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A note on occurrences of nickeliferous and cupriferous mackinawite

TWO occurrences of mackinawite $Fe_{1-x}S$, one nickeliferous, the other cupriferous, examined by the writer so well illustrate the wide variability that may exist in the paragenesis of a single mineral as to warrant brief description.

Nickeliferous mackinawite was identified in the ores and enclosing country rocks of the Scotia nickel sulphide deposit, Western Australia (Ostwald, 1973). The mineral occurs in two associations: as irregular myrmekitic intergrowths with pentlandite of the ore, especially where the ore has undergone incipient supergene alteration; and as elongate 'stringers' and laminae (50 μ m to 0.5 mm wide) in strongly deformed serpentinite layers within and adjacent to the ore body.

The mackinawite is optically spectacular, with bireflection from pale blue-grey to a dull golden-yellow. Anisotropism is very strong with well-defined colours, especially blues, and white. The bireflection is accompanied by a variation in $R\%$ (589 nm) from 22 to 45% (approx.). This range is sufficiently different from that of the optically similar mineral valleriite ($R = 14-22\%$) for optical distinction of the two minerals to be carried out. VHN determinations on the Scotia mineral (at 25 g load) yielded a range of values of 51-82, with a mean of 61 for ten determinations.

Electron probe microanalysis determinations (average of five chemically similar grains) indicated Fe 54.9%, Ni 8.8%, Co 0.4%, Cu 0.1%, S 35.8%, and calculations indicated a metal/sulphur ratio of 1.02 and a formula $(Fe_{0.86}Ni_{0.13}(Co + Cu)_{0.01})_{\Sigma 1.02}S$.

Thus Scotia mackinawite is essentially FeS with part of the Fe replaced by Ni and very minor amounts of Co and Cu. In terms of its metal/sulphur ratio, the derived formula is within the range of values (0.994-1.026) determined by Springer (1968) for this mineral.

The *cupriferous mackinawite* was identified somewhat tentatively in a thin layer of black pyritic mud at a depth of some half metre beneath a water seepage situated at a conglomeratic sand (upper) and shale (lower) contact in a suburb of Newcastle, New South Wales. Attention was drawn to the layer during excavation by the presence of an iridescent coating on the layer (probably due to rapid oxidation of iron minerals in the layer). pH determinations on fresh exposures indicated 6.0 and the occurrence suggested that the mineral was the product of a reducing environment.

Microscopic examination of the dried mud showed the presence of abundant spheres of framboidal pyrite, detrital grains of quartz,

feldspar, mica, and other silicates, a clay fraction, and a poorly defined material best described as a dense gel.

The identification of this latter material as a poorly crystalline cupriferous mackinawite is based on the following three observations:

Scanning electron microscopy and X-ray energy-dispersive spectrometry investigations on the dried gel indicated the presence of major Fe and S and minor Cu.

Select area electron diffraction indicated that the material was largely amorphous but that certain areas gave poorly defined patterns indicating crystalline material.

Electron probe microanalysis on areas of the substance that could be roughly polished indicated Fe 55–8%, S 35–7%, and Cu 5–8%. These results suggest a metal/sulphur ratio of near unity but the nature of the specimens precluded more precise estimations.

This metal/sulphur ratio and the presence of copper suggests that the mineral is mackinawite rather than the closely related mineral smythite Fe_9S_{11} (Taylor and Williams, 1972) or greigite Fe_3S_4 (Skinner *et al.*, 1964) though the latter is known to occur in modern lake sediments (Dell, 1972). The presence of copper, in particular, may be indicative of mackinawite, as Cu has been reported in the mineral by Clark and Clark (1968) and by Springer (1968), and a phase of composition $\text{Cu}_{0.12}\text{Fe}_{0.94}\text{S}_{1.00}$ was tentatively identified by Clark (1970) as a member of a cuprian mackinawite solid-solution series. The origin of the copper in the Newcastle mineral is problematical. A primary copper source is unlikely and it could well be that the original iron sulphide gel scavenged copper ions from superficial ground water that had encountered buried scrap metals, etc.

The mode of occurrence of the Scotia nickeliferous mackinawite suggests that it is a low-temperature alteration product of pentlandite, rather than an exsolution product as postulated by van Rensburg and Liebenberg (1967). Certainly the cupriferous mackinawite is of low-temperature origin though the precise mechanism involved was not studied. It is interesting to consider this occurrence in relation to the experimental work of

Berner (1964), Rickard (1969), and Sweeney and Kaplan (1973). According to these investigations the formation of low-temperature sedimentary pyrite involves reaction of H_2S and dissolved iron to produce an amorphous iron sulphide or mackinawite of formula $\text{FeS}_{0.9}$ followed by alteration of these sulphides to hexagonal pyrrhotine and continued reaction of these monosulphides with elemental sulphur under reducing conditions to form greigite Fe_3S_4 and finally pyrite FeS_2 . Sweeney and Kaplan also concluded that the transformation of the monosulphides to greigite resulted in spherical structures, which were subsequently converted into pyrite framboids. In the light of these results it appears likely that the pyrite framboids found in association with the cupriferous mackinawite were crystallization products of this monosulphide. The fate of the copper following complete alteration of mackinawite to pyrite is a matter for speculation.

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