Mackinawite, pentlandite, and native copper from the Newport pallasite[1]

By Peter R. Buseck

Departments of Geology and Chemistry,
Arizona State University, Tempe, Arizona 85281

[Taken as read 14 March 1968]

Summary. These minerals indicate strongly reducing conditions as well as extremely low sulphur fugacities within the Newport pallasite. They all formed at low temperatures (upper limit 580° C) and in the solid state. This is the first reported occurrence of mackinawite and pentlandite from a pallasitic meteorite; Cu is known from only one other pallasite. Microprobe analyses of a large Cu grain indicate its composition as $98{\cdot}6 \pm 0{\cdot}5$ %, Ni $2{\cdot}0 \pm 0{\cdot}5$, Fe below the limit of detection ($\sim 0{\cdot}3$).

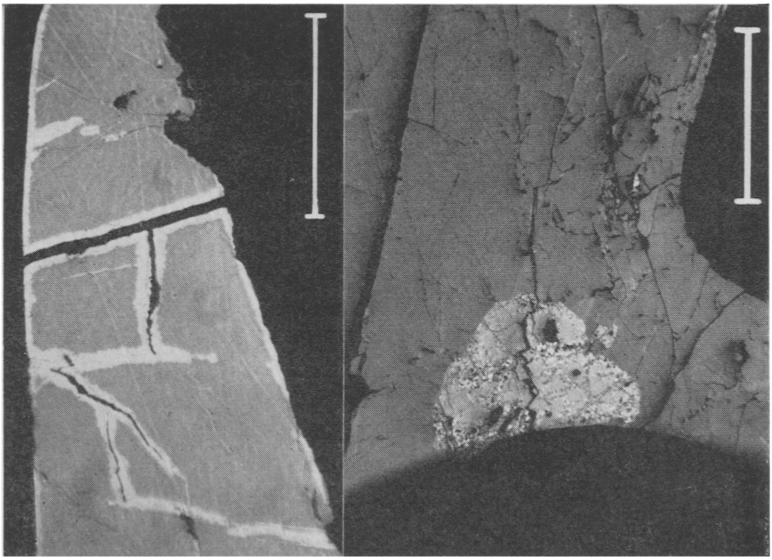
THE pallasites represent the deep interior of their parent body. However, the origin of these meteorites is a matter of controversy (Buseck and Goldstein, 1968); it is probable that a more thorough knowledge of their mineralogy and geochemistry will provide contributory information regarding the physical and chemical environment in which they existed. This report contains mineralogical results of a portion of a continuing study of these stony-iron meteorites.

Like the other pallasites, Newport contains olivine and metal as the main constituents and troilite and schreibersite as widespread minor phases. This apparently simple mineralogy of the pallasites has long made them seem a remarkable group of meteorites. Thus, the paucity of reported minerals resulted in a 'somewhat of a sensation' (Wahl, 1965) when DuFresne and Roy (1961) discovered farringtonite in Springwater. The Newport pallasite is unusual in that it contains three minerals that have not been widely reported from pallasites: mackinawite, pentlandite, and native copper. All occur next to or within troilite, and all formed at moderate to low temperatures and thus furnish data regarding the conditions within the meteorite at a relatively late period in its history.

---

[1] Contribution No. 30 from the Center for Meteorite Studies, Arizona State University.

Pentlandite. Of these three rare minerals, pentlandite is the most abundant; having seen it in Newport, I looked for it elsewhere and have since observed it as a widespread, although minor phase in most other pallasites. Its identification is based on optical properties and, in the case of Newport, this was confirmed by electron microprobe measurements. It has two modes of occurrence, similar to those described by Ramdohr (1963) for the stony meteorites: as an alteration product resulting from terrestrial weathering and as a primary phase. The former is common within troilite in most pallasites: this pentlandite can be identified by its crystallization on the peripheries of troilite areas and especially along limonite-filled fractures within troilite (fig. 1). It is produced when Ni-bearing phases such as taenite, kamacite, and schreibersite are dissolved during weathering; the Fe is then precipitated as the oxide or hydroxide and the Ni, being more chalcophile than Fe, reacts with troilite and thereby precipitates pentlandite.



FIGS. 1 and 2: FIG. 1 (left). Secondary pentlandite (white), produced by weathering, along fractures and grain boundaries within troilite (light grey). The black phase is olivine. Oil immersion; scale bar 50 μ. FIG. 2 (right). Pod of primary pentlandite (white) within troilite (dark grey). Note the white and black flecks of mackinawite within the pentlandite. The black phase is olivine. Crossed nicols. Oil immersion; scale bar 200 μ.

Primary pentlandite characteristically occurs as rounded pods within the larger troilite masses (fig. 2) rather than being localized along zones of structural or chemical weakness. Its stability relations, defined experimentally, indicate that it is unstable above 610° C, decomposing into pyrrhotine and the high-temperature form of heazlewoodite; if Fe-Ni metal is present the highest equilibrium temperature for pentlandite is only approximately 580° C (Kullerud, 1963). Thus, Newport pentlandite must have formed at moderate temperatures by a solid-state reaction, either between pyrrhotine and the high-temperature form of heazlewoodite, or by exsolution as a Ni-rich phase from pyrrhotine. The effect of increased pressure is to depress the decomposition point of pentlandite to even lower temperatures (Bell *et al.*, 1964) and therefore the above are upper limits. This assumes that there are no appreciable shifts in the stability fields resulting from either the absence of vapour or the presence of such minor constituents as Cu.

Mackinawite. A much rarer phase in meteorites than pentlandite is mackinawite, a tetragonal iron sulphide first described by Evans *et al.* (1963). It has not been previously reported from pallasites. It is pronounced in polished sections because of its extreme reflection pleochroism and anisotropism. Although these optical properties are exceptional, valleriite has similarly outstanding optical properties, and, as a result, the two have often been confused. Valleriite has been described from stony meteorites by Ramdohr (1963, 1966), with speculations that it might be mackinawite, and in his 1965 paper Ramdohr does report mackinawite from several mesosiderites. El Goresy (1965) reports it from iron meteorites.

Although I have seen mackinawite in several pallasites, including Imilac and Antofagasta, it is most pronounced in Newport, where it occurs within the primary pentlandite. The mackinawite grains are too small for extraction for X-raying. Consequently, its identification presented difficulties that had to be resolved by electron microprobe study. Electron-beam scans of pentlandite enclosing the presumptive mackinawite were run, with the microprobe set to continuously sweep across an area containing an abundance of the grains in question. Only Fe, Ni, and S were present (detection limit is 0·2 %). The absence of copper precludes the occurrence of valleriite. Line traverses for Fe and Ni, and electron beam scanning photographs for Ni-$K\alpha$, Fe-$K\alpha$, Cu-$K\alpha$, and S-$K\alpha$ support these results, and indicate the presence of mackinawite. The Ni-$K\alpha$ scan photograph appeared mottled, suggesting that these mottlings may reflect variations in the Ni concentration, due to the presence of the small inclusions. Their identification as mackinawite seems reliable.

Mackinawite is a low-temperature mineral. Its upper stability limits, provided the results of heating experiments are reliable, range between 135° and 245° C, the higher temperatures being for the most Ni- and Co-rich samples (Clark, 1966).

Although difficult to prove, it is probable that the Newport mackinawite is a primary phase. It is unlikely that mackinawite is a common product of terrestrial weathering. Berner (1962) pointed out that under near-surface conditions it is unstable, rapidly oxidizing to lepidocrocite and sulphur. Further, at the Muskox intrusion, one of the most thoroughly studied mackinawite occurrences, the sulphides are commonly weathered to marcasite and limonite but never to mackinawite. It does not even persist in surficial samples that are structurally and stratigraphically equivalent to rocks bearing mackinawite at depth (Chamberlain, 1967; Chamberlain and Delabio, 1965).

Terrestrially, mackinawite commonly occurs within pentlandite. Similarly, in Newport it occurs exclusively in pentlandite. It surely formed after the pentlandite and, except possibly for the native Cu, is thus the lowest temperature mineral that has been observed within the pallasites, exclusive of those produced during terrestrial weathering. In view of the lack of primary hydrous phases within Newport, this mackinawite is unique in that, in distinction to terrestrial occurrences, it formed in the apparent absence of an aqueous phase.

Native Cu. With close microscopic work it is becoming increasingly evident that native Cu is a widespread, albeit minor, phase in meteorites (Ramdohr, 1963). However, with the exception of the extremely badly weathered Molong (Ramdohr, 1966), Newport is the only pallasite in which free Cu has been reported. Of the eight pallasites analysed for Cu by Lovering *et al.* (1957), Newport is also the one with the highest Cu content (240 ppm), although several other pallasites do not indicate significantly lower concentrations. Several grains of Cu were observed within Newport; they usually occur along the boundary between troilite (which in some cases encloses mackinawite and pentlandite) and kamacite. In a few places the Cu is enclosed within troilite. The Cu grains typically enclose or are bordered by small grains of taenite (fig. 3). As the troilite in pallasites is normally swathed by kamacite rather than taenite, the occurrence of taenite near to the Cu is anomalous. The textural evidence suggests that the taenite was in solid solution within the Cu and exsolved on cooling. It thus indicates that the Cu is a primary phase, in contrast to the secondary Cu reported by El Goresy (1965) from some iron meteorites.

Using the electron microprobe, a spectrometer scan was run to determine the composition of the Cu. Only minor Fe and Ni and lesser Co were detected. Problems with fluorescence of Fe by Cu-$K\alpha$ are encountered during quantitative analyses for Fe (Duke and Brett, 1965).

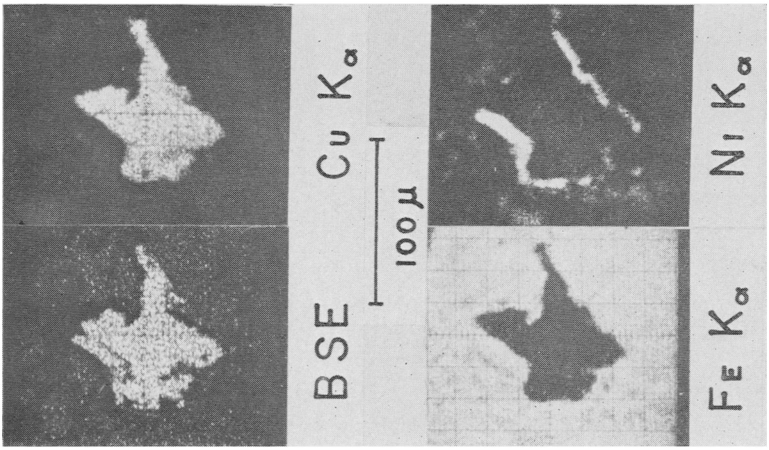


FIG. 3. Electron-beam scan photographs (at 30 Kv and 0·03 μA sample current) of native copper (white area in the photograph for Cu-$K\alpha$ radiation) partly rimmed by taenite (white area in the photograph for Ni-$K\alpha$ radiation) and lying within troilite. The photographs were taken by scanning an electron beam over the area of interest on the sample and recording the signals on the cathode ray tube of an oscilloscope so that the cathode ray beam on the oscilloscope is synchronized with the electron beam scanning the sample. BSE = back scattered electrons; the degree of 'whiteness' is roughly proportional to the average atomic weight.

The measurement for Fe was therefore made by monitoring the Fe-$L\alpha$ peaks. Thus, an anomalous Fe concentration of 3·4 % was determined from the $K\alpha$ peak, whereas no counts above background were detected from the $L\alpha$ peak, i.e. the Cu is effectively Fe-free. The composition of a large grain of Cu in Newport is: Cu 98·6±0·5 %, Ni 2·0±0·5, Fe <0·3 (detection limit). Another, smaller grain indicated 99·4±0·5 % Cu.

Considering the relevant binary systems Cu–Ni and Cu–Fe (Hansen, 1958), it appears probable that solid solution is extensive between the isostructural phases of Cu and taenite, and very limited between Cu and kamacite. Cu within taenite would therefore be exsolved when the alloy is cooled into the kamacite stability field. However, although some Cu may have exsolved from the Fe-Ni, consistent association of Cu with troilite also suggests a genetic relation to the sulphide.

The typical association of kamacite–Cu–troilite (the minor taenite appears to be a late exsolution phase) in Newport approximates the assemblage Fe–Cu–troilite, studied by Yund and Kullerud (1966). Consideration of their experimentally determined phase diagrams of the system Cu–Fe–S indicates that native Cu cannot coexist stably with Fe and Fe monosulphide above 475°±5° C. Instead, a bornite solid solution occurs. Thus, the upper temperature limit for an assemblage analogous to that in Newport is 475°±5° C.

The coexistence of troilite and native Cu requires very low oxygen and sulphur fugacities. It is sufficiently unusual for Garrels and Christ (1965, p. 166) to state that 'the Cu-FeS association is not known to occur in nature'. Actually, in addition to the present occurrence, it has recently been described from a highly reduced zone within the Muskox intrusion (Chamberlain *et al.*, 1965), one of the few reported places where mackinawite is reported to occur naturally.

The oxygen fugacity for the observed assemblages cannot be directly estimated, although limiting values can be ascertained from the lack of observed primary iron oxides or phosphates. Thus, the values given by Olsen and Fuchs (1967) for curve B of their fig. 1 is an approximate upper limit for the oxygen fugacity in the Newport pallasite.

Thermochemical calculations permit evaluation of the limiting sulphur fugacities for the stable coexistence of native Cu and troilite. At sufficiently low fugacities both Fe and Cu will be elemental while at high fugacities both will occur as sulphides. The first Cu-bearing sulphide to form on sulphidization is bornite. However, as free energy data are unavailable for it, the calculations were made for chalcocite, Cu_2S; this should serve as an upper limit for the sulphur fugacity. The thermochemical data are from Kubaschewski, Evans, and Alcock (1967) and the results are shown in fig. 4. The calculations assume that the activity of the Fe in the metal is unity, i.e. that the Ni has no great effect on the equilibria. The curves are terminated at 475° C, the upper temperature limit for the stable coexistence of Cu and troilite. Note the surprisingly narrow range of permissible fugacities (table I) required to get coexisting Cu and FeS. If the Cu and troilite did indeed coexist from 475° C down to present temperatures, rather than the Cu resulting from low-temperature exsolution, this would suggest a well-buffered system to maintain the sulphur fugacity within the required limits. Presumably the abundant kamacite fulfilled this role, thereby suggesting that the actual

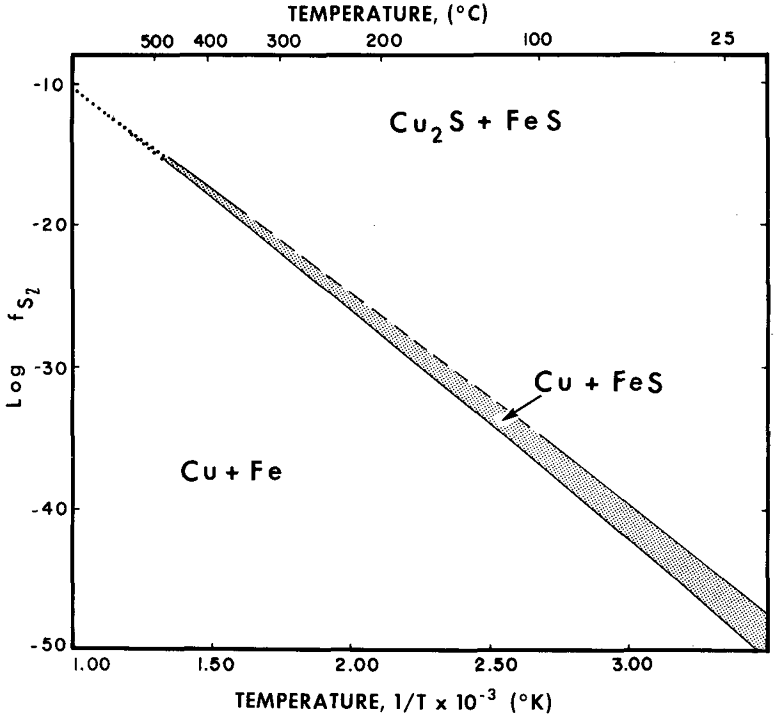


FIG. 4. Calculated field of stability (shaded) for coexisting troilite and native Cu as a function of the sulphur fugacity and temperature.

TABLE I. Calculated limiting values of $\log_{10} f_{S_2}$ for coexisting troilite and native Cu

T	*Lower limit* ($Fe + \frac{1}{2}S_2 \rightleftharpoons FeS$)	*Upper limit* ($2Cu + \frac{1}{2}S_2 \rightleftharpoons Cu_2S$)
475° C	−15·5	−15·2
400°	−17·8	−17·3
350°	−19·7	−19·0
300°	−21·9	−20·9*
200°	−27·7	−26·1*
100°	−36·7	−34·7

*Estimated by interpolation.

change in the fugacities would be indicated by the lower curve in fig. 4. These results indicate that in no event did the sulphur make a major contribution to the total pressure within the meteorite.

Conclusions. Pentlandite and mackinawite have not been previously recorded from pallasites; native Cu was known only from Molong. In the case of Newport, all these minerals occur, and formed in the solid state. Experimental work and terrestrial field relations indicate that the upper temperature limit for the pentlandite is 580° C, for native Cu it is 475° C, and for the mackinawite it is 245° C and perhaps even 135° C. The sulphur fugacity could not have been greater than 10^{-15} atm. and it was surely many orders of magnitude lower at temperatures below 400° C. Thus, the occurrence of these minerals indicates that new phases were forming in the Newport pallasite even at relatively low temperatures and that extremely low sulphur fugacities and highly reducing conditions obtained.

Acknowledgements. The specimens of Newport came from the Nininger Meteorite Collection of the Center for Meteorite Studies, Arizona State University. Dr. Joseph Goldstein kindly provided advice with the microprobe measurements and correction of the microprobe data. The use of the microprobe of the Goddard Space Flight Center is gratefully acknowledged, as is the assistance of Frank Wood and Charles Lewis with the sample processing. Helpful discussions were held with Drs. Joseph Goldstein, Carleton Moore, and Michael O'Keeffe. The research was supported in part by grants from NASA (NsG-399) and the Arizona State University Grants Committee.

References

Bell (P. M.), England (J. L.), and Kullerud (G.), 1964. Ann. Rep. Geophys. Lab., Carnegie Inst. Wash. Year Book 63, pp. 206–207.

Berner (R. A.), 1962. Science, vol. 137, p. 669.

Buseck (P. R.) and Goldstein (J. I.), 1968. Science, vol. 159, pp. 300–302.

Chamberlain (J. A.), 1967. Can. Journ. Earth Sci., vol. 4, pp. 105–153.

—— and Delabio (R. N.), 1965. Amer. Min., vol. 50, pp. 682–695.

—— McLeod (C. R.), Traill (R. J.), and Lachance (G. R.), 1965. Can. Journ. Earth Sci., vol. 2, pp. 188–215.

Clark (A. H.), 1966. Neues Jahrb. Min., Monatsh., vol. 10, pp. 300–304.

DuFresne (E. R.) and Roy (S. K.), 1961. Geochimica Acta, vol. 24, pp. 198–205.

Duke (M. B.) and Brett (Robin), 1965. U.S. Geol. Surv. Prof. Paper 525–B, B101–B103.

El Goresy (Ahmed), 1965. Geochimica Acta, vol. 29, pp. 1131–1151.

Evans (H. T., *Jr.*), Berner (R. A.), and Milton (Charles), 1963. Geol. Soc. Amer., Special Paper 73, p. 147.

Garrels (R. M.) and Christ (C. L.), 1965. Solutions, Minerals, and Equilibria: Harper & Row, New York, 450 pp.

Hansen (Max), 1958. Constitution of Binary Alloys: McGraw-Hill, New York, 1305 pp.

Kubaschewski (O.), Evans (E. Ll.), and Alcock (C. B.), 1967. Metallurgical Thermochemistry: Pergamon Press, New York, 495 pp.

Kullerud (G.), 1963. Can. Min., vol. 7, pp. 353–366.

Lovering (J. F.), Nichiporuk (Walter), Chodos (Arthur), and Brown (Harrison), 1957. Geochimica Acta, vol. 11, pp. 263–278.

Olsen (Edward) and Fuchs (H.), 1967. Icarus, vol. 6, pp. 242–253.

Ramdohr (P.), 1966. Proc. Roy. Soc. New South Wales, vol. 99, pp. 45–55.

RAMDOHR (P.), 1963. Journ. Geophys. Res., vol. 68, pp. 2011–2036.
—— 1965. Monatsb. deut. Akad. Wiss. Berlin, vol. 7, pp. 923–938.
WAHL (WALTER), 1965. Geochimica Acta, vol. 29, pp. 177–181.
YUND (R. A.) and KULLERUD (GUNNAR), 1966. Journ. Petrology, vol. 7, pp. 454–488.

[*Manuscript received 21 August 1967*]