

deposits (50–200 °C) of the Gringuro Band (0.2–1.6% Fe, 36 samples) and Kanizawa (0.3–2.4% Fe, 29 samples) (Hattori, 1975), from Western Canada (0.9–5.0% Fe, 20 samples; Evans *et al.*, 1968) and from the epithermal deposits of the Upper Mississippi Valley, Illinois–Kentucky district and SE Missouri (1.4, 2.5, and 0.5% Fe respectively; Hall and Heyl, 1968).

The trace elements found in the Ishiagu sphalerites are compared with data from other epithermal and hypothermal deposits in Table II. The data indicate that the trace elements of the Ishiagu sphalerites are similar to epithermal deposits elsewhere. The epithermal deposits have low Ag, In, Mn, and Sn, but higher Ge than the hypothermal deposits (Fleischer, 1955). Cd levels are erratic. However, the data are still scanty and many factors other than temperature may affect the trace element levels.

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Comments on the validity of badenite and epigenite

In a recent review of the literature, JCPDS, the international centre for diffraction data, has been unable to find X-ray powder diffraction data for either badenite or epigenite. These are the only sulphides given species status by Fleischer (1980) where no powder diffraction data has been found. Palache *et al.* (1944) consider that badenite needs confirmation and epigenite needs further study. Neither of these minerals are given species status by Strunz (1970) and badenite is not given species status by Embrey and Fuller (1980). Since the original descriptions of badenite in 1900 and epigenite in 1869 no further descriptions have been found by the author. From X-ray powder diffraction data of epigenite (Royal Ontario Museum specimen M11582) from the type locality, Berry and Thompson (1962) indicate its similarity to tetrahedrite.

The chemical formula of badenite given in Palache *et al.* (1944) as $(\text{Co,Ni,Fe})_3(\text{As,Bi})_4$ is different from that given by Dana and Ford (1909) as $(\text{Co,Ni,Fe})_2(\text{As,Bi})_3$. The chemical analysis given

has 61.54 As, 4.76 Bi, 0.27 S, 20.56 Co, 7.39 Ni, 5.98 Fe, and 100.50% total. This chemical analysis may be calculated into a chemical formula of $(\text{Co,Ni,Fe})(\text{As,Bi,S})_{1.47}$. Since the atomic size of Bi is significantly greater than As, Bi is highly unlikely to substitute for As. If Bi occupies a discrete crystal structure site then the chemical analysis may be calculated into a chemical formula of $(\text{Co,Ni,Fe})_{25.5}(\text{As,S})_{36.5}\text{Bi}_{1.0}$. Such a chemical formula is unlikely due to the high ratios involved. The binary alloy diagrams given by Hansen and Ånderko (1958) do not show intermediate compounds between FeAs and FeAs₂, CoAs and CoAs₂, and NiAs and NiAs₂. Neither does the investigation of a natural Ni–Co–As assemblage by Misra and Fleet (1975). Therefore both the metal: non-metal ratios of 3:4 and 2:3 are unlikely in these chemical systems. Calculations show that a mixture of 5% bismuth, 55% safflorite (CoAs₂), and 40% moderite (CoAs) would fit the chemical analysis of badenite.

The chemical formula of epigenite given in

Palache *et al.* (1944) as $(\text{Cu,Fe})_5\text{AsS}_6$? is based upon the chemical analysis of 40.68 Cu, 14.23 Fe, 12.75 As, 32.34 S, and total 100.00%, after deduction of 2.12% Bi as Cu_3BiS_3 (wittichenite) and recalculation. This chemical analysis may be calculated into a chemical formula of $(\text{Cu,Fe})_{5.3}\text{AsS}_{5.9}$ or $(\text{Cu}_{2.17}\text{Fe}_{0.86})(\text{S}_{3.42}\text{As}_{0.58})$. The metal:non-metal ratios of 3:4 is identical to that of greigite Fe_3S_4 , which has a spinel-type structure. This structure formula is unlikely, because, first Cu has only been observed to occupy one of the three metal sites (e.g. carrollite-fletcherite series, $\text{CuCo}_2\text{S}_4\text{-CuNi}_2\text{S}_4$), and secondly As has not been observed to substitute for S in such a large quantity. Experimental phase diagrams have been published in the Fe-As-S system by Clark (1960) and in the Cu-Fe-S system by Taylor and Kullerud (1971). Phase diagrams for the Cu-Fe-As-S system have been proposed by McKinstry (1957) based upon literature descriptions of natural assemblages. The chemical analysis of epigenite falls within the quadrilateral of tennantite-chalcocopyrite-pyrite-arsenopyrite in this Cu-Fe-As-S phase diagram. Calculations show that a mixture of 60% tennantite $(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$, 30% chalcocopyrite CuFeS_2 , and 10% pyrite FeS_2 would fit the chemical analysis.

In order to question the validity of badenite and epigenite, specimens were sought from numerous national museums, and replies were received from London, Aachen, Berlin, Bonn, Clausthal, Göttingen, Marburg, Vienna, Toronto, Chicago, New York, Philadelphia, and Washington. No reply has been received from the University of Jassy, where Poni described badenite. No specimen was available from the University of Würzburg, where Sandberger described epigenite. One badenite specimen AM17962 from the type locality of Badeni-Ungureni, Muscel, Romania was obtained from the American Museum, NY. Three epigenite specimens (AM26761, NMNH R1172, NMNH 138163), all from the type locality of Neuglück mine, Wittichen, Baden, West Germany, were obtained; one from the American Museum, NY and two from the National Museum of Natural History, Washington. X-ray diffraction studies supported by electron probe analysis have been made of these sulphides.

An electron probe analysis with a Kevex solid-state detector of the badenite specimen showed not only Ni, Co, and As, but also distinct Bi inclusions. Powder X-ray diffraction of the specimen shows rammelsbergite, nickeline, and bismuth. These observations support the available theoretical evi-

dence that there are no intermediate compounds in the Co-Ni-As-Bi system between $(\text{Co,Ni})\text{As}$ and $(\text{Co,Ni})\text{As}_2$, and also that Bi does not substitute for As in either of these compounds. Although this specimen contains amounts of Fe, Co, and Ni different from those of the original specimen, these elements are chemically similar since they are adjacent in the periodic table. Substitution within the Co-Ni-Fe diarsenides has been experimentally determined by Roseboom (1963).

The epigenite specimen (AM26761) was identified as arsenopyrite; (NMNH R1172) as skutterudite; and (NMNH 138163) was found to be a mixture of arsenopyrite, pyrite, and tetrahedrite or tennantite. Although chalcocopyrite was not found in these specimens, it was in the original description (Palache *et al.*, 1944).

Every reasonable effort was made to obtain the type specimen and also specimens from numerous national museums, which is the correct procedure to discredit a mineral. All the theoretical evidence and available observations indicate that badenite is a mixture of bismuth, safflorite, and modderite, and that epigenite is a mixture of tennantite, chalcocopyrite, and pyrite. Therefore the International Mineralogical Association voted recently to discredit both of these mineral species.

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