

# Single crystal galena pillars as highly anisometric dissolution forms

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## Abstract

Remarkable single crystal galena formations in the unique form of cylindrical or steep conical 'pillars' with 'capitals' of small rhombododecahedral single crystals of sphalerite, are described. It is suggested that the pillars result from a highly specific process of anisotropic mineral dissolution controlled by a system of internal channels in the original skeletal crystals and represent a kind of dissolution whiskers.

KEYWORDS: galena, crystal morphology, dissolution, whiskers.

## Introduction

GALENA is one of the most widespread and economically important ore minerals and shows notable morphological variety. Here, we characterize and discuss the nature of galena formations with the unique shape of oval 'pillars' with 'capitals' of small single crystals of sphalerite. It is suggested that the pillars are the result of a highly specific process of anisotropic mineral dissolution. Although completely different in size and material, they show surprising morphological similarity to the well known 'earth pillars'. As far as we know, similar extremely anisometric dissolution forms of natural minerals are not known from the literature (Givargizov, 1986; Sangwal, 1987, and personal communication, 1995). It is particularly surprising to find them in a highly symmetrical material such as hexoctahedral PbS. However, extremely anisometric crystals and whiskers of galena can arise under suitable hydrothermal conditions as non-equilibrium growth forms (Bonev, 1993).

The sample studied is a striking ore druse of skeletal galena belonging to the mineral collection of the Department of Geology and Petroleum Geology at the University of Aberdeen, Scotland. Unfortunately the source of this specimen (N 9966) is not known. A sulphur isotope study (galena  $\delta^{34}\text{S} = +0.8\text{‰}$ , sphalerite  $\delta^{34}\text{S} = +1.1$  and  $0.9\text{‰}$ ) indicates

that the most likely UK sources are base metal mineralization associated with granites in NE Scotland (late Caledonian), the Lake District and Cornwall (A.J. Boyce, pers.comm.). The sample is about 8 cm long, 6 cm wide and 4 cm thick. The galena has a dull, black lustreless surface indicating that the sample is of some antiquity. A small amount of sphalerite occurs as minute crystals together with scarce zinc sulphate as an oxidation product.

## Experimental procedures

The specimen was examined by a stereomicroscope, and small fragments of it were separated by a diamond drill for additional studies. Uncovered and gold-coated samples were examined by JEOL scanning electron microscopes (SEM) JSM T-300 and Superprobe-733. An ORTEC energy dispersive system (EDS) was used for local microanalyses, and a Gandolfi camera for X-ray characterization.

## General characteristics

Galena pillars usually occur in groups (Fig. 1) in some of the larger internal cavities of the skeletal crystals comprising the druse (Fig. 2a). The skeletal crystals, up to 7 mm along *a*, are bounded by cubic {100} faces. They have hopper-like morphology with concave, stepped faces. Mostly, their three-fold axes

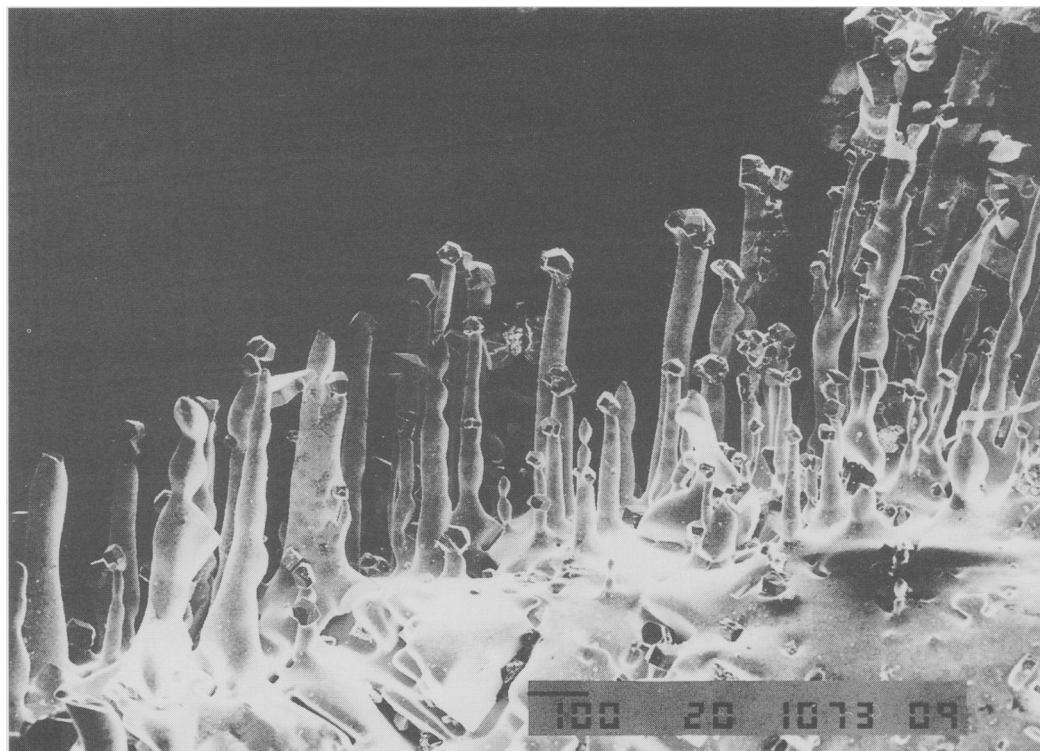


FIG. 1. A 'forest' of galena pillars on the strongly corroded rounded surface of a large galena crystal, on which small open pits and channels are also seen. The pillars have protective capitals of single sphalerite crystals. SEM microphotograph.

are perpendicular to the outer surface of the sample, and so the upper cube vertices and their frontal edges are best developed, while the back ones are reduced. The crystals have numerous elongated or rectangular voids parallel to the edges, especially well revealed in broken and cleaved surfaces (Fig. 2*b*). They have the characteristics of primary fluid inclusions in galena crystals (Bonev, 1977).

The crystals extend inside the druse transverse to its frontal face, forming a parallel-columnar aggregate. An abundance of mm wide, intergranular, channel-like voids and pores determines its high porosity.

Microprobe analyses indicate the galena is pure PbS with below detection levels of Ag, Bi and Sb.

Sphalerite is a minor but important component of the ore sample, occurring in tiny ( $\leq 0.1$  mm) well-shaped crystals with sharp edges (Fig. 6). It is transparent, colourless with a greenish tint, and has an adamantine lustre. Its crystals are perfect or slightly distorted rhombododecahedra  $\{110\}$  with small additional tetrahedral, positive  $\{111\}$ , and sometimes negative  $\{-111\}$  faces, and perfect

$\{110\}$  cleavage.  $\{111\}$  twinning is common, and re-entrant angles around the twin planes are often seen. Sometimes, the twinning is polysynthetic and  $[110]$  striation is developed. Fine growth layers originating from edges are revealed on some crystal faces under the optical microscope and SEM. Some crystals have skeletal development with depressions and holes on their faces (Fig. 6*d*). No fluid inclusions were seen.

Microprobe analyses indicate pure stoichiometric ZnS with practically no impurities (in wt.% from five analyses: Zn 66.95, S 32.93, Fe 0.03, Cu 0.18). The X-ray pattern confirms the structure and cell-dimension (5.401 Å) of pure sphalerite.

Colourless sphalerite crystals occupy the apices of galena pillars and occur at a level about one centimetre below the front druse surface, where most pillars are localized. In the deeper levels of the druse, inside the internal vugs, light brown and darker sphalerite of more irregular shape occurs. It contains Fe up to 2.0 wt.%, Mn to 1.1%, and Cd to 0.35%.

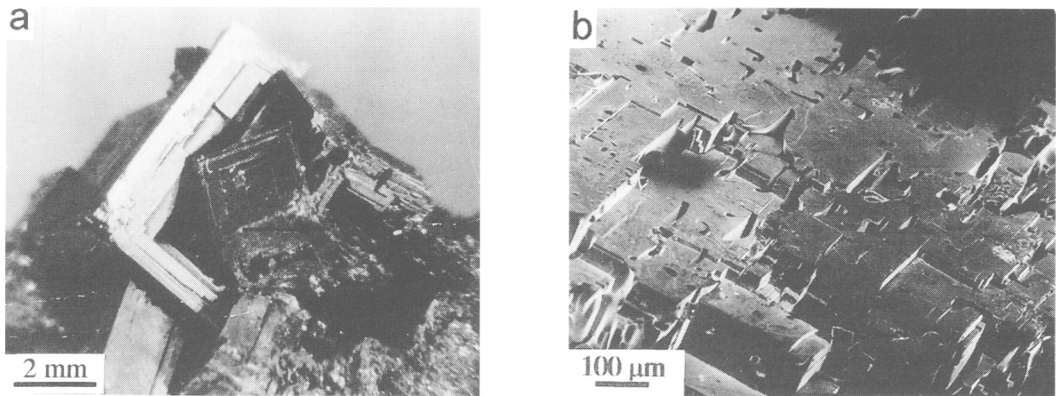


FIG. 2. Morphology of skeletal galena crystals: (a) with hopper outer morphology and internal cavities in which pillar forms have been located (arrow); (b) on a fresh cleavage surface with numerous internal open channels and inclusions.

### Morphology and orientation of pillars

The pillars usually appear in groups, 'forests', of subparallel individuals (Figs. 1,3), located on rounded or more complicated single crystal galena surfaces. The pillars have a rounded, approximately cylindrical or steep conical shape with single crystal sphalerite capitals on their apices (Fig. 3a,c). Some pillars have variable thickness with irregularly alternating, spindle-like knots and necks (Figs. 3a, 5b). No clear correlation between the thin parts of pillars from a group exists. The flat-conical bases of the pillars gradually change to the rounded surface of the substrate crystal.

Flat, terrace-like areas occur on the sides of some pillars, gradually passing to oval or cylindrical lateral surfaces through their rounded edges (Fig. 3b). Clearly these areas belong to the cubic (001) faces and are parallel to the cubic planes bounding the opened internal voids on the galena substrate. Two such opposite parallel traces give the pillar a platy shape. Pillars with rounded-off rectangular cross section are also present (Fig. 5d).

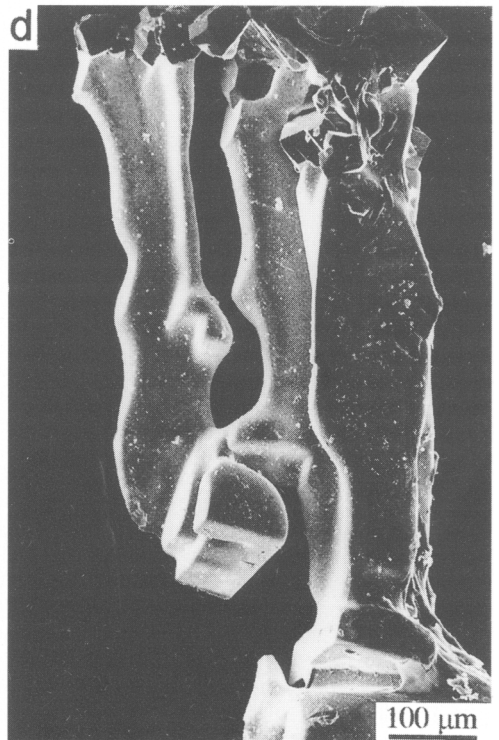
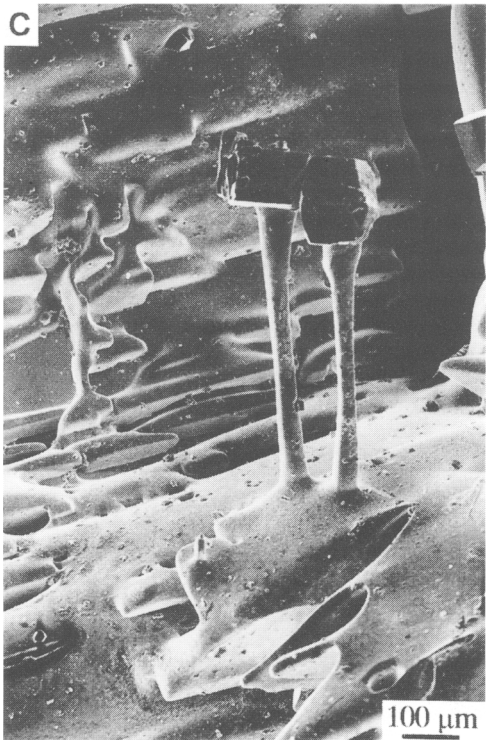
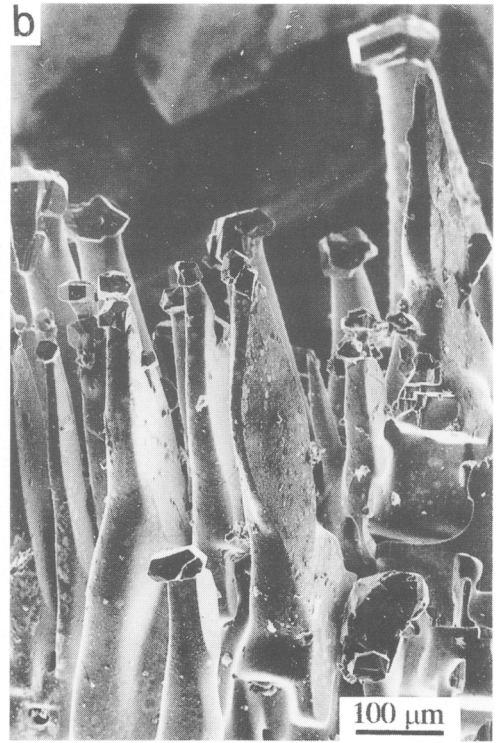
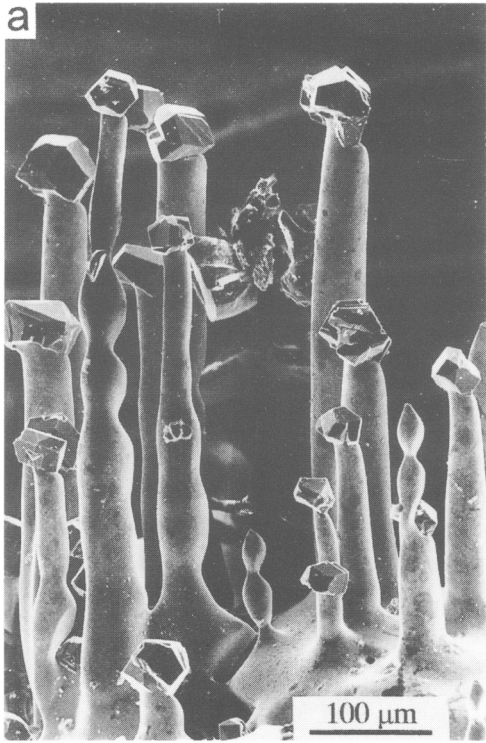
The pillars are mostly 0.4–0.6 mm long and 20–50 μm in diameter. The distances between them in a group are usually of the order of 100 μm. Isolated needles are also present (Fig. 5c,f). The pillars have similar orientation, being nearly perpendicular, or more often, inclined with respect to the rounded non-crystallographic substrate surface. In some larger groups (Fig. 1) a divergent orientation exists, with a deviation between outer pillars of up to 25–30°. Thus, the axes of the pillars do not follow distinct crystallographic directions. Nevertheless, the lattice orientation of the substrate crystal and the pillars, as remnant parts of it, is strongly preserved.

This is clearly indicated by the equal (usually oblique) orientation of the cleavage planes on some broken neighbouring pillars, as well as in the parallelism of some platy pillars mentioned above.

Some groups of pillars have similar bent axes (Fig. 5a,d). More irregular pillars also occur, e.g. with undulating axes (Fig. 5c), with steps, bifurcated (Fig. 1, centre), or of more complicated branching forms (Fig. 3d). The surfaces of pillars are oval, smooth, and without any separated etching figures like etch pits or grooves. Under high magnification they show an even submicron roughness (Fig. 4a). Some corroded surfaces consist of very small (0.2–0.3 μm) rounded, parallel, cubic or more irregular subindividuals (Fig. 4b). Following the local face symmetry, they represent triangular pyramidal kinks in the parts close to (111) and short [110]-elongated domes, when close to (110).

In their morphological characteristics the rounded galena pillars contrast with the highly anisometric needle-like crystals and whiskers formed in growth processes (Bonev, 1993). These growth forms are entirely bounded by smooth and striated crystal faces, and follow crystallographic directions determined by the existing faceting.

The sphalerite crystals on the pillars are not in a mutual parallel position and have random orientation to the galena substrate (Figs. 3, 5d, 6). The upper parts of the capping sphalerite crystals are well formed, with smooth or stepped faces and sharp edges. Their surfaces in contact with galena are rough, irregular and undeveloped (Fig. 6) indicating that their last growth stage has been accomplished on the galena surface. Some shorter pillars have no capitals and their apices are sharp (Figs. 1, 3a).



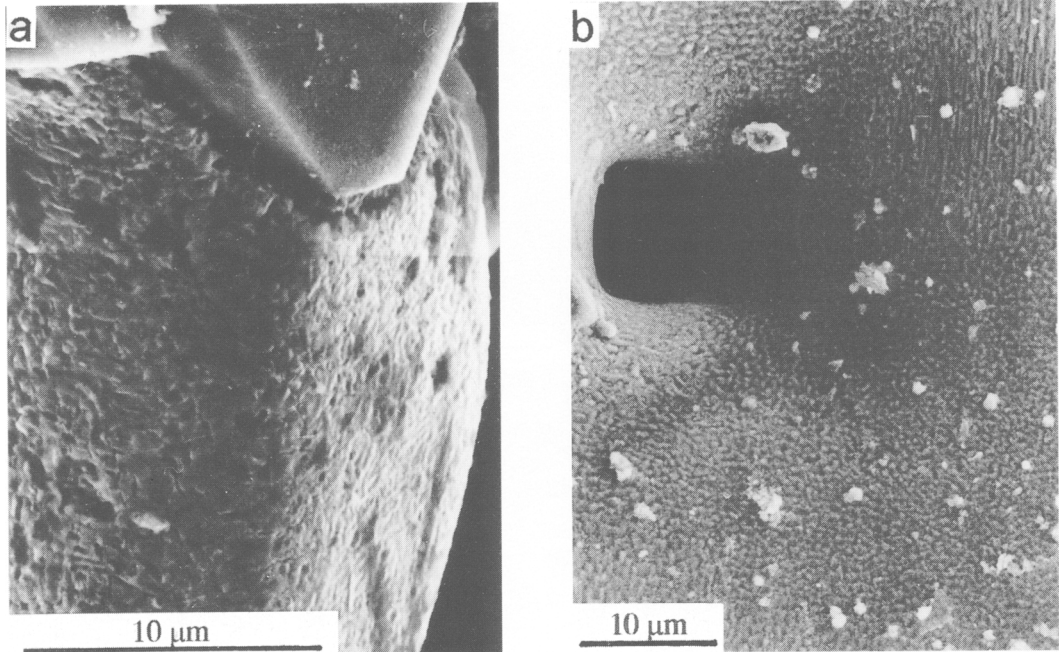


FIG. 4. The rough surface of intensely corroded galena at higher magnification. (a) the apex part of a pillar; (b) the rounded surface in the neighbourhood of an open microcavity.

### Growth and dissolution processes

The galena-sphalerite mineral assemblage and texture of the ore aggregate, together with the essential absence of oxidation minerals, suggest its formation from hydrothermal solutions by crystallization and dissolution processes in open space. The  $\delta^{34}\text{S}$  data are consistent with a magmatic origin for the sulphur and confirm the textural observation that the galena and sphalerite have a sequential relationship, calculated equilibrium temperatures are in excess of 1100°C (A.J. Boyce, pers. comm.). Though the parameters of the actual processes are not precisely known, the observations on the crystal morphology and mineral relationships permit, to a certain extent, a reconstruction of the origin of these mineral formations.

*Character of solutions.* The solubility of Pb, Zn, and other base metals in ore-forming solutions and the type of stable complexes in which they are dissolved and transported prior to precipitating in different environments, have been estimated in numerous recent experimental and thermodynamic studies and reviews (Barnes, 1979; Giordano and Barnes, 1979; Rafalsky and Masalovich, 1981; Seward, 1984; Brimhall and Crerar, 1987; Barret and Anderson, 1988; and others).

The most important complexes for lead transport in the hydrothermal environment are chloride complexes. These are stable in acidic chloride solutions at variable temperature (up to 350°C). The main factors for increasing the solubility of galena are an increase in temperature and chloride concentration, and a lowering of pH. In this case the

FIG. 3. Morphology of galena pillar crystals. (a) A group of subparallel cylindrical and spindle-shaped pillars with protective sphalerite capitals. The uniformly oriented small cavities under them, indicate anisotropic one-sided dissolution by corrosive solutions flowing from right to left. A few shorter needles without protective caps (probably fallen off) have spiked terminals. A detail of Fig. 1. (b) Subparallel pillars of partly flattened morphology, retaining parallel terrace-like flat areas. (c) Two adjacent nearly cylindrical pillars with capitals, projecting over the intensively corroded galena surface. (d) Thick irregular pillars with transitions to rectangular skeletal remnants at their bases and with a group of several sphalerite caps on the tops.

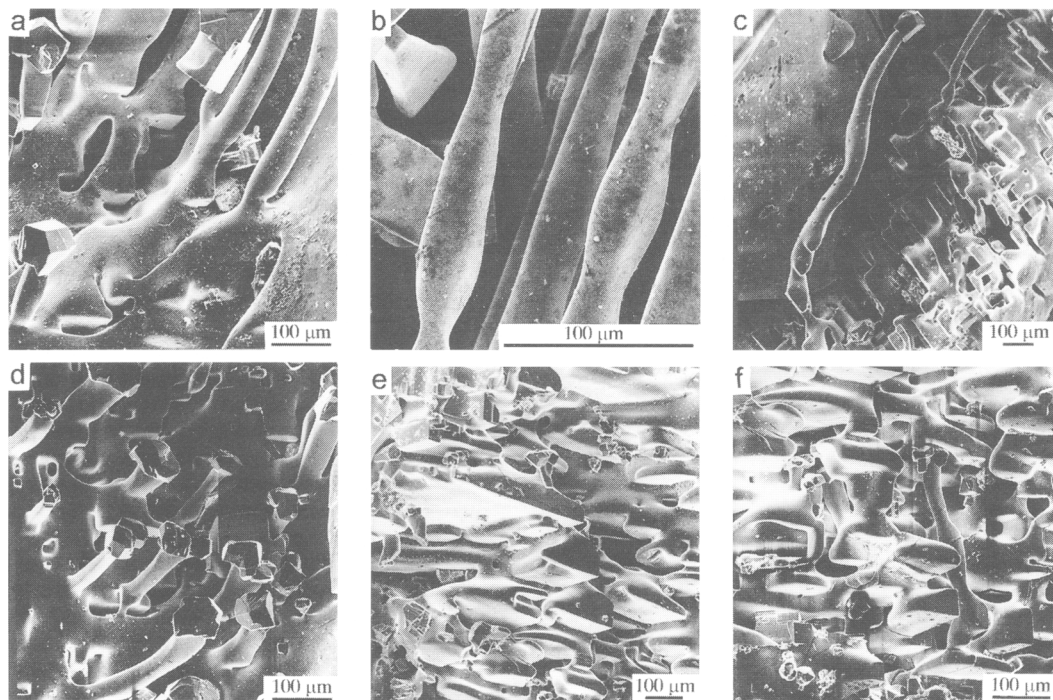


FIG. 5. (a) A rounded corroded porous skeletal galena crystal with many open channels, determining the elongation of a group of projecting arched needles. (b) The central part of the group of subparallel needles with bases partly shown in (a). (c) A single bent pillar protruding over the rounded surface of a corroded highly porous skeletal crystal. (d) A group of subparallel short bent pillars, the elongation of which is predetermined by the system of opened internal channels and pits within the primary porous skeletal crystal. (e, f) The rounded surface of a corroded skeletal crystal with opened inclusion pits and with only one detached needle-like crystal with protective cap (right part of (f)).

temperature of sulphide deposition was probably not high because the isomorphous admixtures in sphalerite and galena are low. Acidic conditions are indicated by the absence of calcite. For acidic solutions of pH 4 or lower, temperature = 160 to 260°C or higher, and total salinity of 1–3 m NaCl equiv., the solubility of PbS is estimated by various authors as 1 to 100 and more mg/kg water. As noted by Barnes (1979), dissolution of sulphide minerals after their precipitation is a common result of the easy reversibility of reactions involving metal complexing.

The hydrothermal dissolution of galena is a phenomenon known from ore deposits of different genetic types, e.g.: carbonate-hosted stratiform Pb–Zn deposits of Mississippi Valley Type (MVT) (McKnight and Fischer, 1970; Clendenin, 1977; Lasmanis, 1989); dolomite-hosted massive sulphide replacement deposits (Thompson and Arehart, 1990); vein Ag–Pb–Zn–Cu deposits (Lacy and Hosmer, 1956); vein and skarn-replacement Pb–Zn deposits

(Bonev, 1992, and unpublished data); skarn-replacement Pb–Zn deposits (Khetchikov, 1960).

Normally in hydrothermal conditions, the equilibrium solubility of ZnS is higher than that of PbS. However, in some of these deposits, corroded galena associates with unaffected sphalerite. This is possible when the solutions are partially undersaturated with respect to the PbS phase, but nearly saturated with respect to ZnS. A difference in the degree of dissolution can also arise from kinetic factors.

*Growth stage.* The main morphological features of the galena aggregate have been formed during its growth stage. The characteristic hopper-like shape is not uncommon for hydrothermal galena (Bonev, 1980), and it is believed to form through rapid, diffusion-controlled growth. The role of restricted diffusion for hopper growth is discussed by Chernov (1984) and others. Hopper crystals have been obtained in hydrothermal growth experiments for galena by Badikov and Godovikov (1966), and in a

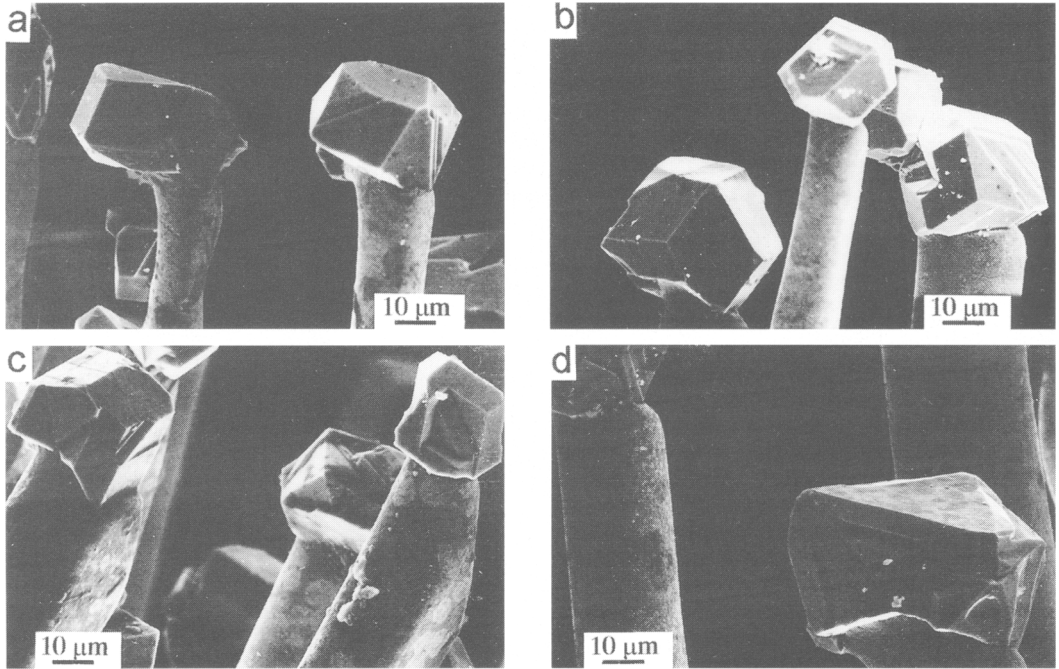


FIG. 6. Sphalerite crystal capitals on the apices of cylindrical pillars of galena. The basal faces of the crystals are uneven and reduced due to growth on the original galena surface. Small uniform cavities seen on the right sides of the pillars under the caps indicate anisotropy of dissolution in the flowing solution. Details of Fig. 1 in the same orientation. (a) Slightly distorted rhombododecahedra {110} with small triangular tetrahedral {111} faces. (b) Well formed rhombododecahedra with partly striated faces. (c) Distorted rhombododecahedra with twinning. (d) Tetrahedral-dodecahedral crystal with concave depressions on (111) and hollows near the edges of (110) due to morphological instability.

gel-diffusion experiment by Garcia-Ruiz (1986). The preferable orientation of the three-fold [111] axes perpendicular to the growth front ensures best feeding of the frontal parts and edges and fastest growth of the cubic crystals. Such conditions, controlled by competition and geometric selection between individual crystals, have been preserved during the whole crystallization process, thus creating the parallel-columnar texture of the whole aggregate (Grigoriev, 1965). The fast, directed growth also generates the high, intergranular, channel-like porosity. This highly anisotropic porosity plays an important role in the later process of dissolution.

*Dissolution stage.* The predominantly rounded faces and edges of the galena crystals are clear morphological evidence that the final state of these surfaces is accomplished by a dissolution process. Several types of corroded surfaces were seen by the SEM studies, more or less inheriting the growth features of the primary galena crystals:

(1) Oval, slightly sloping or undulating surfaces, a result of intensive corrosion of larger flat crystal faces (Figs. 1, 3c and 5a) (Here, we use the term corrosion for nonselective polishing dissolution, in contrast to etching, as a strongly selective, dislocation controlled, dissolution process). During the corrosion process many internal cavities of primary inclusions have been opened, forming numerous rectangular pits and channels, up to 20 and more  $\mu\text{m}$  wide. As seen on a fresh cleavage surface of a large crystal (Fig. 2b), such inclusions are inherent in the skeletal growth of galena crystals. These internal voids, revealed on the corroded crystal surface (Fig. 5a,d), later influence the dissolution process.

(2) Complicated, multisteped, undulating surfaces with oval edges and small open holes on them (Fig. 5c,e,f). These are the corroded, composite, stepped surfaces of the primary hopper crystals and of the irregular intergranular hollows between them. Different transitions between these two types of surfaces occur.

(3) The pillars, as the most specific corrosion forms with fully rounded sides. Appearing mostly in groups on both types of surfaces they represent highly anisotropic corrosion relics.

*Role of sphalerite 'capitals'.* The permanent presence of sphalerite capitals on galena pillars confirms their genetic link, suggesting local blocking of the galena surface during intensive dissolution. The somewhat uniform distribution of the pillars on the galena surface is determined by the initial location of the sphalerite crystals. The dissolution process is selective in that the sphalerite crystals have been preserved nearly untouched. The diameter of the pillars is clearly dependent on the size of the sphalerite crystal caps which are usually (up to twice) larger (Figs. 3, 5c–d, 6). In some pillars additional sideways-attached sphalerite crystals cause distortion and branching (Fig. 1). Rarely, shorter single galena needles with spindle-like shapes and sharp tips are present (Figs. 1, 3a). Clearly, they have lost their protective sphalerite caps by underetching and disruption of their supporting necks. The height of the pillars indicates the depth of galena corrosion — up to 500  $\mu\text{m}$ . The information about positive etch figures in the literature (Heimann, 1975; Sangwal, 1987) is very scanty and none of these figures has such high anisotropy.

*Role of crystal defects.* The rounded morphology and absence of well-defined etch pits on the corroded galena surfaces characterize dissolution processes in slightly undersaturated polishing solutions (Cabrera and Levine, 1956; Lasaga and Blum, 1986; Sangwal, 1987). The preferable sites for dissolution in such conditions are the edges and corners of the crystal, where the dislocation network is inactive. Normally, etch pits appear when fluid undersaturation is larger than a critical value. With advancing corrosion, the system of internal voids and channels available in the skeletal crystals is revealed, so new operating active sites evolve. The influence of the internal openings on dissolution is seen in Fig. 4b, and also in Fig. 5a,d, where the subparallel bent pillars follow the position of the opened oblique channels. The flattened conical shape (Fig. 3b) and some other irregularities, such as the steps on the side surfaces of the pillars, are also inherited from the adjacent cavities. Since in a skeletal crystal the internal inclusion cavities are slightly divergent, the corrosion pillars display a similar orientation, which to some extent follows the anisotropic macrodefects of the primary galena crystal (Figs 1 & 7).

*Mass transfer.* Mass transfer plays an essential role in growth and dissolution processes in aqueous solutions and the diffusion boundary layer around the crystal is the area where the process actually happens. The thickness of this layer, as directly measured by interferometric studies (Sunagawa, 1993, 1994), increases in slowly flowing and stagnant

solutions and reaches a few hundred micrometres (e.g. 200 to 400  $\mu\text{m}$ ). We note that this is approximately the height of the pillars.

A remarkable feature of the skeletal galena crystals is that some of the outermost projecting parts (e.g. Fig. 2a), remain sharp and unaffected by corrosion rounding, in contrast to all other internal crystal parts. One possible explanation is that these external parts were not immersed in the etchant solution. Such a situation is possible if the druse cavity is only partly filled by aqueous solutions during the dissolution process. The presence of sulphide stalactites (e.g. in MVT deposits) is evidence that similar isolated cavities in hydrothermal ore deposits, partially gas and fluid filled, may locally exist in specific, and still disputed, geometric and geologic conditions (McKnight and Fischer, 1970; Motyka and Suwarzynsky, 1989; Cowdry, 1995).

Thus, we propose that during dissolution the druse cavity was incompletely filled and the fluid gradually drained from the system of internal pores and channels in the galena aggregates. The corrosion process occurs only in the water layer covering the crystal surface, i.e. on the crystal-solution interface and not on the inactive crystal-gas boundary of the protruding crystal parts.

Sphalerite and especially galena are amongst the most hydrophobic sulphides. As the dissolution process advances it is possible that the highest parts of the pillars protrude from the solution layer, rapidly dry off and so are preserved from additional corrosion (Fig. 7). Drying should be most effective on the convex lateral surfaces because of their greater curvature.

The flow direction of the corroding solutions is indicated by the small, uniformly oriented, one-sided dissolution depressions on the tips of pillars, just under the protective caps (Figs. 3a and 6).

It is known from experimental studies that equilibrium between hydrothermal solutions and solid galena is reached in a very short time (Giordano and Barnes, 1979). Thus, the fresh undersaturated fluids initially acting as etchant solutions and producing etch pits rapidly transform to slightly undersaturated and nearly saturated polishing solutions, which form the characteristic oval final surfaces of the corroded crystals. The dissolved galena is carried out of the system and no re-growth phenomena are observed.

As an approximation we will assume a moderate solubility of 20 mg/kg PbS in the solution, a single pass system and a time of 9 hours for reaching equilibrium, i.e. for its saturation with a PbS phase (this is 1.5 times longer than the 6 hours accepted by Anderson, 1962, and Giordano and Barnes, 1979, in relation to bulk crystal rather than powder). In reality multiple episodes of dissolution are likely. So, for leaching of 1 mm<sup>3</sup> of solid PbS (density 7.57 g/cm<sup>3</sup>)



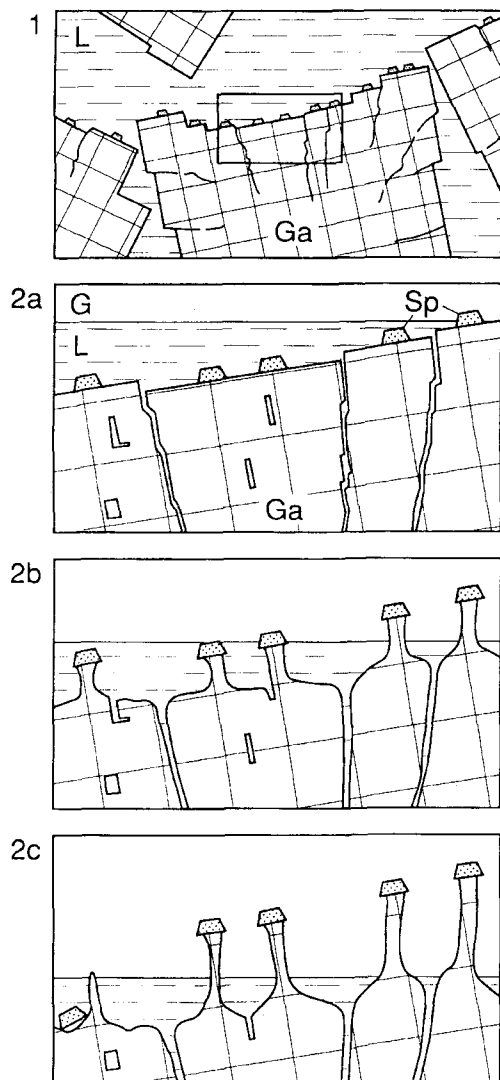


FIG. 7. Model showing the skeletal growth stage (1) of primary galena (Ga), and the successive stages (2a-c enlarged central part of 1) of later dissolution and formation of galena pillars under the protecting spherulite caps (Sp). L and G - assumed liquid and gas filling of the voids.

it is necessary to use 378.5 ml ( $\sim \text{mm}^3$ ) of fresh fluid up to its saturation, which means that an active fluid layer of 200  $\mu\text{m}$  thickness ( $\sim \frac{1}{2}$  of 378.5  $\mu\text{m}$ ) will dissolve 0.5  $\mu\text{m}$  galena in that time. If the solution is inflowing continuously at a relatively slow rate of 1 cm/hour, for 9 hours, it will pass the full length of the specimen and leave the area of reaction nearly

saturated, giving way to fresh portions of fluid. It would take 1000 times longer (one year) to leach a 500  $\mu\text{m}$  thick galena layer. This estimation agrees with the statement of Sunagawa (1993) that crystal dissolution is a fast process, much faster than crystal growth.

### Other pillar structures

It is interesting to note that in nature and in technology similar forms, though involving completely different substances, sizes and occurrences, are known, e.g.:

(1) *Earth pillars* formed by erosion of soft, unsorted sand sediments with protection of columns (10 and more metres high) by overlying stones.

(2) *Ice pillars* and *ice mushrooms*, also with protective cap-stones on their tips, formed by thawing and sublimation of glaciers.

(3) *Pillar* and *cone* textures of micrometer size arising by ion bombardment of metal surfaces with protection of their tips by inert particles (e.g. Pb with Mo, Givargizov, 1986).

In these three cases the processes of surface erosion are partly hindered by inert particles, so the creation of the forms is similar in principle to that of the galena pillars.

### Dissolution whiskers

In terms of their size (diameter 20–30  $\mu\text{m}$ ) and the specific, highly anisotropic, elongated forms the linear galena pillars discussed here resemble whisker crystals. But, in contrast to the whiskers formed by growth processes, they can be considered as *dissolution whiskers*. Such crystal formations have not previously been recorded (Givargizov, 1986).

### Conclusions

The rounded galena 'pillars' with protective spherulite 'capitals' are peculiar single crystal formations. They are a result of highly anisotropic and selective dissolution of skeletal galena crystals, partly blocked by small spherulite crystals, and strongly controlled and directed by the system of pores and channels inside the primary galena crystal. It is suggested that the process is achieved by a limited amount of undersaturated active solution, draining the system of internal pores of the sample. A galena pillar is a kind of hitherto unrecorded dissolution whisker.

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