Non-equilibrium highly anisometric crystals and whiskers of galena

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Abstract

Unusual irregular galena crystals and whiskers were found in close proximity in some druse cavities from the Gradishte hydrothermal lead–zinc deposit in the Madan ore district, Bulgaria. The following crystal forms were observed: (1) straight thin [110] whiskers and thicker needles; (2) kinked whiskers; (3) curvilinear whiskers; (4) complex tortuous whiskers composed of segments with varying directions—[110], [100], [211]; (5) thicker irregular elongated crystals. Combinations of these forms occur also. The detailed SEM study shows that all these formations are single crystals of extreme anisometricity, bounded by octahedral and cubic faces as well as by stepped surfaces of these forms. Surface structures such as longitudinal grooves, jagged edges, striations, pits, etc., are abundant.

It is assumed that these highly non-equilibrium crystals with large surface areas were formed through rapid directed growth from highly supersaturated solutions under a diffusional regime. Such special environments arose in the ore veins as a result of tectonic shocks leading locally to a drastic volume increase and P and T decrease in the solutions.

Keywords: galena, crystal morphology, crystal growth, whiskers, Madan ore district.

Introduction

Well-shaped isometric galena crystals with cubic and octahedral habit are known to be widespread, a natural fact for crystals with close-packed NaCl-type structure. In the lead–zinc deposits of the Rhodope Mountains, Bulgaria, however, unusual elongated straight, as well as crooked and irregular needle-like galena crystal formations and whiskers also occur.

Natural galena whiskers were first described in the ores form the Mogilata deposit in the Madan ore district, Central Rhodopes (Bonev, 1970). The thin (1–3 to 10–20 μm) straight [110] and [100] or kinked whiskers were bounded by cubic and octahedral faces. Thicker needles and irregular dendritic crystals have also been found but their morphology could not be examined by optical microscopy at that time. Such whiskers have also been found in druse cavities of the Govedarnika skarn–ore deposit in the Luki district, Central Rhodopes (Bonev, 1980). Acicular and hollow [100] whiskers of galena from the straitiform lead–zinc deposit Djalta in Northern Tunisia have been also observed by Bogdanova and Bogdanov (1986).

The subjects of this study are irregular needle-shaped galena formations and whiskers found in the Gradishte deposit, again from the Madan ore district, Central Rhodopes. Their morphology and surface structure examined in detail by SEM are a clue to interpreting the specific conditions of their formation in an extremely non-equilibrium hydrothermal crystallisation process.

In the literature, detailed investigations of mineral whiskers and their surface morphology are rare and for the irregularly developed 'pathological' crystals information is almost non-existent.

Geological setting

The Tertiary (30–40 Ma] hydrothermal lead–zinc deposits in the Madan district occur in a Precambrian metamorphic complex of predominantly gneissic rocks and partly in the covering Paleogene breccia-conglomerates. The main ore bodies are steeply dipping veins controlled by six subparallel NNW striking faults 10–15 km in extent. Also important are the metasomatic gently pitching skarn-ore bodies localised in marble layers of the metamorphic complex along the ore-bearing zones. The ores in veins and beds are simultaneously formed and are similar in composition, the following successive mineral

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associations being revealed: a skarn association; early quartz–pyrite; quartz–galena, and quartz–sphalerite–galena (with early large- or medium-sized crystals of galena and of other sulphides); quartz-pyrite–arsenopyrite; quartz–carbonate (with late galena as fine crystals, whiskers and needle formations). The sulphide associations are high- to medium-temperature (360–330–300 °C), while the final quartz–carbonate stage is lower-temperataure (280–200 °C and below). The solutions are slightly acidic, of Cl–Na–K composition and a low salinity (≈5% NaCl equivalent). The mineral deposition is related to neutralisation of the solutions as a result of interaction with the enclosing gneisses and pyroxene skarns, as well as of boiling of the solutions with both open space and replacement deposition (Bonev, 1984).

The Gradishte is one of the economically and genetically most important deposits in the region (Minčeva-Stefanova and Gorova, 1965), now nearly exhausted.

Experimental

The samples collected in the mine were studied by a stereomicroscope in order to determine the mineral relationships and to select material for subsequent studies. Gandolfi and Buerger precession cameras were used for X-ray characterisation. The morphological peculiarities of the crystals were investigated with both uncoated and gold-coated samples by JEOL scanning electron microscopes (SEM) Superprobe-733 and JSM-35 operated at 25 kV. Local microprobe analysis was carried out by an ORTEC energy dispersive system (EDS) directly on natural faces of the galena crytals.

Mineralogical position and characteristics of needle-like galena

The whiskers, tortuous and needle-shaped crystals were found in druse cavities on the deepest 450 level in the Gradishte mine. The associated minerals are long prismatic quartz, early cubic-octahedral galena and bisphenoidal chalcopyrite as crystals up to 0.5–1 cm in size, a few light-brown sphalerites together with baryte, nontronite and calcite. The whiskers and needles (Fig. 1), as the latest gelena formations, have grown on the early polyhedral crystals of galena, and partly on the other sulphides. Many whiskers become overgrown with fine nontronite flakes and nests (Fig. 1*c*). Entirely overgrown galena needles in the form of peculiar tube-like nontronite pseudomorphs were also found.

The X-ray study indentifies the whiskers as ordinary galena, findings confirmed also by microprobe analysis which did not indicate any other admixtures or detectable deviations from the PbS stoichiometry. These determinations are important since in the deposit similar fine fibrous crystals of lead sulphosalt minerals, in particular cosalite and aikinite, are also present.

The thinnest investigated whiskers (below 10 μm) have unusually high elasticity for galena, a fact reported earlier (Bonev, 1970).

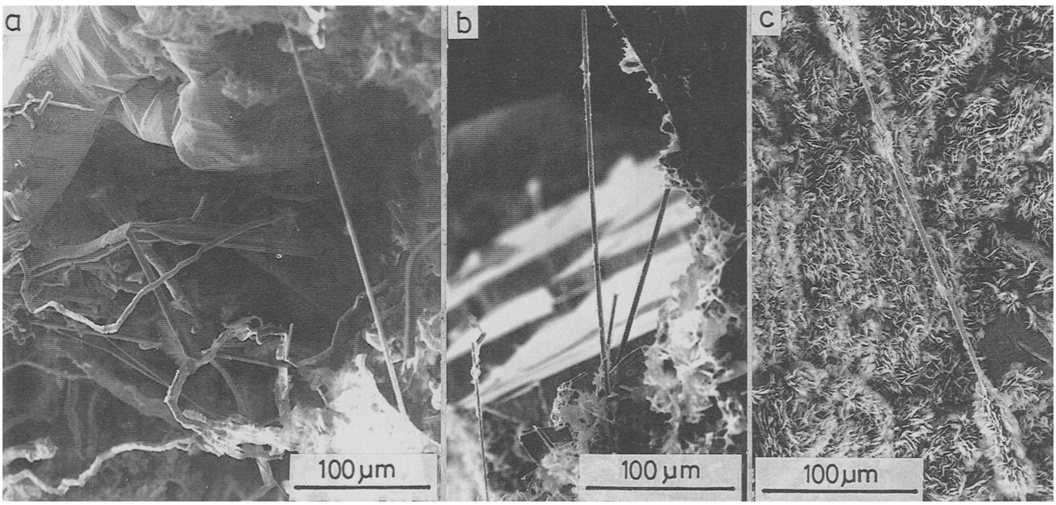


FIG. 1. Location of the galena whiskers. SEM micrographs. (*a*) Adjacent tortuous whiskers with variant growth direction and straight ones. (*b*) A group of straight whiskers. (*c*) A single straight whisker covered at both ends by thin layer of fine flaky nontronite which also covers the substrate of large-crystal galena.

Morphology and orientation

The late galena formations are characterised by complicated and varied morphology: thin and thicker straight whiskers, kinked and arched whiskers, multiple-bended elongated and irregular crystals as well as various combinations of these. According to optical microscopy and SEM studies, all are bounded by smooth or stepwise crystal faces corresponding to both main galena forms, the cube *a* {100} and the octahedron *o* {111}. The octahedral faces prevail strongly, for whiskers obtained in the Gradishte deposit, in comparison with those from the Mogilata where both *a* and *o* forms are developed to almost the same extent (Bonev, 1970), and from the Luki and Djalta where *a* predominates (Bonev, 1980; Bogdanova and Bogdanov, 1986) (Fig. 2).

The alternating uniform steps appearing along an elongated complex-shaped galena crystal shine simultaneously in reflected light, which indicates its single crystal nature. The SEM study also reveals that the corresponding steps and their edges are strictly parallel to each other. The faces

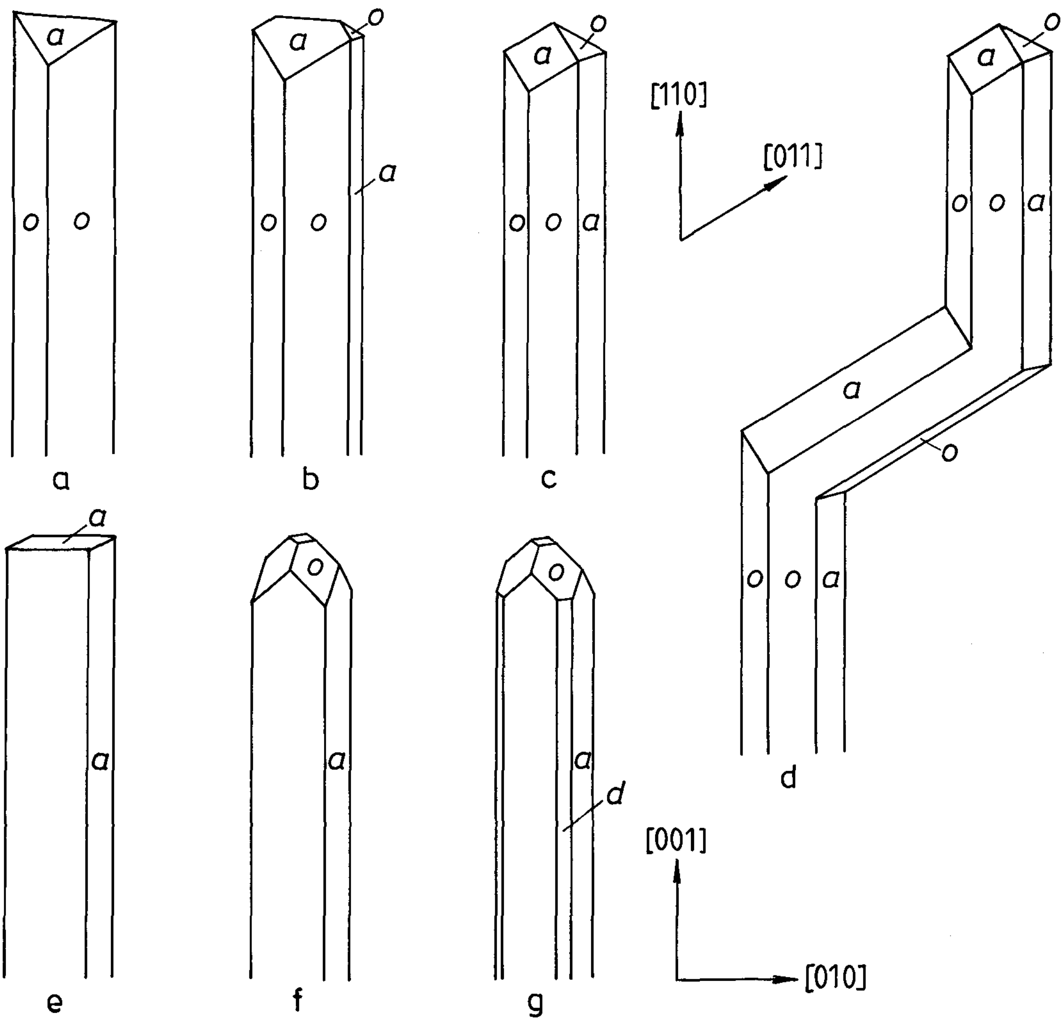


FIG. 2. Idealised morphology of the main types of galena whiskers with different habit ratio of the lateral octahedral *o* and cubic *a* faces. (*a–c*) [110] whiskers: (*a*) with only *o* faces, and (*b*) with *o*>>*a* faces (Gradishte), (*c*) with *o*≈*a* faces (Mogilata). (*d*) Kinked whisker [110]–[011]–[110] (Gradishte, Mogilata). (*e–g*) [100] whiskers: (*e* and *f*) with only *a* faces (Luki), (*g*) with *a*>>*d* {110} faces (Djalta).

are most often covered with a characteristic combined striation in the direction [110] = (111) : (100), outlining polygonal layers and vicinals of different heights. The X-ray diffraction patterns also proved that the complicated crystal formations are undeformed and untwinned single crystals.

The main types of crystals are as follows.

(1) Straight whiskers and needles. They are present either separately or in groups and often together with kinked or more complex crystals (Fig. 1*a–c*). Usually, they are elongated in the [110] direction and are bounded by four octahedral faces with or without two narrow cubic faces (Fig. 2*a,b*, 3*a,b*). Their octahedral faces are sometimes smooth, but more often exhibit a fine triangular striation outlining the growth layers. The bases of the triangles lie along the *o* : *a* edges and their apices are oriented towards the edges *o* : *o* (Figs. 3*a–c*, 6*e*). Thus, two kinds of striations are revealed on the *o* faces: longitudinal, along the whisker axis, and oblique, at angles of 60° towards it. The *o* : *o* edges of some [110] whiskers are imperfect due to the incomplete growth of the oppositely growing triangular layers towards the mutual edge, resembling a saw tooth. In other cases separate pits are found on these edges.

The cubic faces are smooth or more often lined with striations, longitudinal and transverse to the whisker axis [110], forming square and rectangular growth layers which develop from the base to the tip of the whisker and outline a corresponding stepwise profile (Fig. 4*b*).

For the [110] whiskers the direction of cubic cleavage makes an angle of 45° with their axis, which can serve as a simple criterion for estimation of the elongation.

The thin whiskers are from 2 to 10 μm wide and up to 0.5 mm long or more. The thicker straight needles reach 15–30 μm in thickness. On these the longitudinal striation is quite noticeable and is manifested on both type *o* and *a* faces. Well-outlined linear grooves faceted by the same faces are also observed on the needle surfaces (Fig. 3*d, f*).

(2) The kinked whiskers are also widespread. In this case a change in the growth axes is observed along certain crystallographic directions, for example [110]–[011] (Fig. 3*e*), which sometimes takes place repeatedly, resulting in a multiple-zigzag development of the whiskers (Figs. 2*d*, 3*g*) at a nearly constant thickness. These whiskers are also single crystals.

(3) The curvilinear whiskers with a gradually changing growth direction are also observed, often as parts of more complex elongated whisker forms (Fig. 4*a*). They are bounded not by oval surfaces but by multiple alternating cubic and octahedral stepwise portions which maintain the original single crystal orientation. These arch-bended crystals are growth forms which are not affected by deformation.

(4) Complex crooked whiskers with multiple changing directions are also widespread. These bizarrre formations, composing single crystals, are composed of straight, kinked and arched segments passing one into another. Usually the whisker axes coincide with important crystallographic directions like [110], [100], [211], or are close to them, but some stranger shapes also appear. Such is the loop-shaped needle in Fig. 3*h*.

Recently, similar tortuous whiskers of TiN (also of NaCl-type structure) with variant growth direction ([100], [110], [111]) were obtained by Guo *et al.* (1990) in a CVD process. Unfortunately, no data about their surface morphology are reported.

(5) Thicker irregularly shaped elongated crystals of galena are also common (Figs. 5, 6). These are relatively thick, from 15–30 up to more than 50 μm, with a length up to 0.5 mm. Their surface is also formed from stepwise portions and small areas of the *o* and *a* faces with numerous *o* : *a* edges and re-entrant corners. The elongation of these crystals variable, approaching in the separate segments to [110], [100] and [211]. Some crystals are branchy including slab-shaped, platy or more isometric segments (Fig. 6*a*–e). Signs of skeletal growth are seen on some coarse stepped surfaces with crystallographically faceted holes (see upper part of Fig. 5), which are potentially nuclei for generation of fluid inclusions.

The various crystal forms are closely related spatially and sometimes transform into each other. Bases of whiskers and needle-crystals serve as protruded parts of irregularly-grown more massive crystals.

Of particular interest are the whisker tips. In the case of the thin [110] whiskers, the tips are dome-shaped, formed mainly by two large oblique cubic faces, while the corresponding oblique octahedral faces are faintly developed or are missing (Figs. 2*a*, *b*, 3*a*). In many cases the tip is broadened or irregularly-shaped, which possibly delays or even stops the growth (Fig. 3*d*). Also of interest is the gradual thinning of the tip of the trunk-curved crystal shown in Fig. 6*f*. This shape together with the grooves and pits deeply engraved along the edges are probably indicative of a depletion of the feeding substance. The terminations of thicker crystal formations are well-differentiated crystal parts faceted by *o* and *a* forms (Fig. 5).

The edges of some whiskers are rounded (Fig.

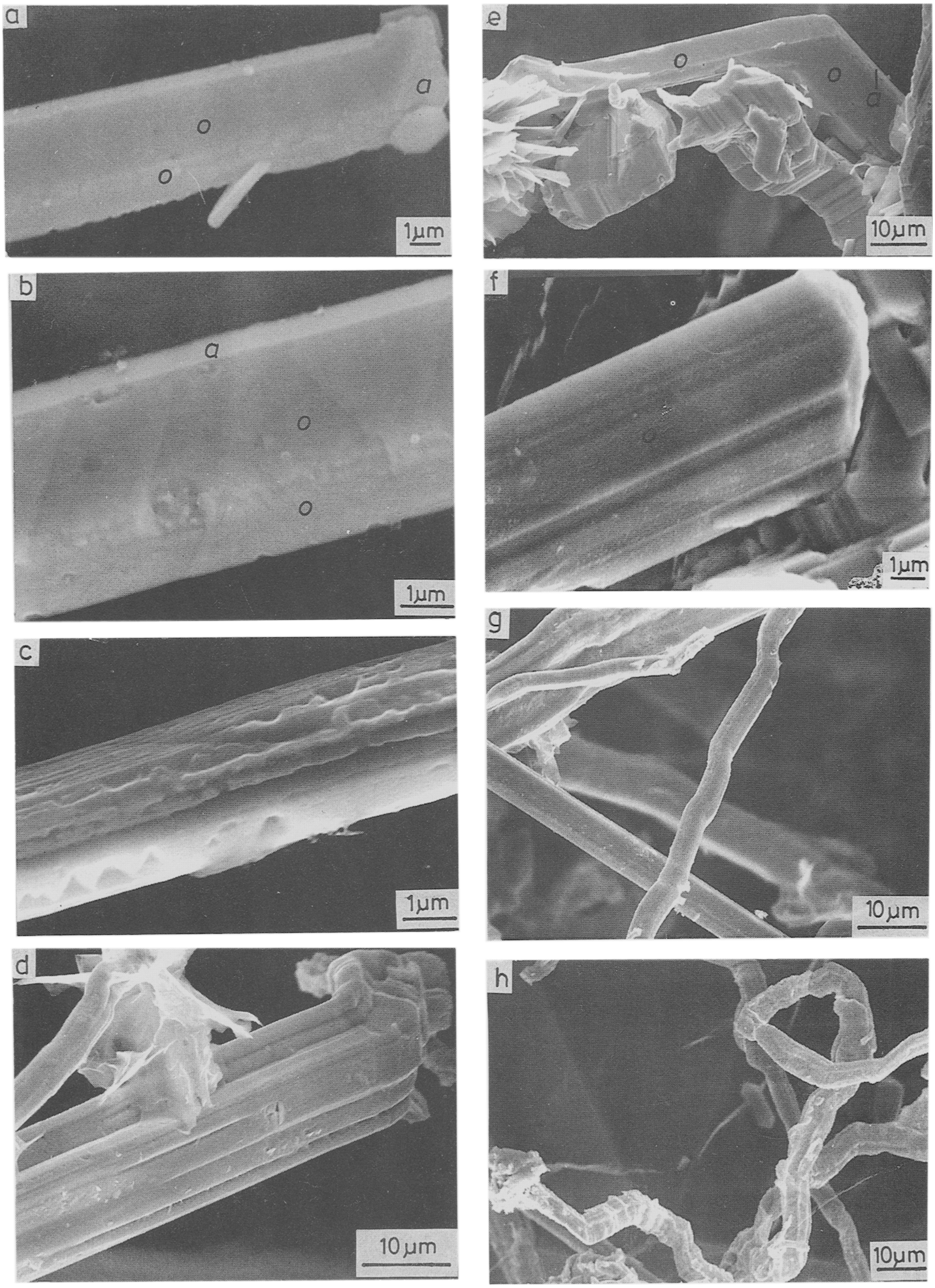
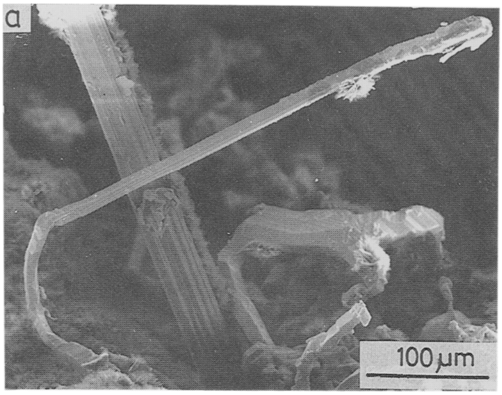


FIG. 3. Morphology of the different kinds of whiskers. SEM micrographs. (*a* and *b*) Straight [110] whisker under lower (*a*) and higher (*b*) magnification. The octahedral *o* faces show triangular surface steps and incomplete, jagged *o* : *o* edge. Cubic faces *a* prevail in the tip faceting (*a*). (*c*) A [110] whisker with logitudinal striations, triangular relief and partial edge rounding due to a dissolution process. (*d*) Longitudinally heavily striated [110] whisker with a complicated and thickened tip. (*e*) A [110]–[001] kinked whisker associated with irregular, striated galena crystals and nontronite flakes (white, on left). (*f*) A thick [110] whisker with longitudinal striations and faceted grooves. (*g*) A kinked zig-zag whisker; straight and irregular whiskers are also seen. (*h*) An irregular knot-like galena crystal.



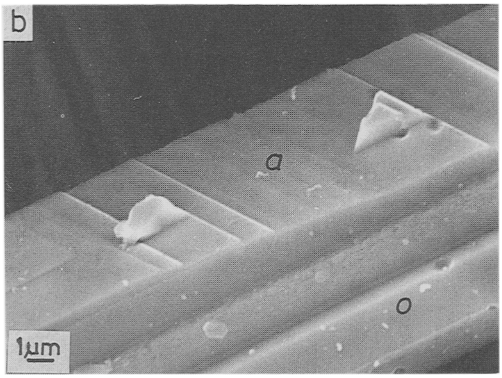


FIG. 4. (*a*) SEM micrograph of a crooked whisker composed of a curvilinear arched base (on left) and a straight [110] part ending with an irregular tip. Other irregular galena crystals are also seen. (*b*) A detail of the straight part of (*a*) with both, longitudinal and transverse steps. The parallel position of all relevant edges proves that this form is a single crystal.

3*c*). In other cases, on the octahedral faces and terraces, small pits with triangular symmetry and a size below 1 µm are also observed (Fig. 5).

Discussion

Equilibrium crystal shapes are convex polyhedra with minimum surface and surface energy, bounded by their densest, F faces (Chernov, 1983; Kern, 1987), In contrast, the unusual galena crystal described, while preserving their cubic structural symmetry, occur as irregular, strongly anisometric growth forms with a substantially enlarged surface and numerous tips with re-entrant corners. It is evident that in this case, non-equilibrium crystals formed. The prevailing development of the octahedral K faces for PbS in the absence of modifying impurities (like Bi and Ag) is an additional indication for growth at a higher supersaturation.

Conditions and mechanisms of growth. Recently, minute (<50 nm wide) [100] whiskers of PbS with right-angle kinks grown inside the nozzle of a kerosene burner were studied using TEM by Mansour and Scholz (1990). They suggested a VLS (vapour–liquid–solid) growth mechanism for those dislocation-free whiskers with Pb-rich droplets on the tips. Obviously, such a mechanism cannot be operative in the hydrothermal environment discussed here.

Originally, a screw-dislocation growth mechanism was proposed for the galena whiskers from Mogilata. However, no dislocations were really observed (Bonev, 1970). In that paper, the formation of associated irregular needle-like and dendritic galena was not discussed. Whiskers from Djalta have also been interpreted as caused by dislocation growth (Bogdanova and Bogdanov, 1986).

A similar example is filamentary cuprite–chalcotrichite. Veblen and Post (1983) have suggested that such whiskers grown through a dislocation mechanism which, supposedly, is different from the still obscure manner of growth of the coexistent platelets and skeletal crystals.

The dislocation mechanism has been considered by many authors (see e.g. Maleev, 1971) as the main factor in the growth of whiskers from solutions, although real evidence has seldom been presented.

There are reasons to suppose that whiskers as well as platelets, needle-like and crooked irregular crystals grow from supersaturated solutions under diffusional regimes (Bonev, 1990). Highly non-equilibrium conditions may occur in various ways including mixing of different solutions, abrupt changes in *P*, *T*, pH and other parameters. A striking example is the submarine mixing of high-temperature hydrothermal solutions with sea-water. Under such conditions, the formation of fine needle-like galena skeletons have been observed by Tufar *et al.* (1984) in the modern 'black smokers' of the East Pacific. Another type of sudden change in the *P–T* parameters of solutions has been performed experimentally by Trufanov *et al.* (1986) who, through an abrupt increase of the crystallisation volume, produced needle crystals and whiskers of pyrite and other minerals.

Signs of phenomena of this latter type were discovered in the course of the present study. It was found that galena whiskers and irregular forms sometimes grew over fresh cleavage surfaces of large broken crystals of early galena. After these, numerous fine flakes of nontronite were also deposited, followed by fine-grained calcite. It is probable that the brittle, rather than

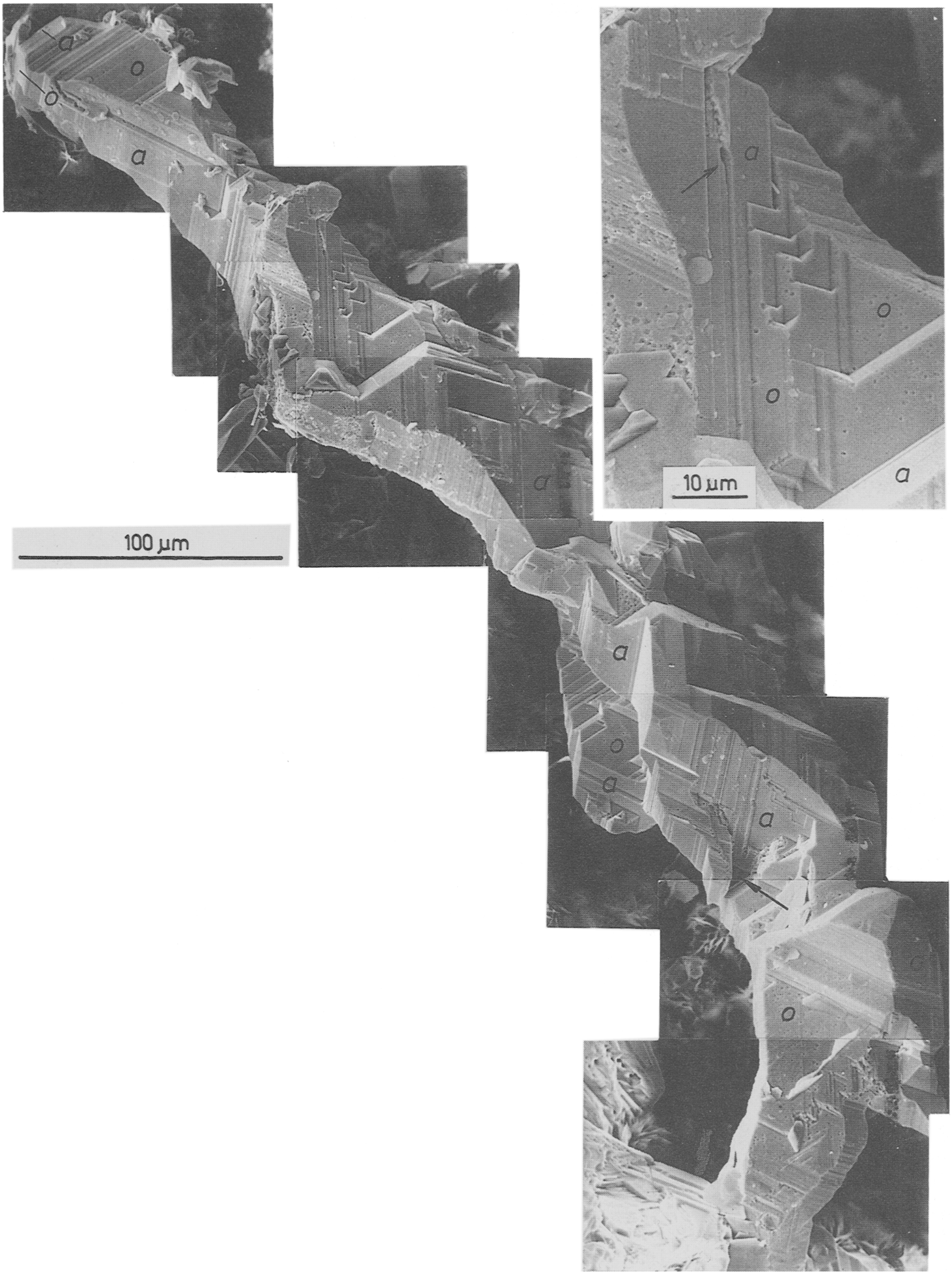


FIG. 5. An irregular, elongated, relatively thick galena crystal bounded by *o* and *a* faces with numerous edges and steps, with reentrant corners and incomplete open cavities (arrows), and with numerous minute triangular negative etch pits on the octahedral surfaces (better seen on the enlarged detail shown in the upper right corner).

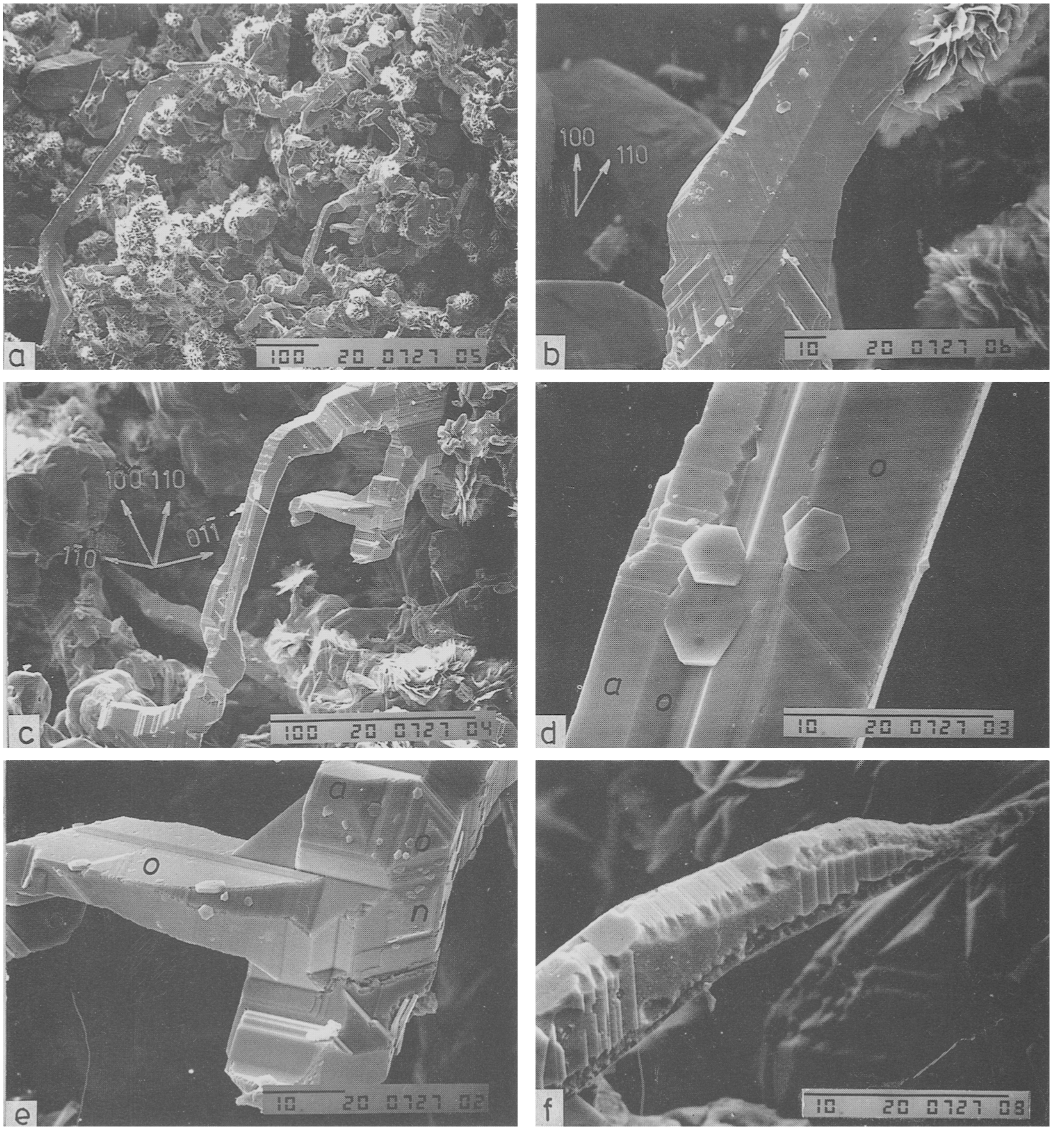


FIG. 6. (*a*) SEM micrograph of a group of irregular crystals shown in some details in (*b–f*), and associating with nests of flaky nontronite (white). (*b*) A kinked part of the left crystal from (*a*) with stepped surface. (*c*) Irregular branched galena crystal bounded mainly by alternating *o* and *a* faces, a detail from the right side of (*a*). (*d*) Enlarged detail of the central, straight [110] segment of the crystal from (*c*), showing the specific surface structure of transversal steps on *a*, triangular 60° steps on *o*, longitudinal striation and grooves between both faces with jagged profile, and small open pits. (*e*) Enlarged detail of the right-side, irregular branched part of the crystal from (*c*) with complex stepped surface formed by *a*, *o* and *n* {211} faces. (*f*) A bent trunk-form termination of a galena whisker with decreasing width, stepped surface and incomplete, uneven and concave longitudinal edges; this morphology most likely suggests diffusion controlled growth and under-nourishment. Scale—in μm.

the usual plastic deformation of galena crystals was caused by short seismotectonic shocks, immediately preceding the whisker growth. It is well known that strike-slip faults are ore-controlling structures in that deposit. The abrupt subhorizontal movements may cause local *V* increase in separate, structually-determined sections, which may produce a sudden drop of *P* and *T*, arising from high supersaturation, and an increase in the diffusional resistance of the cooled solutions. Under such conditions, the thin straight whiskers can grow without dislocations at a very high rate due to their very small cross-sections and minimum consumption of nutrient.

The needle-like, kinked curved and irregular crystals occurring in the vicinity of whiskers form in the same environment. It may be assumed that the changes in their growth directions are controlled by the environmental anisotropy, their growing tips tending to follow the richest portions of the non-uniform concentration field in the crystallisation space (possibly an effect of hydrothermal currents in the fluid). All growth directions deviating from [110], even approaching other crystallographic axes like [111] or [211], are bounded by face combinations of the two forms found (*a* and *o*, and seldom *n*), thus forming the stepped side surfaces of these unusual crystals.

The whisker growth has been observed to stop under the following circumstancs: (1) when an obstruction has been reached (Fig. 1*a*,*b*); (2) when the tip has been blocked by a thickening or some irregularly-shaped crystal formation (Figs. 3*d*, 4*a*); (3) when the feeding material has been depleted which seems to be the case with the whiskers of gradually thinning tips (Fig. 6*f*).

It is likely that the growth of whiskers in the other deposits has taken place under a similar diffusion-controlled regime. In the case of Djalta, the axial hollows observed inside some [100] whiskers may be regarded as due to a difficient supply of material to the starving centres of their rapidly growing frontal faces.

Dissolution. When discussing the physicochemical changes in an open hydrothermal vein system caused by a brief tectonic shock it could be expected that during a period of time the continued inflow of ascending solutions would bring the system back to its former state, approaching the original parameters. In such a situation the supersaturation may drop or be reduced even to undersaturation, and then dissolution of the crystals is also possible.

Some traces of dissolution phenomena were actually observed during this study. The numerous tiny triangular holes seen on the octahedral faces of some irregularly-shaped galena crystals (Fig. 5) apparently represent typical etch pits (Sangwal, 1987). In other less common cases, rounded edges of whiskers were also observed (Fig. 3*c*).

Formations of particular interest are the rare fine tubular nontronite aggregates representing pseudomorphic overgrowths of galena whiskers leached afterwards. Occasionally, they are accompanied by nontronite pseudomorphs after fine baryte platy crystals, sometimes also entirely leached. In so far as the deposition of galena and baryte presumably proceeded in the course of neutralisation of moderately acid chloride solutions, their dissolution indicates the action of acid solutions again (Holland and Malinin, 1979; Kristotakis, 1979), i.e. a backward process restoring the initial physicochemical situation.

Whiskers of other sulphides. Highly anisometric crystals of other sulphides have also been found in the Madan district, including chalcopyrite [111] whiskers (Bonev and Radulova, 1991), and pyrite [100] whiskers and thin (100) platelets (Bonev *et al.*, 1985). They have been also interpreted as grown from unstirred solutions under diffusional regime.

Crystallochemical control. By their appearance and physical properties the thin [110] galena

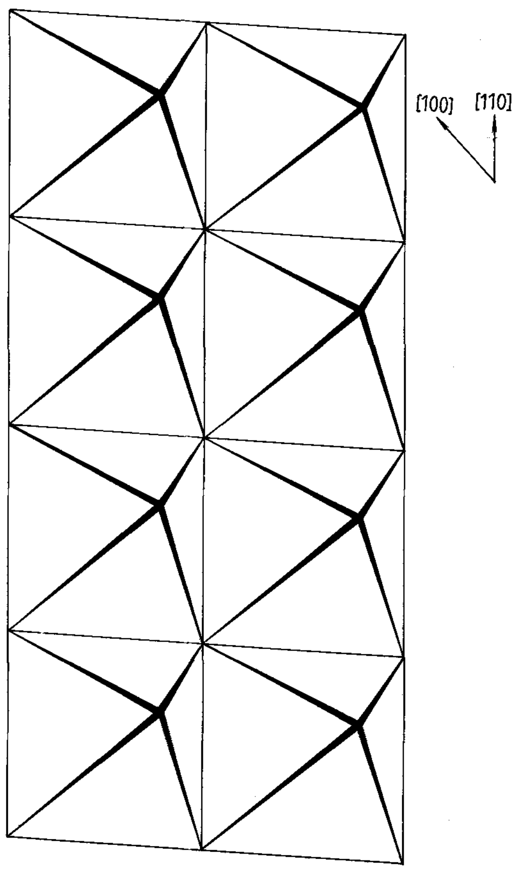


FIG. 7. A polyhedral structural model of a [110] galena whisker relevant to the longitudinal galena like building blocks in the structure of the acicular lead sulphosalt minerals.

whiskers are similar to the needle-like sulphosalt crystals of Pb–Bi and Pb–Sb composition. This similarity is not superficial but is based on some crystallochemical reasons. Indeed, the structures of these sulphosalts include (Takeuchi, 1978; Kostov and Minčeva-Stefanova, 1981; and others) 'tropochemically twinned' galena building fragments of infinite [110] chains of edge-sharing PbS_6 octahedra, extending along the main 4Å-needle axis. The [110] galena whiskers are just of the same structure (Fig. 7).

Conclusion

The thin straight, kinked, curvilinear and complex tortuous whiskers and thicker needle-like or irregular crystals of galena, closely related in space, are bounded by oscillating octahedral and cubic faces with abundant steps and other surface structures. The screw dislocation mechanism cannot be responsible for the growth of such highly anisometric and non-equilibrium crystals. It is suggested that they were formed through rapid diffusion-controlled growth from solutions in which the increased and probably non-uniform supersaturation was the result of abrupt local V, P and T changes caused by seismotectonic shocks in the hydrothermal vein ore-forming systems.

Acknowledgement

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