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# Accessories on Pyrite, Pyrite Zoning, and Zoned Pyrite

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With 6 figures in the text

## Historical note

Crystallo-graphy in its original and etymologically correct sense was, until recently, a science which emphasized the *description* of forms or geometric patterns, exterior, megascopic, microscopic, morphological and since 1912 atomic.

Mineralogy and especially crystallography have been, and are still going through a "renaissance", as WENK stated (1962, p. 151). But this renaissance consists of two different parallel and often happily connected developments: 1) the application of more modern methods of physics, chemistry, and physical-chemistry, and 2) the introduction of a more nomothetic trend, i. e., the introduction of more causalistic analytical thinking.

This development in the mineralogical sciences is not unique. M. HARTMANN called the attention to a similar development in biology (1953, p. 3f.):

„Die nomothetische Forschungsrichtung hat sich aber in neuerer Zeit auch auf dem Gebiete der Biologie ausgedehnt, die früher ausschliesslich die Domäne der idiographisch-systematischen wissenschaftlichen Betätigung bildeten, die Morphologie, die Form und den Formwechsel. Durch planmässige Anwendung der kausal-analytischen Forschung und der experimentellen Methoden auf die Probleme der Form und des Formwechsels wurden nun auch diese Gebiete vom kausalen Denken erfasst. Die biologischen Wissenschaften gehen nun nicht nur darauf aus, die reiche Formenmannigfaltigkeit der Lebewesen und ihrer Teile durch vergleichende Beobachtung in Ordnungssysteme einzugliedern, sondern sie sind auch mit Erfolg bemüht, die kausalen Gesetzmässigkeiten, die die Formen und den Formenwechsel bedingen, zu ermitteln.“

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Perhaps another renaissance is also percolating into common knowledge, although rather slowly, despite the fact that other fields of science have, a generation ago, incorporated this knowledge into their basic principles: The fact that scientific theories originate in, and consist of subconscious patterns. They are therefore subject to the same rules of "normality" or of "disturbances" as are all other domains of human life (behaviour, fine arts, music, etc.).

### Previous work

The present paper is in essence a progress report on an attempt to make use of some morphological details for the understanding of the process of formation of ore deposits and for future exploration. It may afford at the same time a good example for the fact that, today, there is hardly a difference anymore between "the practical" and "the academic" or "theoretical". There is probably hardly any good theoretical work going on which is not already or which may not at one time be of great practical value. And almost all "practical" work bears aspects of interest to a scientific approach. Close cooperation between "applied fields" and "theoretical fields" can, therefore, be only of benefit.

There is little previous work to be mentioned. The only compound which is known quite well with regard to the relationships between the crystal habits and the natural parameters such as  $t$ ,  $p$ , etc. is ice or snow. There is even an international agreement on the terminology on snow flake morphology. The only other minerals of which the crystal habits have been studied in fair detail in relation with natural factors are calcite, cassiterite, fluorite, barite, celestite, and to a certain extent hematite. Recently a Russian paper by SHER and DEMCHENKO (1962) reported a similar application of morphological details to exploration as the one summarized here. The crystal habits of pyrite (skeletal crystals, cubes with concave, normal, and convex faces, cubo-octahedra, pyritohedra, and pseudo-habits) were compared with the different pyrite generations and the relations with the gold mineralisations. The gold appears to be associated with the pyritohedral pyrite.

Another Russian paper by ABDULLAEV (1957) reports a study of pyrite "in order to discover the relationship between the morphology of pyrite crystals and the conditions of their formation" in twenty localities in Azerbaijan. In this last paper only some "new simple forms of pyrite" were reported but no habit-habitat relationships.

### Present study

The present work was started in 1952, when the author was checking and mapping stopes and drifts of the vein-type Cu-Pb-Zn-Ag deposit of Morococha, Peru. The observation was made that the habits of the pyrite showed certain conspicuous changes from one ore zone to another, or one vein to another. The question to which no answer or even reference in the literature could be found, was, whether there was any meaning in the distribution of the different types of pyrite. Obviously, some single factor or probably some set of factors was controlling the habit changes. But it had to be simple enough to be easily recognizable, to be of any practical use in exploration.

The systematic study of some 750 grains from different ore bodies and from drill holes showed that there was some sort of "law" to the distribution. But quite obviously the study would have required more data and perhaps even some computer work. The main obstacle to a simple scheme was probably twofold, the complexity of the mineralisation and the presence of some telescoping and of more than one separate generation and type of mineralisation.

After the stay in Morococha, the author was transferred to Southern Peru and put in charge of the geological exploration work at the porphyry copper deposit of Cuajone. Here, the mineralisation was simple and no evidence for telescoping was found. Accordingly, the pyrite pattern was simple and showed a distinct shift from pyritohedra to cubes, essentially where higher copper values and a certain type of alteration was encountered. Details on the distribution patterns in these and other mines must be saved for a later more extensive report.

A large number of pyrites were recorded between 1952 and 1962 from common rocks of many geological ages and from many parts of the world and certain statistical regularities were observed for pyrite habits in certain rock types. The results of this study will also be reported at a different occasion.

Only a few examples will be quoted here, and the statistical data saved for later.

Over 90% of all pyrite crystals found in sediments and in metamorphic rocks are almost pure cubes. The Carrara marble with its perfect pyritohedra is an exception.

In igneous rocks, hydrothermal and other higher temperature deposits, pyrite exhibits a much larger variety of forms than in sediments and metamorphic rocks.

In the contact metamorphic deposit of Antamina in Peru, the habit changes from pyritohedra in the monzonite to cubes in the granite and back to pyritohedra in the surrounding limestone.

In the present report one special detail will be discussed. This detail had become the crucial key of any work on mineral zoning on the basis of pyrite habits, as early as in 1952 in Morococha.

### **Vicinals and vicinaloids — the key to face symmetry**

Many of the pyrite grains available in the mine samples and most of those from diamond drill cores and from churn drill cuttings consisted of crystal fragments. The pyrite habit zoning method required a knowledge of the predominating habit. Without the presence of fairly complete crystals the habit could not have been determined and most of the fragments would have been lost, if a special method for the determination of the "face symmetry" would not have been found.

This method which was started in Morococha, made use of the vicinals and vicinaloids on the faces, which reveal the symmetry of the faces and therefore of the form.

Since, in Morococha, the papers of WACKER (1933) and SEAGER (1953) were not known to the author, an "atlas" of vicinals on definite faces had to be made first. Soon it became clear that, except for border cases, there was no similarity between vicinals on  $\langle 100 \rangle$  and on  $\langle 210 \rangle$  (see figure 1). Since only very few good octahedra were available in Cerro Mines, the atlas of vicinals on  $\langle 111 \rangle$  had to be completed later by observations in the collections of the Natural History Museum in Vienna, and the large pyrite collection in the Mineralogical Institute of the University of Rome. The vicinals on  $\langle 100 \rangle$  and  $\langle 210 \rangle$  on pyrites of these collections were also recorded and differed only in minor details and in abundance from the collection of forms made in Peru. The drawings on figure 2 therefore contains mostly patterns from other areas, whereas figure 1 consists only of patterns observed in Morococha.

The photographs of figures 3, 4, 5 illustrate some typical habits with characteristic vicinals. On synthetic pyrite made in test tubes (Re. STRAUMANIS, AMSTUTZ, and CHAN, 1963) the striations were always quite irregular and the accessories not distinct.

The shape of vicinals and other accessories on crystal surfaces has been the object of many papers and discussions. The most useful and clear classification of patterns of accessories was given by R. L. PARKER

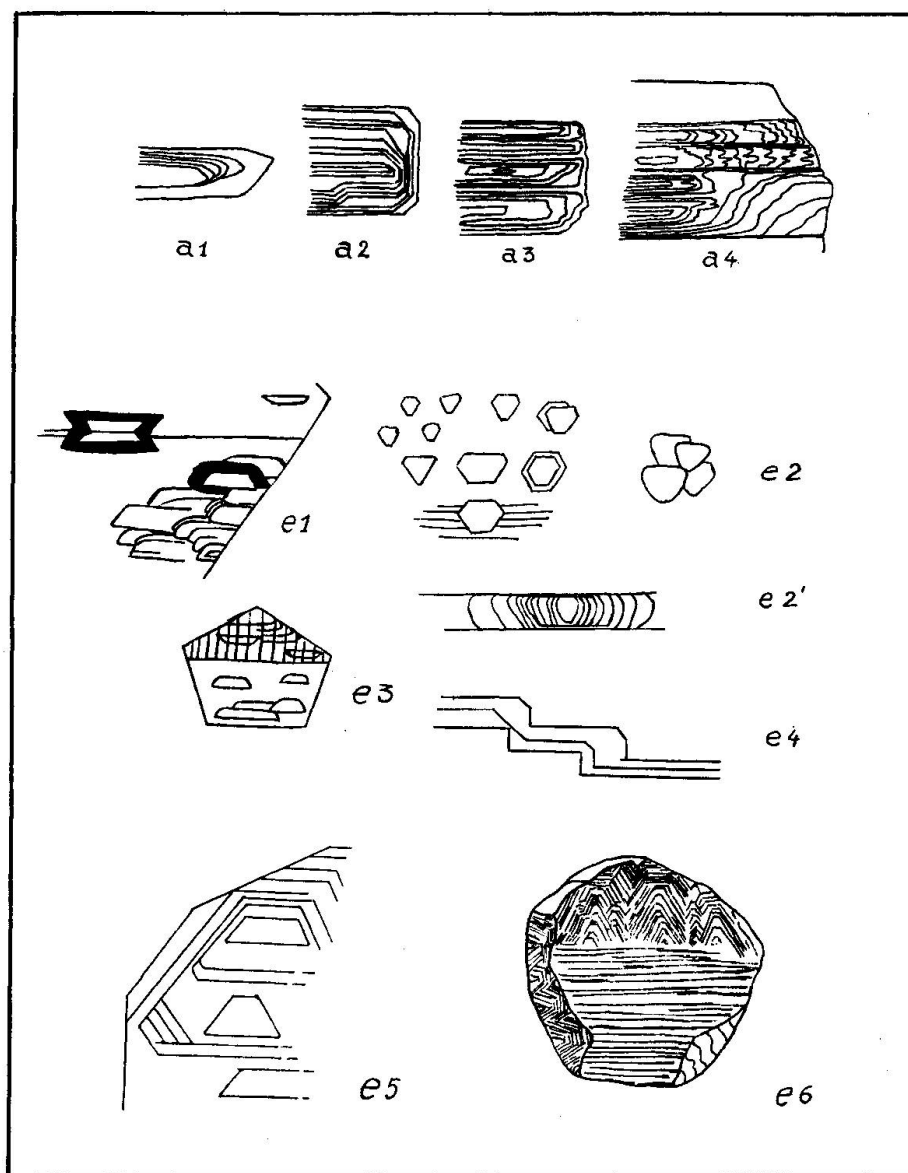


Fig. 1. "Atlas" of accessories on crystal surfaces observed in Morococha and neighbouring Mines, Central Peru. The top row shows the variability of accessories on cube faces ( $a_1$ — $a_4$ ), the other patterns ( $e_1$ — $e_6$ ) were all observed on faces of pyritohedra. Note the striking similarity with patterns pictured by WACKER (1933, fig. 7, 9, 10, 11, 13).

in 1932. He differentiated between four distinct types of accessories on crystal faces. The accessories pictured on figure 1 to 6 fall either into PARKER's group 3 or 4, since all of them show at least one straight boundary, many even four.

A comparison of the "local atlas" of accessories on pyrite made in Morococha (fig. 1) with the extensive study of pyrite from many different

localities made by WACKER (1933) showed that virtually all patterns observed by him on the cube and on the pyritohedron occurred in Morococha. It should be noted too that most of the good examples of pyrite with clear large vicinal patterns came from one large pyrite rich portion of the Morococha Mine. This portion is called Ombla Manto.

Vicinals on pyrite were studied in detail by WACKER (1933) and later by SEAGER (1953). P. HARTMANN (1953) discussed the pyrite morphology on the basis of P. B. C.-vectors and KLEBER (1955) examined the applicability of the P. B. C.-vectors to the relationships observed on vicinals and other accessories.

In two remarkable papers SUNAGAWA (1960a, 1960b) offered a modern demonstration of how a detailed study of accessories on crystal surfaces can lead to conclusions on the mechanism of crystal growth. The ample information on accessories contained in SUNAGAWA's paper remains to be studied also from a "minerogenetic" and paragenetic point of view, and so does the atlas of microstructures on diamond by TOLANSKY (1955).

At this point two things have to be brought into the discussion. First, this may well be the time and place to emphasize how useful it would be to have a closer cooperation between "Science" and "Technology" in regard to this topic of controlling factors in ore genesis. For this reason, a form has been prepared which lists the parameters that may influence directly or indirectly the formation of different pyrite habits. This form (available from the author) contains space for observations such as:

- the stratigraphic horizon, or,
- the igneous rock unit
- the geometric type of the deposit as a whole
- geometric type of the local unit (vein, bed, geode, etc.)
- wall rock composition and alteration
- mineral association (broken down in KUTINA-type generations)
- size of crystals, a. o. information.

### **Zoned pyrite**

So far the pyrite zoning study may appear to be an ideal and simple tool. This would be the case if there would never be a change in the habit during the growth of pyrite. This problem of habit changes is almost identical with that of zoning in pyrite. Habit changes can be



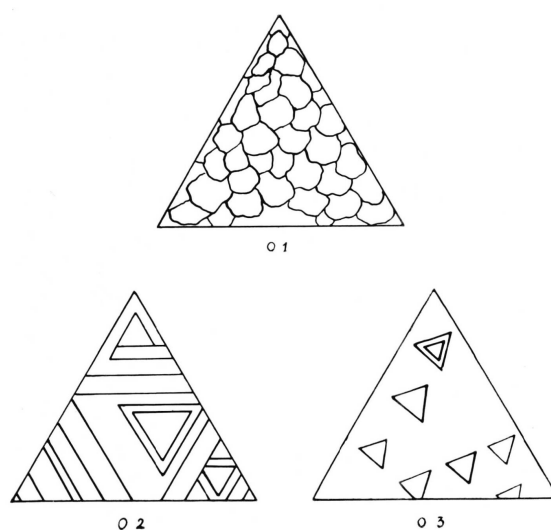


Fig. 2. Basic patterns observed on octahedral faces. O<sub>1</sub> on samples from Cerro de Pasco Mine, O<sub>2</sub> and O<sub>3</sub> on samples from Elba and other localities. This range of variations is virtually identical with that reported by WACKER and by others (see PARKER, fig. 5 on table 8; and WACKER, fig. 15, 16, 17 and 18; or SEAGER, fig. 39, 40, 41).

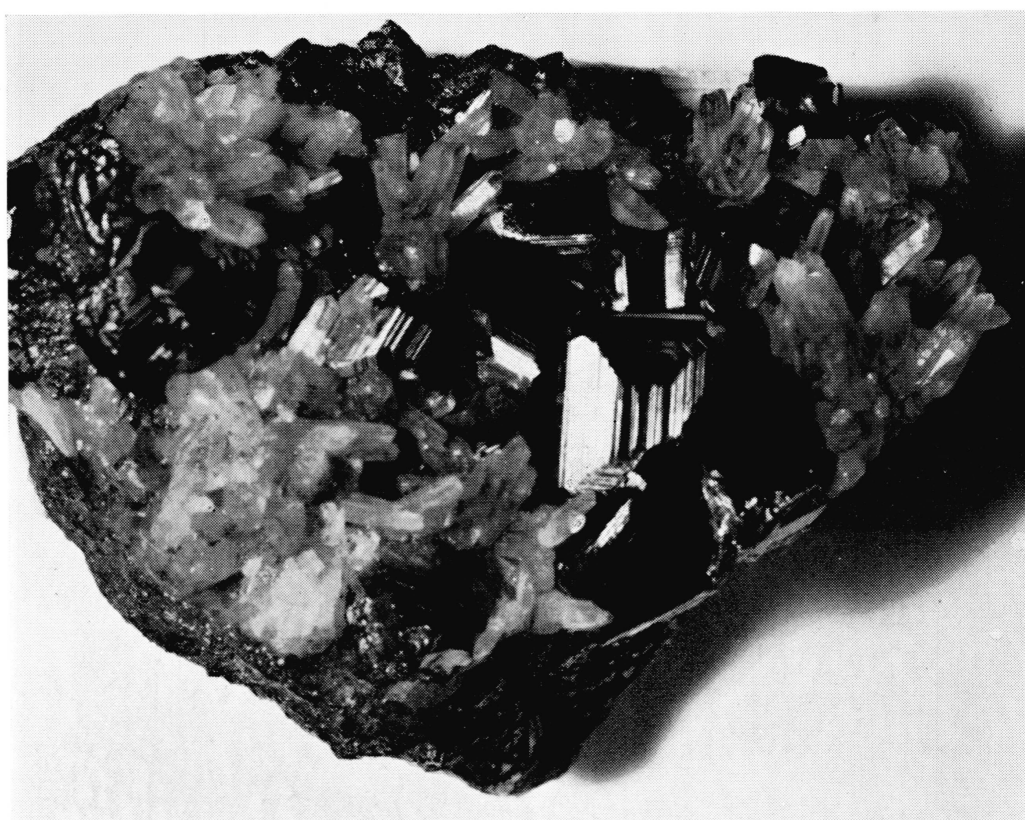


Fig. 3. Example of accessory type a<sub>2</sub> as a simple pattern on cubes intergrown with quartz in a cavity of the Ombla Manto, Morococha, Peru. The length of the clearest and largest pyrite cube is 1 cm.



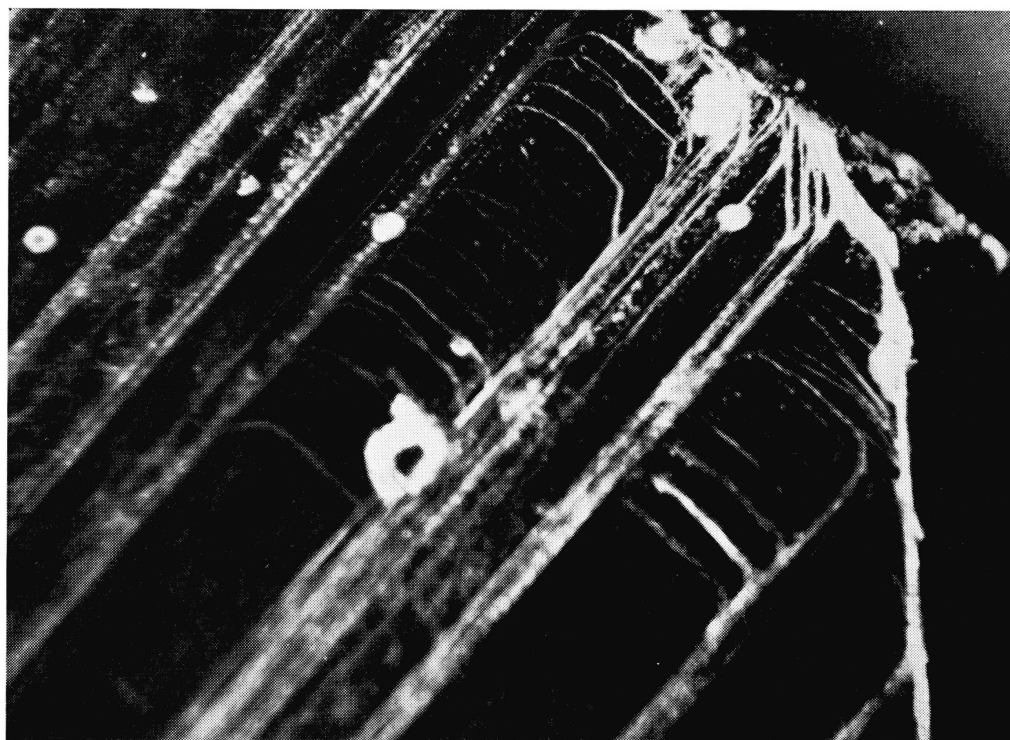


Fig. 4. "Polysynthetic" pattern of the  $a_3$  type on pyrite cubes from Morococha, Peru. The vertical extension of the figure is 1 mm.

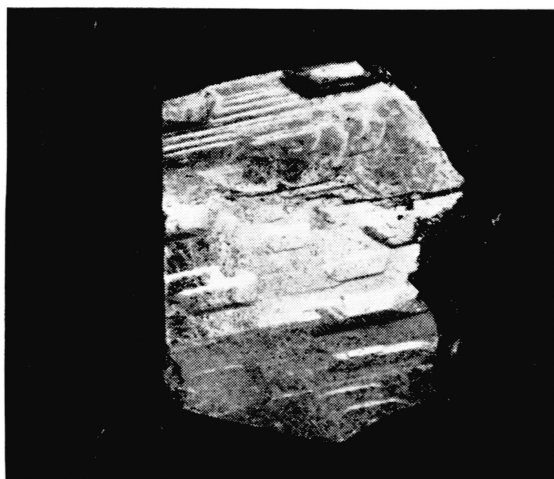


Fig. 5. Typical trapezoidal patterns on a pyrite-hedral face of a large pyrite crystal from Ombla Manto, Morococha, Peru. Size of the face:  $3 \times 4$  cm. Compare WACKER, fig. 20.

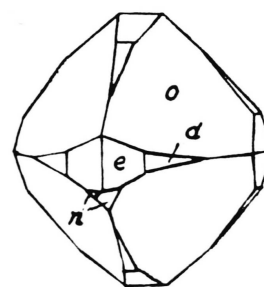


Fig. 6. Habit of pyrite occurring in cavities with native sulfur, in a massive pyrite body, 2300 level, Cerro de Pasco Mine, Peru.

considered as one sub-case of zoning. The second sub-case consists of compositional changes (content in S or changes in the Fe : Ni : Co ratio), and the third one merely of physical or quality changes (pits, inclusions, etc.).

In other words, the problem of pyrite zoning is closely linked to the question of zoned pyrite. One problem can not be investigated without a careful consideration of the other. This is at the same time a complication and an advantage, because a habit change or another type of zoning provides us with more information on a  $\Delta c$ ,  $\Delta t$  or  $\Delta p$ , i. e. a change of the composition or of conditions during the history of crystal growth.

In order to test the possible meaning of zoning, and the factors involved in it, an extensive pyrite-bravoite study was undertaken. A preliminary report of a statistical study of some 4500 bravoite grains will appear elsewhere (EL BAZ and AMSTUTZ, 1962). At this time only some basic statements will be added in connection with the historical remark made at the beginning. It has been stated in a paper on the genesis of congruent ore deposits (1962) that the Deus Ex Machina, i. e., the belief that everything is caused by changes *from without*, i. e., by exogenetic causes, is gradually disappearing.

The old theory on zoning is also exclusively exogenetic because it explained the formation of different zones as formed by compositional or physical changes in the surroundings of a crystal.

The bravoite-zoning study mentioned above showed quite conclusively that this exogenetic theory is ruled out in many cases by the co-existence of different zoning sequences in one and the same stratigraphic layer or in spots. Moreover, the classification of zoning types and the statistical results showed that only an increase in Fe is possible in gradational zones and that, as far as could be observed by oil immersion systems, Ni richer zones always start abruptly.

These and other results eliminated the "feeder-theory", as the only possible theory on zoning in pyrite. A new "model" had to be sought and this "model" or analogue may well provide an explanation for both, some major factors in the formation of zoning and also the formation of the different patterns of accessories on the surface.

It is almost definite that this model should basically be inherent or "endogenous," i. e., the controlling factors must be first of all sought within the crystal and especially its surface. What is known of the surface energy relationships in saturated conditions or in response to pH or Eh changes, plus the knowledge of donor and receptor property

changes appears to fit the observed variability, combination, and statistical distribution of zoned pyrite-bravoite as well as zoned minerals much better than a simple "deposition zoning theory." Simple "deposition zoning," of course, does take place, but the above criteria rule it out as an overall explanation for the genesis of zoning.

Sulphides are semi-conductors and the processes on the surface, including the acceptance of atoms during crystal growth, are a function of the distribution, strength and type of the electrical field on the surface of a crystal. The excess of metal ions in a lattice will thus produce a tendency towards an n-type of conductivity, i. e., "the electron concentration... is increased by excess of metal in the sulphide over the stoichiometric proportion and is also increased by the foreign metal atoms in the crystal lattice" (PLAKSIN, 1960, p. 390). The excess metal atoms or "impurity" metal atoms act as "donors" and a p-type lattice is produced. A deficiency of metal atoms, i. e., an excess of S-atoms will create a receptor or p-type crystal and surface.

Mixed donor-receptor surfaces are possible as shown experimentally by PLAKSIN, and may perhaps be reflected in the distribution of accessories or of pits on the surface of crystals.

Changes from p- to n-type lattices or surfaces are possible, not only through the change of the ratio sulfur to metal, but also through changes in the immediate vicinity of the crystal and the adsorption of oxygen on the mineral surface.

Whereas it is obvious that the experimental methods of PLAKSIN and others should now be applied to different zones and accessories to obtain an answer to the present suggestions, it was only the purpose of this concluding section to offer suggestions for future work and a reasonable working hypothesis.

It is interesting to note that PARKER (1932, p. 251) questioned the overall validity of GOLDSCHMIDT's theory on the growth accessories as being caused by special conditions outside of the crystal. Perhaps here too, the surface energy distribution is a more concrete model for the formation or absence of accessories and for their pattern and number than a mere random distribution of left-overs from crystallisation. In this sense the inherent properties of a crystal and its surface again offer a better model.

Here too, future research has to concentrate on the study of the surface itself instead of indulging in assumptions on the possible movements and supplies of matter from unknown outside sources, this *Deus ex Machina* par excellence.

In *conclusion* and *summary*, the work on pyrite zoning required first a detailed "atlas" of occurring accessories, in order to allow a determination of the dominant habits. This first approximation yielded useful results only in "simple" deposits, i. e., in deposits with only one major generation of "mineralisation." In complex deposits the observations need to be refined and the major additional "dimension" is a study of zoning and especially of habit changes in pyrite.

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