

VARIOUS ASPECTS OF ATOMIC DISPLACEMENTS IN METALLIC SULFIDES

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ABSTRACT

Movements of atoms can be observed and even brought about in metallic sulfides. A change in the structure may result from a large number of these movements. These displacements can be studied by various methods. Three examples are given: 1) atomic displacement involving another cell, causing a polymorphic form to appear; 2) atomic displacement bringing about the unmixing of several phases; and 3) artificial introduction of a new metal into a given mineral, where the introduced atoms either enter into solid solution or cause the appearance of new phases. The distances traveled by the atoms can be estimated. Such displacements can explain a number of commonly observed phenomena.

The most common metallic sulfides still pose numerous problems, which become obvious when the minerals are examined under a polarizing metallographic microscope. Many optical anomalies, many features of their mutual arrangements, and the occurrence of unidentified phases make optical interpretations difficult (Prouvost, 1959).

We attribute these surprising features to the facts that, when they were formed, the nutrient material was not so well determined as those which we reproduce in the laboratory, and numerous elements were present in variable quantities. As a result of this variation, each distinct phase contains a certain number of elements, probably in the form of a solid solution, which will be stable under certain conditions. Since conditions vary in the course of geological ages, the balance tends to shift. New phases appear or disappear, certain crystalline states can no longer exist and are replaced by others. All this is accompanied by a regrouping of the atoms and, consequently, by movements of atoms which leave their previous positions to reach new equilibrium positions.

To study these phenomena, it is normal to resort to methods which grasp each of the variables arising from the above observations: the variation of thermodynamic energy is clearly shown by the differential thermal analysis; crystalline modifications are indicated by x -ray diffraction; changes of reflecting power (in quantity and quality) and appearance or disappearance of new phases can be seen with the aid of a metallographic polarizing microscope. Finally, there is the analysis, at specific locations, of the elements of the different phases.

Let us consider each of these experimental techniques. DTA, for our purposes, must be particularly sensitive. In fact, it is advantageous to modify the heating rate during the observation of the phenomena, thus permitting the control of their reversibility.

The analysis must be sensitive in order to show very slight variations of energy. (Both the dilution techniques and the protection of thermocouples generally used for sulfides are to be avoided, even if it means the destruction of these thermocouples during each experiment.) It should be added that the instability of sulfides heated in an oxidizing medium necessitates the use of an inert gas.

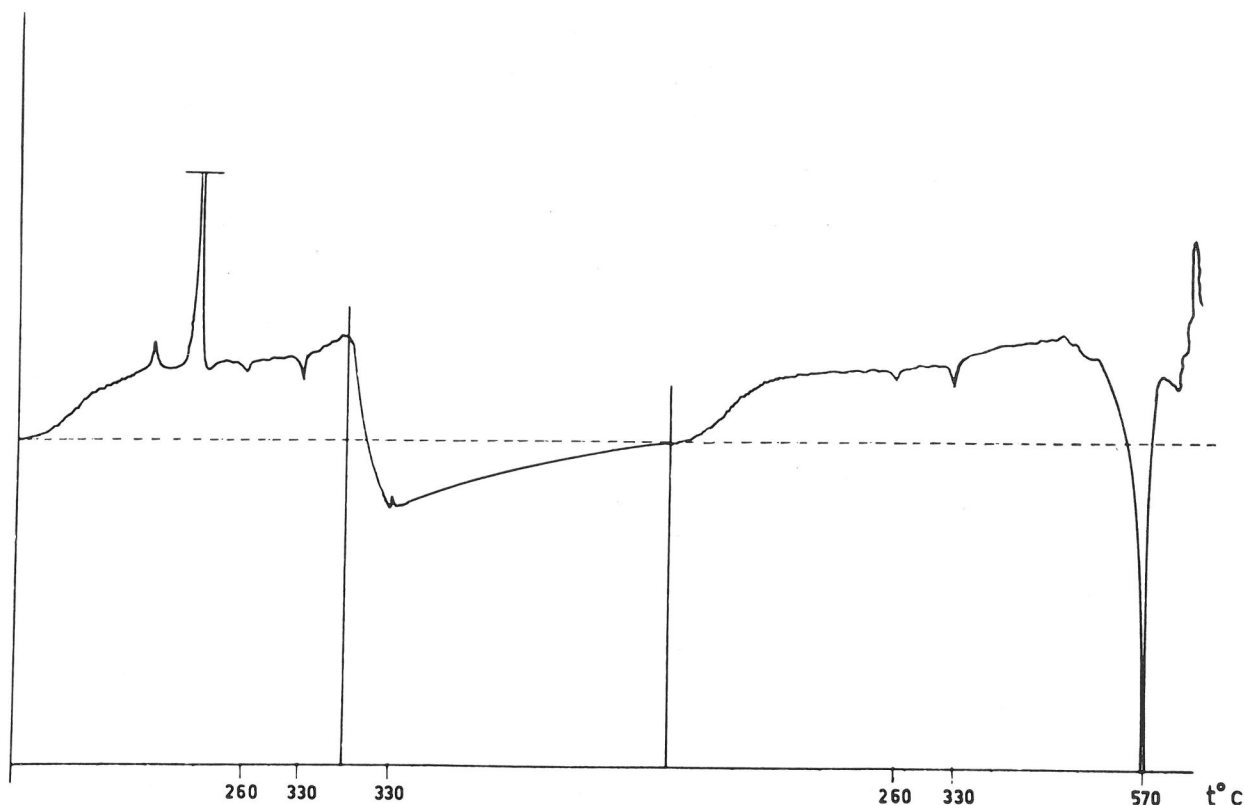
The x -ray examination of phases that are stable only in a fixed range of temperatures requires the use of a high-temperature camera, and up to now, with the apparatus at our disposal, we have succeeded only in obtaining Debye-Scherrer powder patterns.

Optical study, in its present form, falls short of giving the results we could expect to obtain with the apparatus that we eventually intend to build, *i.e.*, a heating stage for polished sections. Now we can observe the samples only before thermal treatment and after cooling.

The chemical study of a certain location is effected with the Castaing microsonde, an apparatus based on the emission of x -rays, which permits optical observation simultaneously with an analysis of the elements. In some cases it can be supplemented by the scanning apparatus.

Let us recall the results that such a combination of techniques has enabled us to obtain. Let us first examine the case where no arrival or departure of any element is to be expected during thermal treatment. As an example, let us take antimony trisulfide, which we have particularly studied and which can be obtained from pure chemical substances (Prouvost, 1960).

After the transformation at 215° C. of the red precipitate to an orthorhombic crystalline sulfide with $a=11.229$, $b=11.310$, $c=3.839$ Å (Swanson, 1955), we observe, by DTA (Fig. 1), two endothermic peaks at temperatures of 260° and 330° C. By


 FIG. 1. Differential thermal analysis curves of antimony trisulfide, Sb_2S_3 .

stopping the heating almost immediately and by letting the sample cool, we can observe an exothermic peak corresponding to 330° ; then, as the temperature rises again, the two peaks are reproduced at 260° and 330° C. This example is particularly striking. It is an almost perfect example of reversibility: in the region under consideration, the two curves of thermoanalysis are superimposable. The high-temperature polymorphic phase has probably never before been observed, since it is stable only in a restricted range of temperatures, from 330° C. to the comparatively low melting point, recorded at 570° C. under our conditions. An x -ray investigation with the aid of a heating camera seems to indicate that this phase must be cubic, with $a = 5.57 \text{ \AA}$.

The above phenomena, which are commonly observed when different stable phases exist, are certainly very frequent, and each case studied has revealed interesting observations. The passage from one form to another is accompanied by atomic displacements, the magnitude of which is always very slight.

We can now treat the more complex sulfide, bornite (Cu_5FeS_4), in the same way. In this case the sulfur is

combined with two different metals, and we have a greater number of possibilities: different forms of bornite; formation of other compounds, either of iron or of copper with incidental exclusion of the other metal; and ordered or disordered compounds (Frueh, 1950).

We have analyzed by DTA the purest sample available to us (Fig. 2). The chemical analysis shows close agreement with the chemical formula:

	<i>theoretical</i>	<i>sample</i>
Cu	63.33	62.8
Fe	11.12	11.3
S	25.55	25.5

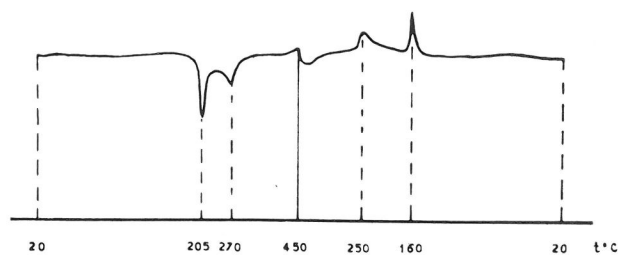


FIG. 2. Differential thermal analysis curves of bornite.

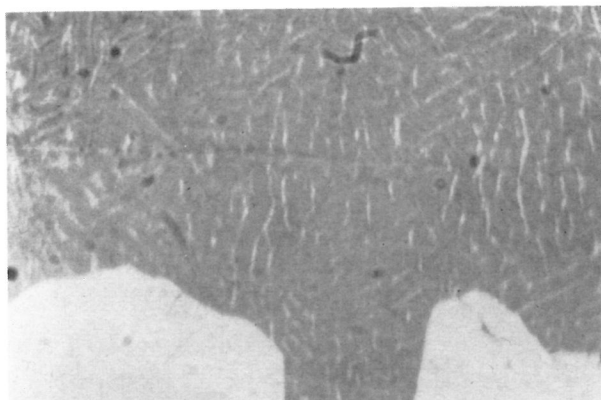


FIG. 3. Micrograph of bornite after thermal treatment. Note two specks of chalcopyrite and segregation of copper sulfide forming Widmannstätten patterns. Ordinary light, $\times 1000$.

The first endothermic peak is noticed at 205°C ., and the balance is not yet restored when a new peak is traced at 270°C . The temperature continues to rise without incident to 450°C ., when the heating is stopped. Analogous phenomena are observed on cooling, but at lower temperatures.

The run was repeated several times, and the same phenomena were observed each time. There are, therefore, two points of energy change. Since it was impossible to carry out an optical investigation at these temperatures, *x*-ray diffraction was used. Powder photographs were taken at temperatures of 20° , 230° , 270° and again at 20°C . At 230°C . (*i.e.* above the endothermic peak), chalcopyrite lines appeared, and above 270°C . chalcocite lines were also noted. These lines disappeared on cooling to room temperature. Therefore, the formation of chalcopyrite and then of chalcocite must encounter some difficulty, since the diffraction pattern of bornite still persists, with only the main lines of chalcopyrite and chalcocite showing, and since the return to the low-temperature state was considerably delayed.

In order to carry out an optical examination, we used quenching in the hope that it would freeze the structure at a fixed point. The polished sections, which initially consisted only of one phase (bornite), showed, after treatment, minute specks of chalcopyrite scattered in the center of the bornite. Crystallographic planes of chalcopyrite often formed the boundaries of these statistically distributed specks. One could also observe, albeit with great difficulty, the segregation of the copper sulfide. This difficulty arises from the fact that we are dealing with very thin elongated zones, probably oriented along the

planes of the original bornite and forming Widmannstätten patterns (Fig. 3).

The examination of such zones with the Castaing microsonde did not give satisfactory results, because we had reached the limit of resolving power. A drop in iron content was nevertheless ascertained when the electron beam embraced such a zone. The scanning process did not yield any better results.

The transformation just described is completely different from the one previously studied. Here we are dealing with unmixing, with the appearance of several solid phases. The atomic displacement, which is relatively large judging by the photographs, takes place only comparatively slowly, which probably explains the difference in the temperatures at which the individual peaks occur on heating and on cooling.

In the course of some other work, we noted particularly interesting phenomena in Cu-Ag-S. Unfortunately, equipment was not available for a study of this compound either by DTA or by *x*-ray diffraction at elevated temperatures. It is known that a mixture of these three elements shows quite different optical properties depending upon the temperature at which they are combined. If we assume that the total composition remains constant, this compound must obviously occur in several forms.

Let us now study the transformation obtained when a new element is introduced from the outside. In this case we increased the energy either by raising the temperature or by applying an electric field. So far, all the experiments which I have attempted, to bring about transformations by the action of an electric field compatible with natural conditions, have ended in failure. The presence of at least one liquid has always proved indispensable. Electrolytic phenomena, therefore, seem in this case to control the movement of the ions (Prouvost, 1960).

By raising the temperature, we were able to make a metal enter the crystal structure of a mineral, and thus bring about the transformation of the latter. It again was the Castaing microsonde that gave the proof of the atomic displacements. Curves of established percentages along lines cutting through the transformed parts give us an idea of the concentration of the various elements at each point (Prouvost, 1962).

As an example, let us consider the deposits of silver and tin on chalcopyrite. On the photograph (Fig. 4) we can see, adjoining the transformed areas, the percentage curves of the constituent elements. These curves show that the enrichment is not

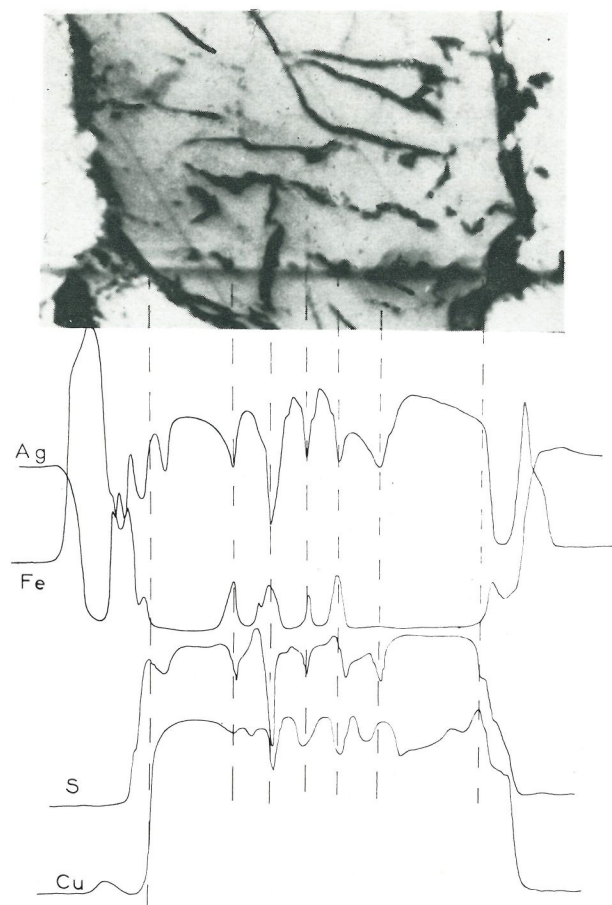


FIG. 4. Examination with Castaing "microsonde" of chalcopyrite treated by silver. Silver is white (some on the left and on the right). Chalcopyrite is gray. The black specks are the transformed areas. The horizontal dark line is the trace of the electron beam. Ordinary light $\times 350$.

gradual; that, on the contrary, there is a sudden variation in concentration at the boundary of the transformation. The percentage of the particular metal is remarkably constant throughout the crossing of the chalcopyrite, and in the case of silver it is about 5 to 8%. The presence of silver in solid solution is probably the reason for the greenish appearance of the treated chalcopyrite, which has been observed in some samples from Peruvian silver deposits. This is a third type of diffusion of the atoms. In this particular case we deal with a supernumerary element. The percentage curves give some information as to its movement.

We have thus shown three aspects of the movements of atoms in metallic sulfides. In the first case, which is the simplest and the most completely

studied, the movement of atoms develops quickly, but is slight: because the crystal structures of the two forms are only slightly different from each other, the atom will move to a neighboring position without circulating through the crystal structure. The other cases are different. Let us examine the areas of thermally treated bornite, in which chalcopyrite and copper sulfide have appeared. The segregation points of chalcopyrite are rarely more than 0.1 mm apart. We must not forget that their organization is statistical. We are led to think that, under the conditions of our experiments, the ferrous ions taking part in the regrouping have traveled about 0.1 mm; in the present state of our research we have reason to believe that the material is homogeneous between the particles of chalcopyrite. Finally, in the case of the deposition of a new element, the greater number of parameters makes our study more uncertain. With the same mineral, results are different according to the metal deposited. The thickness transformed under our experimental conditions (8 days at 300°C ., or a bit less in the case of tin to avoid fusion) was about 0.01 mm. However, we must distinguish several problems. Up to a certain concentration, movements can take place in a solid solution, without transformation, over distances which can be large. If there is a change of phase, we must take into account the fact that other atoms must occupy the areas in which a new mineral crystallizes. This is possibly the explanation for the slight penetration of the total transformation with appearance of a new phase.

In conclusion, it may be said that the atomic movement of elements or of groups of elements trying to reach a state of equilibrium takes place very slowly as compared to our own time scale. However, the atomic velocities are sufficient to account for the textures commonly encountered in polished sections of ore minerals. In some cases, bornite for instance, we have succeeded in producing typical microstructures in a comparatively short time and under very similar conditions.

ACKNOWLEDGMENTS

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DISCUSSION

B. J. SKINNER (Washington, D. C.): What is the composition of the yellow mineral, which you called chalcopirite, that appeared in the heated bornite sample?

AUTHOR'S REPLY: (Lille): The yellow mineral that I called chalcopirite has not been chemically analyzed by classical methods because the specks were too small. I determined the optical properties by means of the dispersion curve of the reflecting power, and the lattice parameters from x-ray powder patterns. I also used the Castaing microsonde to obtain the ratios of the elements.