

## OBSERVATIONS ON THE SYMPOSIUM ON SULFIDES

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Assisted by the panelists: A. J. Frueh, *University of Connecticut, Storrs, Connecticut*; E. R. Nickel, *Department of Energy, Mines and Resources, Ottawa, Canada*; P. Cloke, *University of Michigan, Ann Arbor, Michigan*.

In dedicating a symposium to the topic "Sulfides," it is not surprising that the contributions should be extremely diverse in character. It is very difficult to distill and summarize a program so broad. Yet, in spite of the enormous scope of such a field of study, rather little work is being done today, in comparison to studies that would come under the heading of "Oxides." The oxides encompass the "rock-forming minerals," which are today receiving a rapidly expanding amount of attention; but it would seem that the "ore-forming minerals," which include the sulfides, should be of somewhat comparable interest, especially from an economic point of view. Because of this dearth of effort, it does seem worthwhile to bring together workers on sulfides from various disciplines in order to encourage a better coordination of study. Each of the contributions, for example that on crystal structure studies, could in itself easily be the subject of a larger program than we are permitted for this symposium; but one of the main objects at present is to remind petrologists and thermodynamicists of the inroads of structure problems on their area of work, and vice versa.

Thus, contrast is the main characteristic of the papers here presented. Perhaps the two most nearly related, but still rather contrasting in character, are those of Professor Pauling and Dr. Pickart, on structure and properties respectively. There was much discussion of interatomic bonding, but in a confusing variety of languages; that of valence bond and electronegativity theory, emphasized by Professor Pauling; valence and molecular orbital theory used to describe magnetic properties; and band theory used to describe electrical properties. We should remind ourselves that all these languages are equivalent and applicable to any given phenomenon that occurs when atoms are brought near to each other. To mineralogists, petrologists and geochemists, perhaps the language of physics used by Dr. Pickart was the least familiar; yet an understanding of the physical properties can hardly be underestimated for such workers for an appreciation of sulfide minerals from any fundamental point of view, and this understanding comes today largely from the solid-state physicists. In other directions, too, the seeming contrasts may be lessened somewhat, for example, by translating the thermal studies of the phase chemists referred to by Dr. Kullerud into terms analogous to the activity functions used by Professor Helgeson.

An interesting factor that appears in these discussions is the lack of certain basic experimental data that has somehow escaped investigation to this late date. For example, although many very complex sulfide structure determinations are now being carried out, such as No-

wacki's beautiful studies of the sulfosalts, certain elementary structures such as pyrite, chalcopyrite, enargite and covellite have not been refined by modern methods. Much work needs to be done to bring such measurements to modern standards of accuracy. (Enargite is currently under study by Nowacki's group; pyrite has just been cleared up by Brostigen and Kjekshus [*Acta Chem. Scand.* 23, 2186, 1969], who find the distances Fe—S =  $2.262 \pm 0.003$  Å and S—S =  $2.177 \pm 0.004$  Å). The same observation applies to thermodynamic data; a large amount of well-chosen experimental studies are required to supply free energy and activity data required to strengthen the theoretical interpretations offered by Prof. Helgeson, especially at higher temperatures and pressures. Of course, many systems that formerly were regarded as simple turn out to be very complex when subjected to modern experimental techniques.

At this point we may remark on another contrast, namely that of breadth of viewpoint. On the one hand, we have people like Dr. Pickart and Professor Pauling studying the fine details of atomic phenomena, and on the other Dr. Thode who is interested in the general behavior of sulfur isotopes in various broad rock types, or Professor Helgeson who applies sweeping generalizations to geochemical systems that are breathtaking in scope. Professor Helgeson is not the least disturbed if some portion of his event-phase diagrams violate information provided by the details of a chemical phase study; a small adjustment of the parameters will eliminate the difficulty. But the overall general principles of rock-forming phenomena discovered by his calculations are, of course, invaluable as guides to other scientists attempting to account for more localized details.

Much interest was shown during the panel discussion in how much modern theoretical chemistry and solid-state physics can help to account for various phenomena observed in sulfide systems. Subtle magnetic forces certainly have considerable effect on the structure types assumed by certain sulfides, and so may indirectly affect the phases that appear in mineral suites. The manner in which the addition of certain atoms to a given structure fills up a Brillouin zone can impose sharp limits on the chemical composition of a berthollide, and thus affect the topography of a phase diagram. Such avenues to the elucidation of mineral stabilities have so far been little studied, and offer fertile fields of research.

Another deficiency in current sulfide mineral research was emphasized by Dr. Barton's summary of ore petrology. He reminded us of the rich source of information, concerning the phenomena of mineral stability and se-

quences of deposition, that lies in the fabric of mineral textures themselves, as revealed by field studies and examination of mineral sections. Little attention was paid to these data by the other contributors, who mainly concentrated on the results of theoretical or laboratory investigations, and yet a glance through the microscope will raise a host of strange problems, suggesting phenomena that often are far from being resolved in terms of our present understanding of ore genesis. Much attention is devoted to predicted systems based on complete equilibrium, but the kinetic processes are often important in interpreting local textures. Reconciliation of the broad results of thermochemistry and the details of ore petro-

graphy will require much patient collaborative effort in the future.

The overall impression produced by this symposium is one of optimism, and even satisfaction with the fine progress that has been made up to now. Remarkable advances have been made in the last fifteen years on several fronts in our understanding of the sulfide minerals. It is perfectly natural to find that when we come together to review their present state, large areas of study are waiting to be opened up, and great rewards can come from increased interchange of ideas and experiences among the different disciplines.