

the liner is placed in the autoclave, and the annular space between the liner and autoclave is charged with sodium hydroxide solution and about one-half gram of silica. In this way a layer of acmite, a sodium ferric iron silicate, is formed on the internal surfaces of the autoclave making them impervious to attack from the aqueous solution up to 425°C. There is no attack at this temperature. The autoclave is sealed, and the system brought to proper temperature. During heat-up the liner bellows can expand or contract if a pressure difference develops between the internal fluid and the annular fluid. With proper selection of the percent fill of the liner and the annular space, the change in linear dimension of the liner is negligible. The final pressure can be adjusted as desired by addition of fluid to the annular space with a fluid pump or by withdrawal of fluid.

The liner has several additional advantages. Heliarc welding is not required to seal the liner, and the flared silver disc and steel collar, plug and machine screws are easily replaced. The liner can be removed easily from the autoclave, facilitating repairs and charging and clean-up procedures. The design allows scale-up to any size autoclave, making commercial application feasible. The exposure of dangerously corrosive potassium hydroxide solution is confined to silver surfaces only.

Silver liners as described have been used successfully hundreds of times up to 400°C for the hydrothermal growth of crystals of potassium metal phosphates and related substances. A wide variety of metals including platinum and gold can be formed into bellows and thus lend themselves readily to the basic design. Physical and chemical requirements of the system under investigation together with economic considerations would dictate the choice of material.

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NICKELIAN MACKINAWITE FROM VLAKFONTEIN, TRANSVAAL: A DISCUSSION

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I would like to present some published and new observations on naturally-occurring mackinawite, which complement those of Vaughan (1969), who has described an unusually nickel-rich specimen of this mineral from the Transvaal.

Vaughan's conclusion that the cell size of mackinawite varies inversely with the degree of substitution of nickel and, probably, other transition metals for iron, is based on his own data for the Vlakfontein material, and on those of Kouvo, Vuorelainen and Long (1963) for a mackinawite from Outokumpu, Finland. The present author (in Clark and Clark, 1968) obtained tetragonal cell dimensions of $a=3.673\pm 0.002$ and $c=5.034\pm 0.002$ Å for an end-member, iron-mackinawite, with a composition of $\text{Fe}_{1.064}\text{S}$ (Ni, Co, and Cu not detected), from the Ylöjärvi deposit, Finland (Clark, 1966; cf. Kouvo, Vuorelainen and Long, 1963). The few available determinations, therefore, support Vaughan's conclusion that replacement of iron by nickel and cobalt results in a marked decrease in the cell size; the a -dimension, however, apparently remains essentially constant over a wide composition range, from *nil* to 22 weight percent Ni+Co. Clark and Clark (1968) concluded that solid solution of nickel and cobalt in mackinawite is accompanied by a significant diminution in c , but suggested that a concomitantly increases slightly. This tentative conclusion was based only on a comparison of the data for mackinawites from Ylöjärvi and Outokumpu.

Consideration of the cell dimensions reported by Berner (1964) for synthetic iron mackinawite ($a=3.679\pm 0.002$; $c=5.057\pm 0.002$ Å) would lead to the conclusion that *both* a and c decrease with increasing Ni and Co content. However, the significant differences in the cell dimensions of the synthetic and Ylöjärvi mackinawites introduces some uncertainty. While Berner (1964) assumed that his "tetragonal FeS" was in fact iron-rich, it is possible that these natural and synthetic iron mackinawites exhibit differing departures from stoichiometry. The potential existence of marked variations in the metal:sulfur ratios of "polymetallic" mackinawites should encourage caution in the assessment of the precise interrelations of mackinawite composition and cell dimensions.

In this context, it should perhaps be pointed out that the cell edge values determined by Kouvo, Vuorelainen, and Long (1963) are in one respect somewhat ambiguous. The quoted parameters are stated (p. 519) to be "valid . . . for a material having about 5 percent nickel," on the basis of an X-ray fluorescence analysis of similar *euhedral* crystals associated with, among other sulfides, nickel pentlandite. On the other hand, these authors found only ~ 0.7 percent Ni+Co (their Table 2, p. 518) by electron microprobe analysis of *euhedral* mackinawite from the same locality in the mine, suggesting either that such crystals are compositionally zoned, or that the fluorescence analysis was made on impure material. In any event, Vaughan is incorrect in assigning the cell edge measurements to the *anhedral* mackinawite with Co, 0.2 and Ni, 5.4 ± 0.3

percent (microprobe analysis; Kouvo, Vuorelainen and Long, 1963; Table 2, p. 518). A combined nickel and cobalt content of less than one percent for the Outokumpu mackinawite would be in rather better agreement with the proposed cell dimension *vs.* composition relationship than would one of 5.4 percent.

The suggestion (Vaughan, 1969, p. 1192) that the Vickers micro-indentation hardness of mackinawite increases with increasing nickel content was previously advanced by both Clark (1966) and Schidlowski and Ottemann (1966), albeit on the basis of fewer quantitative data. Although Vaughan employed a load of 25 gram, whereas Chamberlain and Delabio (1965) and the author (1966) used one of 50 gram, his new data clearly demonstrate the markedly greater hardness of mackinawite rich in nickel than that of specimens poor in that metal.

In view of the undoubtedly marked dependence of micro-indentation hardness on mackinawite crystal orientation, it would seem to me that the determination of the precise relations between composition and hardness in this sulfide would best be carried out by measurement of hardness variations on one or more *selected* crystal faces. In practice, non-birefractant and weakly anisotropic surfaces, assumed to be approximately perpendicular to the *c*-axis, may be observed in polished sections of most natural assemblages of anhedral or subhedral mackinawite. For this reason, the author (1966) made micro-indentation hardness measurements for the Ylöjärvi iron-mackinawite on such faces, obtaining a comparatively small hardness range ($VH_{50} = 52 \pm 3$; mean value 50.6) for 16 grains showing subdued anisotropism. However, if, as suggested above, the *a* cell dimension of mackinawite changes little with nickel substitution, basal sections of mackinawite have the disadvantage in this context of potentially exhibiting only minor changes in hardness with varying composition.

Continuing studies of mackinawite from the Kilembe Cu-Co deposit, Uganda, indicate that cobalt has a comparable effect on the hardness of this mineral. Coarse-grained mackinawite (grain diameters up to 4–500 μm) has been shown by microprobe analysis to contain only traces of nickel (≤ 0.5 percent) and minor copper (~ 0.3 –1.3 percent), but between ~ 4 and more than 18.5 percent cobalt. Individual grains are occasionally zoned with respect to cobalt:iron ratios, but the greater proportion are essentially homogeneous, with cobalt contents ranging over less than one percent.

Vickers micro-indentation hardness values have been determined (Fig. 1) for five analysed mackinawite grains, containing from 4.9 (± 0.5) to 16.5 (± 0.6) percent cobalt, and exhibiting only weak anisotropic

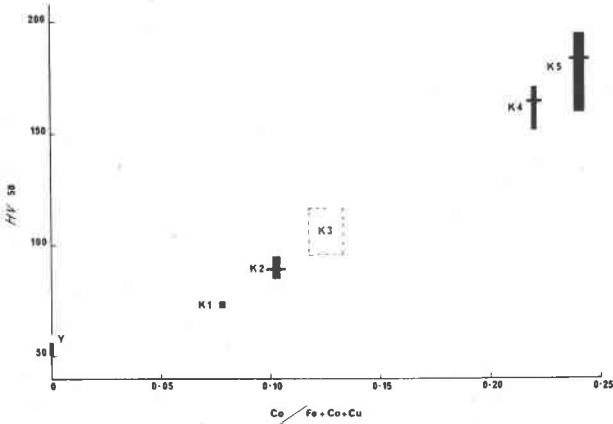


FIG. 1. Relationship between Vickers micro-indentation hardness (VH_{50}) and cobalt content of mackinawites from Kilembe, Uganda. The vertical and horizontal bars indicate, respectively, the overall and mean micro-indentation hardness values for each specimen. The combined nickel and copper contents of the mackinawites do not exceed 1.5 weight percent in any case. Specimen K3 exhibits compositional zoning and relatively poor micro-indentation hardness value reproducibility. The VH_{50} for the nickel- and cobalt-free Ylöjärvi mackinawite is included for reference.

effects. One of the grains tested (K3) showed an appreciable compositional zonation. The indentations, obtained with a Leitz Durimet-Pol instrument and a 50 gram load, are consistently of good quality, each with diagonals of almost equal lengths. Only a single indentation could be made on the softest, and most cobalt-poor grain, but between two and four were accommodated on the remaining specimens without apparent interference between indentations. Where more than one indentation was measured, the VH_{50} values were calculated for each indentation, and the individual determinations combined to yield a mean hardness and an overall hardness range (the "convention 1" of Leonard, 1969).

From Figure 1, it will be seen that there is a systematic, but not necessarily linear increase in VH_{50} with increasing cobalt content, from 74 to 160–195 (mean, 183). Since the copper and nickel contents of these mackinawites are low and relatively constant, the increase in hardness may reasonably be ascribed to the substitution of cobalt for iron. Cobalt, therefore, has an effect comparable in kind and degree to that of nickel (Vaughan, 1969). Precise comparison of the hardening effects of cobalt and nickel on the mackinawite structure must await a clarification of the variation of micro-indentation hardness with crystal orientation.

This marked increase in micro-indentation hardness of mackinawite

in *near-basal* sections may imply that, with increasing cobalt content, the *a* dimension of the tetragonal cell decreases together with the *c* dimension, in contradistinction to the apparent effect of nickel substitution. Cell-edge measurements are clearly needed for cobaltian mackinawites.

Vaughan's observation that naturally-occurring mackinawite is confined to a "relatively restricted" compositional area remains valid in the sense that iron apparently consistently exceeds other substituting metals, but it is becoming evident that this sulfide may accommodate a wide range of transition metals. Thus, H. Zôka, A. H. Clark and S. Takeno (in preparation) have found up to 8.8 percent copper in mackinawite by microprobe analysis, and the author (1969) has described a mackinawite with a significant chromium content.

There is probably little compositional overlap, in terms of Co:Ni:Fe ratio, of the pentlandite and mackinawite series in the system Co-Ni-Fe-S. However, Petruk, Harris and Stewart (1969) have shown that a cobalt pentlandite from Cobalt, Ontario, has the composition, $(\text{Co},\text{Ni})_{1.025}\text{S}$, departing significantly from the 9:8 atomic ratio normally accepted for pentlandite. This composition is *metal-poor* with respect to at least some naturally-occurring mackinawites, suggesting that the cubic π structure may have a lower thermal stability limit at low to moderate temperatures.

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NICKELIAN MACKINAWITE FROM VLAKFONTEIN, TRANSVAAL:
A REPLY

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Clark has added some useful data to the authors' original comment on nickelian mackinawite (Vaughan, 1969), especially by his work on cobalt-rich phases.

Recently, the author and M. S. Ridout (unpublished) have gained some insight into the nature of mackinawite through the study of Mössbauer spectra of the pure synthetic iron end member at 300°, 77° and 4.2°K. These spectra, with their very low isomer shifts and absence of quadrupole and magnetic hyperfine interactions even at low temperatures, suggest extensive delocalisation of electrons in mackinawite. On the basis of X-ray powder data, Berner (1962) ascribed to mackinawite the structure of tetragonal PbO with sulphur occupying the lead positions and iron the oxygen positions. This is a very unusual structure, with layers of metal cations tetrahedrally coordinated to sulphur layers above and below resulting in a Fe—S—S—Fe layer structure. The close metal-metal distances (2.6 Å) in the *x* and *y* directions in the layers suggest considerable overlap of metal 'd' orbitals which would account for the Mössbauer spectra and the absence of a magnetic moment for iron in neutron diffraction experiments (Bertaut *et al.*, 1965).

The structure of mackinawite can probably accommodate cations in additional layers between S—S layers in tetrahedral coordination with sulphur. This would explain reported Fe:S ratios in excess of 1:1. Also, such additional cations would tend to be more prevalent in phases formed (or synthesised) at low temperatures. Such nonstoichiometry should affect the value of the *c* cell parameter and may be the origin of the high values in synthetic FeS. It encourages caution in correlations of composition and cell parameters.

Extensive overlap of metal 'd' orbitals in the *x* and *y* directions sug-