they should not be overruled, and the Mezica specimen suggests a relationship. The habit change in the "ridges" (but not in the "valleys") is accompanied, as already described, by a change in colour from yellow to amber-red towards the dipyramidal (W) end of the specimen. It follows that red colouration is somehow related to lead-rich environments. Under highly oxidizing conditions, a lead-rich environment has locally dropped red lead oxides in addition to wulfenite at Mezica (Strucl, 1984). Boncroft et al. (1991) specifically note that brownish red crystals occur on galena.

Development of dipyramids

Whereas the pinacoid sensitivity to reactant ratios has demonstrated itself in the whole wide range of experimental conditions, preferential development of three major dipyramids has been observed in certain restricted intervals of nitric-acid concentrations. The relationship is shown in Fig. 3 which combines the laboratory observations (Vesselinov, 1995) with the Mezica evidence valid for a pH range not covered in the experiments. It should be pointed out again that pH, given in the figure as a measure of nitric-acid concentrations, does not exhaust the solution-chemistry effects in this case. In addition to the acid action as an oxidant, its increasing concentration provokes complexing in molybdate solutions and, combined with other well-known complexing agents such as Si, P, As, etc., leads to the formation of iso- and heteropolymolybdate species (Gmelin, 1976; 1987; 1989). In particular, silicomolybdates has been found to cause the lemon-yellow colour in tabular wulfenite grown in silicagel (Vesselinov, 1977; Vesselinov, 1995), and molybdate complexing in silica-free solutions has most likely controlled some growth directions of dendritic lead molybdate (Vesselinov, 1996). Thus, the decreasing pH in Fig. 3 reflects also an increasing oxidation potential and growing chemical complexity of solutions at least with respect to molybdate solutes. The possible effect of the latter on dipyramidal growth forms has been discussed in Vesselinov (1995).

The morphological diagram in Fig. 3 shows four pH ranges. In silica-free solutions below pH about *1,5* (high acidity, oxidation potential and chemical complexity) the habit dipyramid is of the {hkl} type with curved faces and {hk0} areas in the [001] zone, whereas between pH *1,5* and about *2* the dominant dipyramid is of the {hhl} type; in the medium pH range and in silica-bearing solutions the {0kl} type becomes a habit form, too (Vesselinov, 1995). This scheme quite naturally extrapolates itself to the habit dipyramid in the Mezica specimen occurring in neutral and, by implication, less complex solutions. The occurrence of e{112} in addition to n{011} in the final pyramidal overgrowth is explained by it as a response to a chemical change involving molybdate complexing in more acid solutions. It is interesting to note that the lemon yellow colour of the tiny crystals in the “valleys” closely resembles that of silicagel-grown wulfenite (Vesselinov, 1977) so that an increase of the silica content of solutions during the final stage of growth seems quite probable. At the same time the absence of red colouration in these dipyramidal crystals, in contrast to the red dipyramids in the “ridges”, may indicate a parallel decrease of the oxidation potential as discussed in the previous section.

It may be seen that the scheme in Fig. 3 generally fits the paragenetic scheme of Williams (1966) with respect to the features of dipyramidal development. Indeed, that author has observed that with the increasing acidity and oxidation potential the stability of {hhl} increases while that of {0kl} decreases, and {hk0} becomes increasingly important and even dominant in the wulfenite-plattnerite assemblage.

Conclusion

The specimen in this study shows that solution-chemistry effects on wulfenite morphology observed in growth experiments can form a basis for a deeper understanding of wulfenite formation in nature. Laboratory results stress the significance of the chemical complexity of solutions and the specific and very sensitive response of crystal interfaces. Although the artificial conditions have not reproduced the rich variety of natural environments and crystal shapes, they have given valid clues to the mechanisms underlying some elusive features of wulfenite morphology, such as its habit development and hemimorphism, by distinguishing factors acting separately on pinacoid and dipyramidal surfaces. The results of this study have a number of verifiable implications that may throw more light on crystallization processes in nature and the behaviour of crystal surfaces in different environments.

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