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A STUDY OF DISTORTED PYRITE CRYSTALS FROM SPAIN

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ABSTRACT

In Fuente Valoria, Province of Soria, Spain, medium-sized crystals of pyrite with a pronounced distorted cubic habit occur in calcareous rocks that are mined for ornamental use. The variations of the angles between the cubic faces have been measured. A qualitative spectrographic analysis, as well as an x-ray study by single-crystal and powder methods, have been carried out. A study of the faces of these crystals has been made by means of a reflecting microscope. From the data obtained it is deduced that the deformation of these crystals was due to irregularities in their growth.

INTRODUCTION

On the border between the provinces of Soria and Logroño there are, in a zone of about 30 km by 10 km, four localities in which perfectly crystallized pyrites occur in the calcareous rocks of the Wealden beds. The pyrite crystals exhibit cubic habit in Fuente Valoria, Villerijo and Valdenegrillos (Soria), and have less well-developed pyritohedral and cubic habit in Muro de Aguas (Logroño). Only in Fuente Valoria are the deformed crystals found.

The Wealden, in this region discordant with the Lias, has a thickness of 800 m and is formed by alternating layers of limestones and clay-marl. The pyrites appear only in some layers of the limestones, and never in the clay-marl. Cuttings were observed in which the limestone layers abounded in pyrite cubes whose edges ranged from 1 cm to 25 cm in length.

In Valdenegrillos, the blackish limonitized pyrite cubes, called "negrillos" in this region, are surrounded by twinned (swallow-tail) gypsum crystals that reach a size of 20 cm. These gypsum crystals are produced by the reaction of sulfuric acid, released in the process of the limonitization of the pyrite, with the calcium carbonate of the limestones.

In a preliminary, unpublished study of the deformed pyrite cubes of Fuente Valoria (José F. de Villalta), it was indicated that the distortion of these crystals seemed to result from homogeneous deformations attributable to external pressures. This particularity aroused our interest.

MAGNITUDE AND REGULARITY OF THE DEFORMATION

A group of 250 was chosen from among the thousand or so distorted crystals that were placed at our disposal by the mining company. From this group a second selection was made, eliminating those crystals whose face irregularities did not permit measurements to be made with sufficient accuracy.

The dihedral angles of the 200 selected crystals were measured with a contact goniometer. Although the goniometer could be read to 0.1°, the accuracy of the measurements was estimated to be $\pm 0.5°$. Forty-three of the crystals were found to be completely regular and were eliminated from further consideration. Only the remaining 157 were used for calculations.

A distribution curve (Fig. 1) was plotted by grouping the values at intervals of 1 degree, so that those measurements falling between 89.6° and 90.5° were plotted at the value 90°. The average value of all values less than 90° (between 81° and 89°) is 87°, and the average of all values over 90° (between 91° and 107°) is 93°. The overall average value is 91°. These results immediately caused us to doubt that a question of homogeneous deformation was involved.

X-RAY AND SPECTROGRAPHIC STUDY

X-ray Laue diagrams were obtained from different parts of various crystals. None of them showed the spot deformation typical of a crystal lattice distorted by pressure. In addition to the characteristic diffraction lines of pyrite, the x-ray powder diagrams of these pyrites revealed some very weak lines attributable to calcite. This calcite is found as an inclusion in the distorted pyrite crystals.

For the spectrographic analysis, specimens were chosen that were representative of all types of crystals occurring in the pyrite deposits of Fuente Valoria. Only those portions of the pyrite were analyzed that were found, by microscopic observation, to be free of any inclusions. A carbon arc using direct current, graphite electrodes, and a Hilger spectrograph were employed. The film used was Mafe positive, sensitive only to the ultra-violet region of the spectrum.

Al, Si, Mg and Ag were present as minor elements in all of the crystals. Ti was present in a quantity that permits us to say that the pyrites from Fuente Valoria are "titaniferous pyrites." The samples from the other deposits of this region do not contain as large a quantity of Ti.

Microscopic Study of the Crystal Faces

The deformation of the pyrites of Fuente Valoria may be due to phenomena occurring during the growth of these crystals. Should this be so, the microscopic observation of the irregularities existing on the faces, as well as of the lines and surfaces of growth, which give us information about the conditions of crystallization, will clear up the problem.

A series of crystals with faces of varying nature were chosen for this study. They were all treated with H_2O_2 and washed with water acidulated with HCl and alcohol to bring out the features of the faces and remove the impurities contained thereon.

The microscopic examinations were carried out with a Zeiss photomicroscope fitted out with reflected-light and dark-field equipment. The photomicrographs (24×35 mm) were taken on a 13° DIN Adler film, and the exposure times were estimated automatically. The photomicrographs were enlarged to the size 90×120 mm on glossy paper of high contrast.

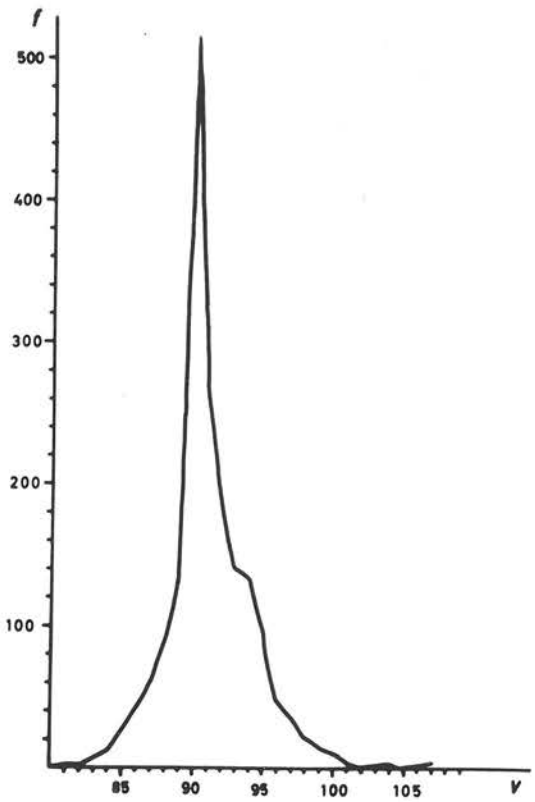

FIG. 1. The distribution curve of the deformation (frequency of occurrence, f, *vs.* angle between cube faces, v.)

FIG. 2. General view of the crystal face of a pyrite from Fuente Valoria. The growth steps are of irregular outline; however, they follow two general directions corresponding to the cubic faces (100) and pyritohedral faces (320). ×75.

On studying the surfaces of these crystals we can distinguish: a) growth features, and b) dislocations.

Growth features. A general view of the cubic faces is shown in Figs. 2 and 3. In these low-magnification photomicrographs it is observed that the crystalline surfaces are formed by blocks limited by real cracks. In each of these blocks the growth steps are of a different form, a fact which accentuates the differences of the various blocks. The faces of these crystals are of

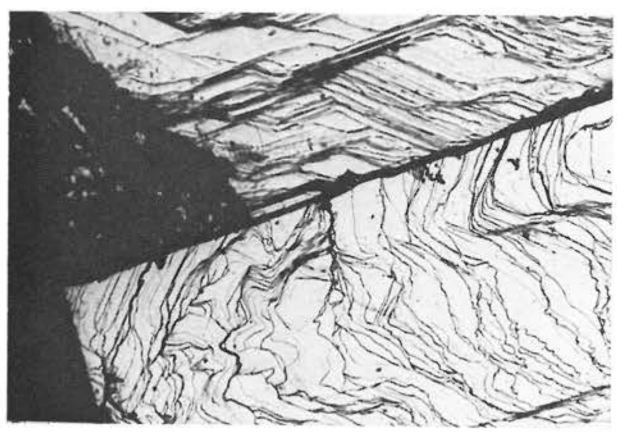

FIG. 3. General view of crystal face exhibiting two blocks outlined by surfaces closely parallel to the cubic faces (100). The growth steps in the two blocks are of different types. On the upper block the steps are straight and regular and are parallel to the (100) and (320) faces. On the lower block the steps are of warped and irregular outline but tend to develop into (100) and (320) faces. The blocks are separated by a split in the crystal faces. ×75.

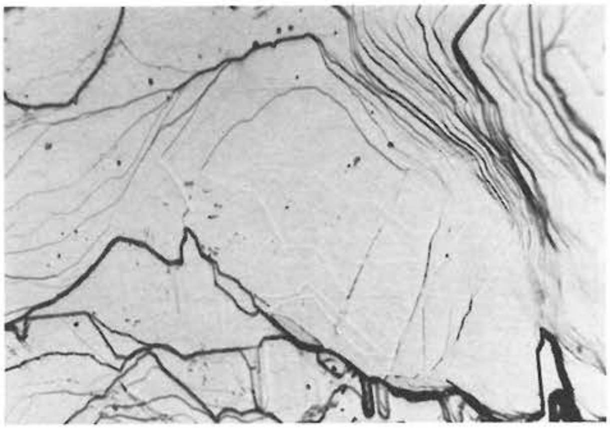

FIG. 4. Details of growth steps showing triangular disposition of the primary steps and dislocation lines. ×480.

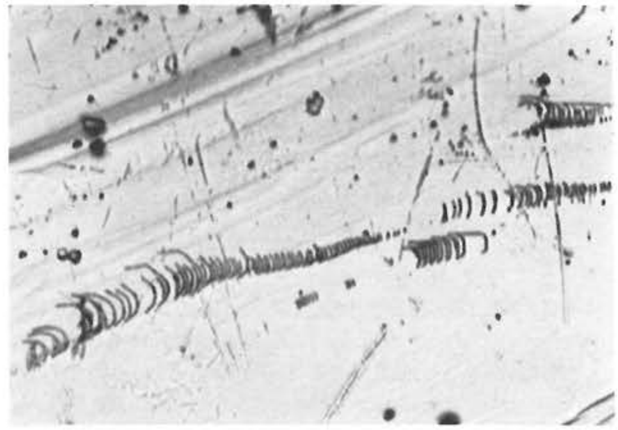

FIG. 6. Lineal series of dislocations lying nearly parallel to the (320) faces. ×750.

mosaic type due to the "lineage structure" type growth as described by Buerger.

These differences in the blocks of the crystalline faces are increased in the case of the pyrites of Fuente Valoria through the existence of abundant inclusions of $CaCO_3$ in the interior of the crystal. The inclusions of $CaCO_3$ are located in the small cracks and force the crystal to grow with exaggerated distortion. The final result is complete deformation of the crystal.

In some blocks the growth steps are of irregular form, although they tend to develop in the direction of the (100) and (320) faces. In others, the steps are straight and develop parallel to the above-mentioned faces. Figures 4 and 5 show the growth steps with a higher magnification. In Fig. 4 it is possible to observe the triangular disposition of the primary steps and also some dislocation bands, which are independent of the growth of the crystal and cut the growth steps (Fig. 5).

Dislocations. Two kinds of dislocation were observed: one kind independent of the lines of growth, and the other closely related to them. The former are disposed in a linear series lying almost parallel to the (320) faces. Figure 6 shows these dislocations highly magnified, and in Fig. 5 bands of the same kind of dislocation can be observed cutting the growth steps without mutual interference. Figures 7 and 8 illustrate the type of dislocation closely related to the growth lines. The dislocations are on one side of the step and can be perpendicular to and develop along it as in Fig. 7, or they can be parallel to the step and develop perpendicular to it as in Fig. 8. Figure 9 shows a series of dislocations starting from the edge of a crystalline block. A growth step arises from them, and another one is being formed.

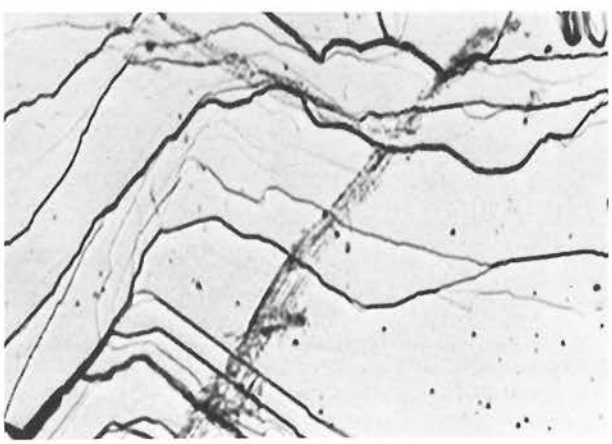

FIG. 5. Dislocation bands cutting growth steps. ×750.

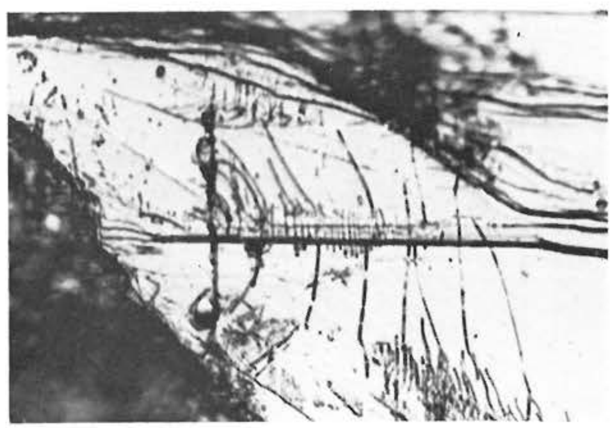

FIG. 7. Dislocations lying parallel to a growth step. Note that the dislocations are on only one side of the step—the side which is growing. ×750, with green interferential filter.

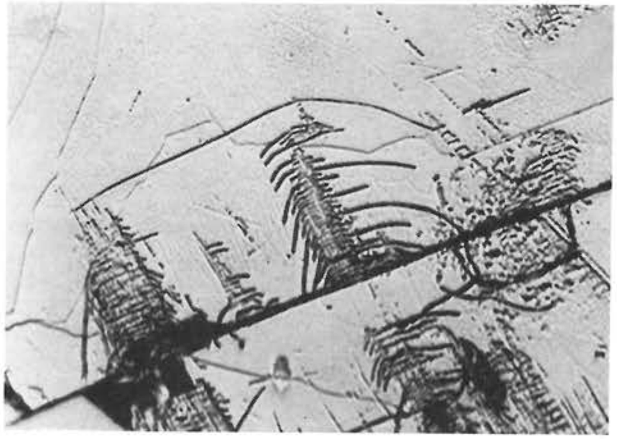

FIG. 8. Series of dislocations lying perpendicular to a growth step and parallel to the direction of the step. ×1200, with green interferential filter.

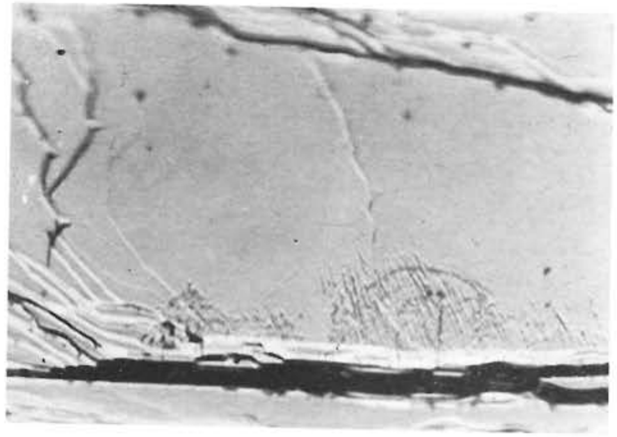

FIG. 9. Dislocations starting from the edge of a crystalline block. Note the growth step which arises from them, and another that is in process of formation. ×1200, with green interferential filter.

CONCLUSIONS

The morphological, x-ray and microscopic study of the pyrites of Fuente Valoria does not support the idea that the crystals are distorted as a result of homogeneous deformation attributable to external pressures. From the observation of nearly three thousand specimens carried out at the deposit, and from the study of a series of crystals chosen in such a way that the greatest number of different types would be found amongst them, we have deduced that the deformation of these crystals was due to irregularities in their growth, chiefly produced by the abundant inclusions of $CaCO_3$.

On studying the local geological conditions of the deposits where the distorted pyrite cubes occur we did not observe in the limestone layers any signs of pressure great enough to produce the deformation found in the crystals. The microscopic examination of the crystal faces indicated that these crystals grew from a liquid phase. This agrees entirely with their sedimentary origin. As the Wealden is of continental facies (in Spain it presents the typical facies of Numancia), it can be supposed that these pyrites formed under reducing conditions during lacustrian deposition. This explains why the pyrites appear only in certain layers while in others there is no trace of them.

The conditions producing the simultaneous formation of pyrite and calcite that existed when the limestone layers of the Fuente Valoria deposits were formed determined the deformed cubic habit of the pyrites and explain the existence of abundant calcareous inclusions in these crystals.

ACKNOWLEDGMENTS

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REFERENCES

AMORÓS, J. L., M. A. BRANDOLY AND PEREZ PEÑASCO M. (1955) *Publ. Dept. Crist. Min.* **2**, 89.

A.S.T.M. *X*-ray powder data file, 6-0710 and 5-0586.

DANA'S SYSTEM OF MINERALOGY (1946). Elements, sulfides, sulfosalts and oxides. I, 282.

FRONDEL, C. (1936) *Am. Mus. Nat. Hist.* Nov. **829**.

INST. GEOL. MIN. ESPAÑA, *Hojas y memorias explicativas del Mapa Geológico.*

LÓPEZ DE AZCONA, J. M. (1961) *Notas Com. Inst. Geol. Min. Expaña*, **63**, 119.

SHANNON, F. (1922) *U. S. Natl. Mus. Proc.* **62**, 9.

VILLALTA, J. F. DE (1961) Private communication.