

Günter H. MOH *

PHASE EQUILIBRIA STUDIES IN MULTICOMPONENT SULPHIDE AND OXIDE SYSTEMS AND THEIR APPLICATIONS

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Abstract. In this paper many aspects of the application of sulphide phase diagrams have been presented. These diagrams can be used to the reconstruction of conditions which occurred at the formation of natural ore minerals assemblages. They are also useful for the purposes of modern technology.

SPHALERITE-TYPE STRUCTURE MINERALS AND THEIR REACTIONS UNDER VARYING TEMPERATURE-PRESSURE RELATIONS

Mineralogists frequently observe (under the reflecting microscope) conspicuous ore textures which have formed during or after deposition upon cooling from elevated temperatures. When compared with silicates, the reaction kinetics of sulphides are much less sluggish and equilibration may take place even at very low temperatures, depending on the cooling rates of the ore bodies in which the minerals occur. In addition to, for instance pyrite and pyrrhotite-type minerals, the most common minerals in typical sulphide ores are those which are structurally related to sphalerite and chalcopyrite. In view of observations made in some high-temperature deposits or deposits of metamorphic origin, the mutual reactions between such coexisting minerals were investigated in the laboratory under various temperatures and pressures up to 5 kb. Besides sphalerite and chalcopyrite other minerals have also been considered, e.g. hawleyite and greenockite, cubanite, gallite, germanite, renierite, briartite, stannoidite, mawsonite, stannite, tetrahedrite, etc.

If the minerals do not show any structural transition within the respective temperature-pressure range, the reactions can easily be explained. At the temperature of deposition commonly an extensive solid solution

* Mineralogisch-Petrographisches Institut der Universität, (Berliner Strasse 19, 6900 Heidelberg, BRD).

series exists between the minerals which diminishes with decreasing temperature. Thus, simple mutual exsolution textures may develop, unless the appearance or disappearance of certain minerals causes more complex reactions, controlled by their specific t-p stability and/or sulphur fugacity.

However, in case one or more minerals of the considered assemblages occur in different polymorphic modifications, the sequence of mutual reactions becomes complicated. The reactions are influenced by the pressure-dependent inversion temperature of the respective minerals and by the traces of other minerals dissolved or their presence in excess. Textures of exsolutions in more than one generation can be observed.

Chalcopyrite was found to be the most affected ore mineral, particularly under varying pressures. At elevated temperatures but low pressures, the high-temperature α -chalcopyrite can dissolve remarkable amounts of other minerals forming a compositional range which can be expressed by the simplified formula: MeS ($\text{Me} = \text{Cu, Fe, Ga, Ge, Sn, Zn}$, etc.). On cooling when passing through the phase transition temperature, this solid solution series breaks down to tetragonal β -chalcopyrite and other minerals, producing various kinds of exsolution textures and replacements in all stages.

If the high-temperature chalcopyrite solid solution series is allowed to cool under high confining pressure, the α - β inversion appears to be incomplete, even at very low temperatures. Thus, the α -phase may remain as *chalcopyrrhotite* or relics of it, displaying β -chalcopyrite exsolution lamellae and eventually other oriented exsolved break-down products visible under the microscope.

Pa₃-TYPE STRUCTURE MINERALS AND RELATIONS WITHIN THE Cu-Ni-S SYSTEM

Pyrite, FeS_2 , is the most frequent sulphide mineral, whereas other Pa₃-type sulphides are much less common or a mineralogical rarity as, e.g., vaesite, NiS_2 ; catterite, CoS_2 . The stability relations of these simple sulphides as well as the intermediate solid solution series of the FeS_2 - CoS_2 - NiS_2 system were studied by various researchers in great detail. Bravoite, $(\text{Fe, Ni})\text{S}_2$, is a mineral deposited from low-temperature hydrothermal solutions and a characteristic is its strongly zoned appearance caused by compositional variations in the Ni:Fe contents. The alternating zones of bravoite often contain appreciable amounts of cobalt. The mineral villamaninite $(\text{Cu, Ni, Co, Fe})\text{S}_2$ is known from Providencia Carmenes, Spain, and its appearance shows many similarities with bravoite. However, pure $(\text{Cu, Ni})\text{S}_2$ can be synthesized and shows an upper stability temperature of at least 500°C.

In order to study the stability relations, the ternary Cu-Ni-S system was investigated at various temperatures and the experimental results were later applied, i.e. compared with natural ores. Figure 1 shows the phase diagram of the system in the 100 to 150°C temperature range. At these temperatures, the ternary villamaninite phase forms an extensive solid solution series and is stable with excess sulphur. The Ni-rich end of this series coexists also with vaesite, the Cu-rich end with covellite, CuS .

The intermediate solid solution series, depending on the composition, is connected by tie lines with *blaubleibender* covellite, Cu_{1+x}S , and with digenite, Cu_9S_8 . All these intergrowths could be observed in polished sections of the type locality of villamaninite mentioned above.

An example for the univariant field digenite-vaesite-polydymite (Ni_3S_4) was found in an ore specimen of Shinkolobwe, Katanga/Zaire, and for digenite-polydymite-millerite (NiS) in material from Grube Königszug, Dillenburg (West Germany).

In the temperature range presented in Figure 1, the mineral djurleite, $\text{Cu}_{1.97}\text{S}$ was not found; it is stable at or slightly below 100°C and occurs, due to its composition, between digenite and chalcocite (Cu_2S). Djurleite was found intensively intergrown with millerite in a polished section from Siegen (West Germany).

Godlevskite (Ni_7S_6) is very similar in its optical behaviour to millerite or heazlewoodite (Ni_3S_2), and it can occur stably either with millerite or with heazlewoodite, forming also stable assemblages with chalcocite. Such intergrowths have been observed in traces in the serpentine of the Allalinhorn (Switzerland).

Heazlewoodite-chalcocite-copper intergrowths have been investigated, for instance, in a pikrite near Braunfels, Lahn (West Germany), and in serpentine near Kraubath/Austria. In both cases the copper was microprobed showing Ni contents up to nearly 0.5%. Metallic nickel and heazlewoodite intergrowths are known from Bogota Canala, Nouvelle Calédonie.

SOLID SOLUTION SERIES OF SULPHIDES AND OXIDES AND THEIR GEOCHEMICAL APPLICATIONS; THE DISTRIBUTION OF GERMANIUM IN TIN AND LEAD ORES

The 4A-group elements show many distinct similarities with respect to their chemical properties, although these elements are, as reported, paragenetically separated in their natural occurrences. Extensive laboratory investigations were performed in order to study the mutual reactions between stable phases in some systems, e.g.: Fe-Sn-S-O; Ge-Sn-S-O; Ge-Pb-S; Sn-Pb-S. The experimental results yielded the formation of remarkable or even complete solid solution series between coexisting phases. Mutual solid solubility of much less extent was found in the Ge-Pb-S system, probably because of the different atomic radii of Ge and

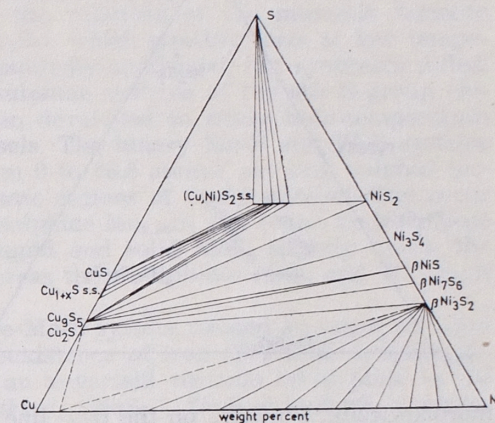


Fig. 1. The Cu-Ni-S phase diagram for the temperature range of approx. 100 to 150°C

Pb. However, a number of ternary phases were synthesized, as schematically illustrated in Figure 2. Tetravalent germanium was found to be more stable than bivalent Ge, and most of the phases contain either only tetravalent or 4- and 2-valent Ge. The only exception seems to be the mineral

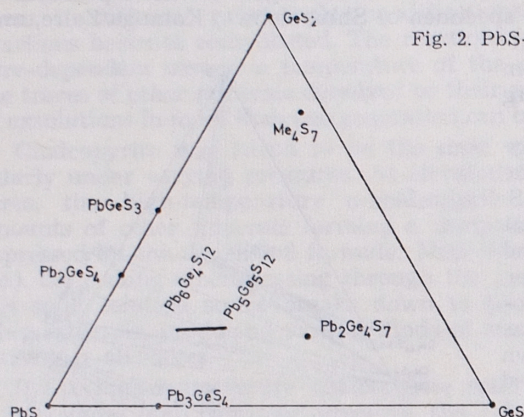


Fig. 2. PbS-GeS₂-GeS compositional scheme

morozewiczite, Pb₃GeS₄, on the base line between PbS and GeS; its synthesis failed as yet.

Tin and lead occur together in some of the hybrid Bolivian ore deposits of which a number of complex sulfosalts is reported; for instance, teallite (PbSnS₂), franckeite (Pb₅FeSn₃Sb₂S₁₄), cylindrite (Pb₃FeSn₄Sb₂S₁₄) and another one with a similar formula containing traces of Ag. Of tin-lead oxides only one secondary mineral has been reported as a Bolivian rarity: hochschildite, PbSnO₃·nH₂O.

Tin and germanium together are known of the rare minerals canfieldite (Ag₆SnS₆) and argyrodite (Ag₈GeS₆) and some naturally occurring members of their mutual mixed crystal series.

Recently numerous tin and lead-tin sulphides were spectrochemically investigated, yielding e.g. for some Cornish stannites Ge contents up to a few thousand p.p.m. Also for spectrochemical studies, several hundreds of tin ores were collected from all known tin provinces over the world (mainly cassiterites, wood tin and varlamoffites), and in some provinces remarkable Ge concentrations of several thousand p.p.m. were recognized, particularly in Cornwall, Bolivia, Japan, and in some Australian occurrences. The highest germanium concentrations were found in wood tin specimens and in some varlamoffites. In very few cases the natural formation of GeO₂ was recognized as an exsolution product of partly recrystallized varlamoffites.

REFRACTORY SULPHIDES, HIGH-TEMPERATURE REACTIONS

Modern techniques require in increasing proportions the application of high-temperature resistant steels and metal alloys containing titanium, chromium, molybdenum, tungsten etc. For examples, blades of turbojet

engines have to withstand oxygen and sulphur corrosion, due to the sulphur contents in kerosene. Another point is the use of mineralic lubricants, for instance for bearings, at elevated temperatures. MoS₂, a typical layer structure mineral, is such a lubricant, although sometimes the appearance of sudden corrosion phenomena was noticed. But also mineralogical problems exist concerning, e.g., titanium and chromium minerals in lunar samples or in meteorites, or the solid solution series between molybdenite (MoS₂) and tungstenite (WS₂) with view to frequently observed ReS₂ contents. Further questions regard the relations of the minerals femolite (FeMo₅S₁₁) and castaingite (CuMo₂S₅), which possibly form at low temperatures; both minerals were undoubtedly confirmed, but syntheses failed.

With the aim to investigate sulphide systems of the 6th B-group elements, a new technique has been developed to study high-temperature relations in molten reaction vessels. The binary Mo-S and W-S systems were completed in the range from 0 to 66.6 atomic per cent sulphur (disulphide composition); in both cases regions of liquid immiscibility occur at high temperatures. The sesquisulphide Mo_{2.06}S₃ was found to decompose incongruently to a metal-rich liquid and solid MoS₂ slightly below the melting point of silica glass, whereas the disulphides MoS₂ and WS₂ melt congruently far above 2000°C.

Reactions performed in the Fe-Mo-S system yielded an upper stability temperature of 677°C for the coexistence of iron (Fe) with molybdenite (MoS₂). Above this temperature an unvariant reaction takes place in the presence of a vapor phase: ~3Fe + 4MoS₂ = 2FeS + FeMo₄S₆ + vapor. The formation of the ternary sulphide can already take place at temperatures above 535°C, depending on the starting materials and the reaction time. It may appear in pseudomorphs after molybdenite or the sesquisulphide, Mo_{2.06}S₃, but it has no layer structure and consequently is no lubricant. This ternary compound can also be synthesized in a straight reaction between Fe and the molybdenum sesquisulphide.

A similar compound was found in the Cu-Mo-S system: ~CuMo₂S₃; both ternary compounds form complete solid solution series, and these complex molybdenum sulphides show interesting superconductive properties.

Günter H. MOH

STUDIA NAD RÓWNOWAGAMI FAZOWYMI W WIELOSKŁADNIKOWYCH UKŁADACH SIARCZKOWYCH I TLENKOWYCH I ICH ZASTOSOWANIA

Streszczenie

W pracy wskazano na szereg aspektów zastosowania diagramów fazowych układów siarczkowych. Pozwalają one na rekonstrukcję warunków w jakich tworzyły się naturalne zespoły minerałów rudnych jak też mogą być wykorzystane dla celów współczesnej technologii. Pierwszy aspekt został omówiony m.in. na przykładzie minerałów o strukturze typu sfalerytu. Podano również związki między układem Cu-Ni-S (fig. 1) a minera-

łem villamaninitem. Badania w układzie PbS-GeS₂-GeS (fig. 2) zwróciły uwagę na możliwość występowania większych koncentracji Ge w rudach Sn lub Pb-Sn. Pierwiastek ten może pojawiać się w postaci kilku trójskładnikowych faz bądź też w formie roztworów stałych. Znaczenie technologiczne mają np. badania w układzie Fe-Mo-S. W układzie tym występuje MoS₂, który wykazuje wysoką ogniotrwałość jak też ma własności smaru mineralnego. Powoduje to, że siarczek ten jest wykorzystywany przy eksploatacji łożysk urządzeń pracujących w wysokich temperaturach.

OBJASNIENIA FIGUR

Fig. 1. Diagram fazowy układu Cu-Ni-S w zakresie temperatur od około 100 do 150°C
Fig. 2. Schematyczne zestawienie związków występujących w układzie PbS-GeS₂-GeS

Гюнтер Н. МОХ

ИЗУЧЕНИЕ ФАЗОВОГО РАВНОВЕСИЯ В МНОГОКОМПОНЕНТНЫХ СУЛЬФИДНЫХ И ОКИСЛОВЫХ СИСТЕМАХ И ИХ ПРИМЕНЕНИЕ

Резюме

В работе указывается ряд аспектов применения диаграмм фазовых сульфидных систем. Они разрешают реконструкцию условий, в которых образовались натуральные комплексы рудных минералов, и могут применяться в задачах современной технологии. Первая проблема рассматривается на примере минералов со структурой сфалерита. Приводятся тоже связи между системой Cu-Ni-S (фиг. 1) и минералом вилламанинитом. Исследования в системе PbS-GeS₂-GeS (фиг. 2) обратили внимание на возможность присутствия довольно больших концентраций Ge в рудах Sn или Pb-Sn. Этот элемент может появляться как несколько трёхкомпонентных фаз или как твёрдые растворы. Технологическое значение имеют исследования в системе Fe-Mo-S. В этой системе присутствует MoS₂ который характеризуется большой огнеупорностью и проявляет свойства минеральной смазки. Из-за этого этот сульфид используется во время эксплуатации подшипников машин работающих в высоких температурах.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Фазовая диаграмма системы Cu-Ni-S в диапазоне температур 100—150°C
Фиг. 2. Схематическая сводка связей, которые можно наблюдать в системе PbS-GeS₂-GeS