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MACKINAWITE FROM THE WITWATERSRAND CONGLOMERATES

Manfred Schidlowski and Joachim Ottemann,
Department of Mineralogy, University of Heidelberg, Germany.

Introduction

Investigations by several workers (Evans *et al.*, 1962; Kuovo *et al.*, 1963; Chamberlain and Delabio, 1965) have shown that mackinawite, tetragonal iron sulfide containing varying amounts of Ni and Co, is a common though minor constituent of a great variety of rocks and economic mineral deposits. Until recently known as "valleriite" (Blomstrand, 1870), it has been lately separated from the latter, since the "valleriite"-type has proved to consist of two distinct mineral phases, namely valleriite proper, having a chemical composition close to $CuFeS_2$, and tetragonal FeS, mackinawite (Evans *et al.*, 1964). Although differing both in crystal structure and chemical composition, these two minerals are very similar in their appearance under the microscope and in their paragenetic associations which rendered a distinction between them rather difficult. Once familiar with the subtleties of their optical properties, however, it is in most cases possible to separate them without diffiiculty in polished section. Chamberlain and Delabio (1965) have tabulated certain optical and physical properties which help to serve as distinguishing features.

Microscopic Physiography and Chemical Composition

In the course of an ore-microscopic investigation of Witwatersrand gold conglomerates from the Orange Free State goldfield (South Africa) we had an opportunity to observe a peculiar mineral occurring only in traces or minor amounts and displaying a very strong, graphite-like anisotropism. Moreover, it was generally characterized by a rather high bireflectance varying from pinkish-white to gray (Figs. 1-1, 1-2), although, on the other hand, cases have been encountered where this pleochroism was insignificant. As a rule, the mineral forms minute flakes or very small grains commonly showing indications of crystallographic terminations (Figs. 1, 2). Small particles usually exhibit a fairly smooth surface (Fig. 1) whereas large ones take only a moderate polish and are commonly badly scratched (Fig. 2). The hardness appears to be of the order of chalcopyrite or slightly higher. This is neither in accord with the findings of Kuovo *et al.* (1963) nor with those of Chamberlain and Delabio (1965), but apparently bridges the gap between conflicting opinions expressed in these two papers. The hardness of mackinawite probably depends on the chemical composition (Ni and Co contents) as well as on its crystallographic orientation within the polished section.

These properties in connection with the common occurrence of the phase along with sulfides left very little doubt that the mineral in question was actually mackinawite. In order to confirm the optical diagnosis, a microprobe investigation has been carried out, the results of which are summarized in the scanning pictures of Figs. 1 and 2. As is known from previous chemical and microchemical investigations (Kuovo *et al.*, 1963; Evans *et al.*, 1964; Chamberlain and Delabio, 1965), mackinawite contains some Ni, as already inferred from paragenetic considerations by Schneiderhöhn (1929). This Ni content ranges from mere traces up to about 8%. Besides, minor amounts of Co (normally <0.2–1.5%) have been reported by most analysts.

It is evident from the scanning pictures that in the areas underlain by mackinawite conspicuous $\mathrm{Ni}_{\mathrm{K}\alpha}$-intensities were recorded, whereas the neighboring sulfides (chalcopyrite, pyrrhotite) show no indication of nickel at all. In Fig. 2 the measurements have been extended to include cobalt. The distribution pattern of cobalt—although weak due to the minor amounts present—coincides excellently with the outlines of the mackinawite grain investigated, this being proof that cobalt is restricted to this mineral. Accordingly, the results of the microchemical analyses corroborate the observation that mackinawite is present among the constituents of the Witwatersrand conglomerates.

In the case of the grain depicted in Fig. 2 a quantitative determination of nickel and cobalt has been carried out. As a standard, a mackinawite sample from Outokumpu, Finland, was used, whose chemical analysis had been given by Kuovo *et al.* (1963, p. 517, sample II). Compared with this standard (containing 8.17% Ni and 0.37% Co) the Ni and Co con-

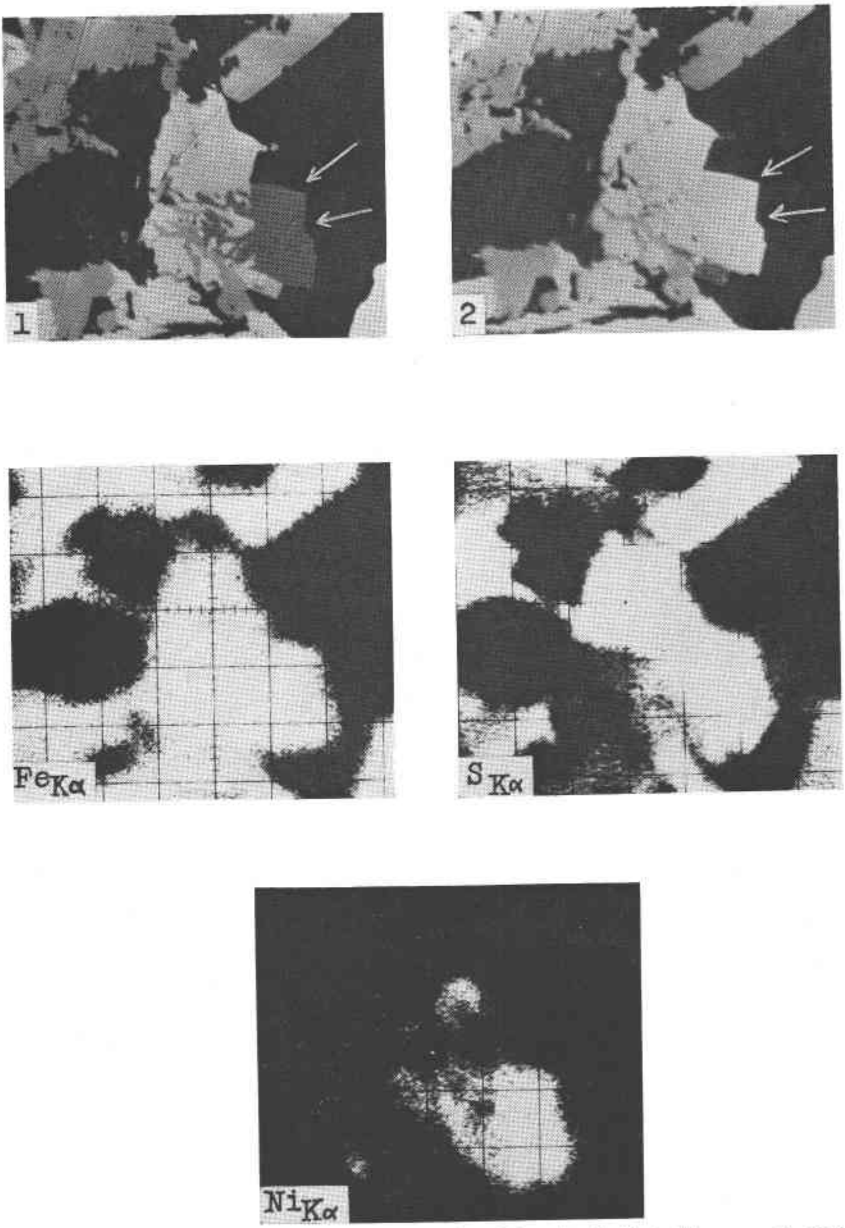

FIG. 1. Assemblage of sulfides consisting of mackinawite (indicated by arrows), chalcopyrite and pyrrhotite (note big lath in the NE). Mackinawite is partially intergrown with chalcopyrite; attention is drawn to its extremely strong pleochroism (pictures 1 and 2). Below: Scanning pictures for Fe, S and Ni. Basal Reef, Free State Geduld Mine, Orange Free State goldfield. 850× (1 and 2 taken in oil immersion).

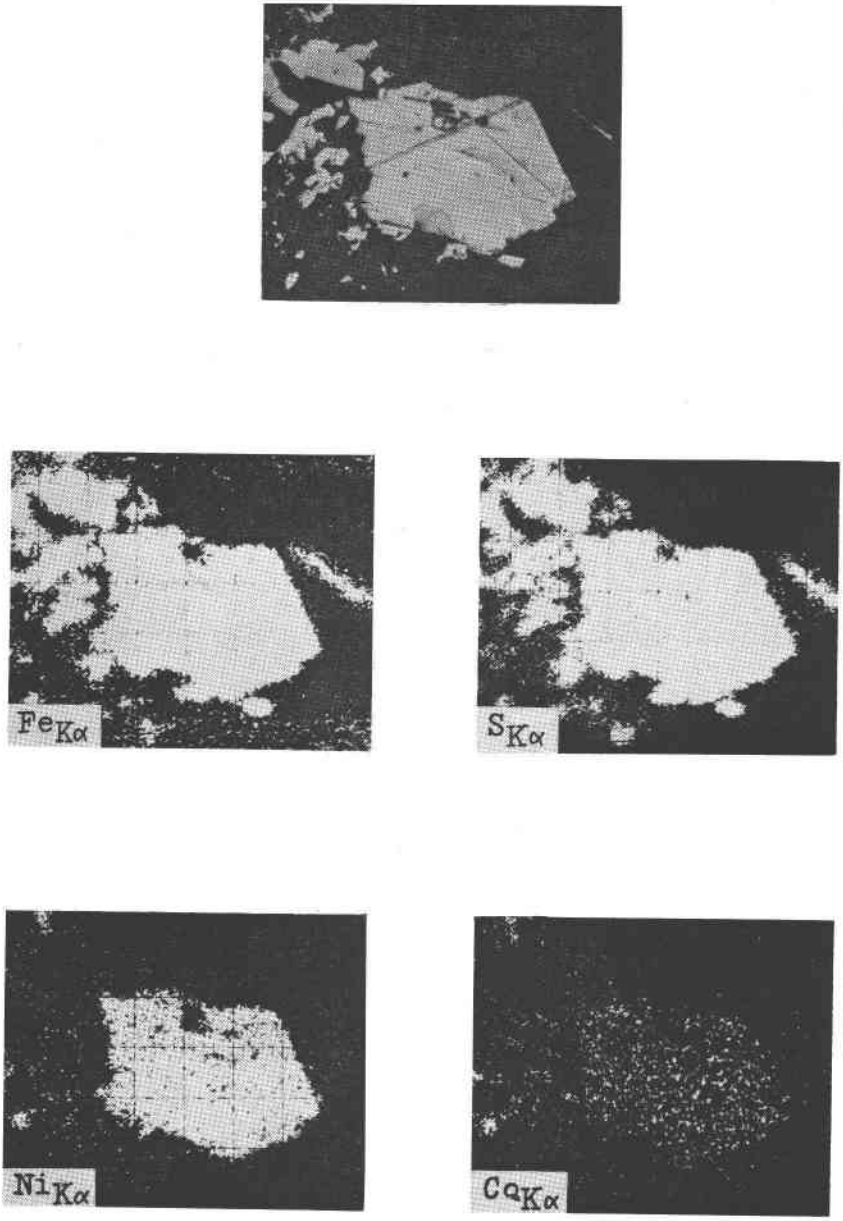

FIG. 2. Big grain of mackinawite (with scratches) surrounded by minor pyrrhotite particles. Below: Scanning pictures for Fe, S, Ni, and Co. Basal Reef, Free State Geduld Mine, Orange Free State goldfield. 385× (optical picture in oil immersion).

tents of the Witwatersrand grain were slightly higher. As an average of six measurements we found for Ni 9.462 and for Co 0.65 weight %. These results lie well within the range of values reported for mackinawite.

ORIGIN AND OBSERVED PHASE RELATIONS

It is well known that the conglomerates of the Witwatersrand System contain certain amounts of sulfides (about 3% average), the bulk of which usually consists of rounded grains of pyrite. These grains have been convincingly interpreted as detrital constituents by Ramdohr (1958 a), although some authors (*e. g.*, Davidson, 1957) regard them as replacements of primary quartz grains and, accordingly, the whole sulfide assemblage as being of hydrothermal origin. It is outside the scope of this communication to deal at length with the so-called "Witwatersrand controversy" concerning the origin of sulfides, uraninite and gold; it should be stated, however, that one of the authors, during an extensive ore-microscopic investigation performed in recent years, has come to conclusions similar to those first advanced by Ramdohr (1954) and Liebenberg (1955).

In their further geological history the sediments of the Witwatersrand System underwent certain changes, however. During a later phase of metamorphism (the peaks of which coincided with the period of the Ventersdorp volcanism and the intrusion of the Bushveld Igneous Complex) it is postulated that circumstances were created which closely resembled genuine hydrothermal conditions, thereby giving rise, *inter alia*, to a partial recrystallization of the primary detrital sulfide fraction as well as to a certain mobilization and redeposition of gold; furthermore, brannerite (UTi_2O_6) is believed to have been formed from allogenic uraninite and rutile (Ramdohr, 1957). Due to this "pseudohydrothermal" activity a number of secondary sulfide phases (pyrite, pyrrhotite, pentlandite, chalcopyrite, linnaeite, etc.) are present in the conglomerates, all of which are regarded as resulting from an extensive reconstitution of the primary allogenic sulfide fraction.

In its occurrence, mackinawite is almost always associated with these secondary or "recrystallized" sulfides. Shape as well as paragenetic affiliations of the individual grains indicate beyond doubt that the mineral has formed *in situ*. In Fig. 1 it is found in contact with, and partially intergrown with, chalcopyrite, the latter forming part of the sulfide aureole of a so-called "uraninite ghost," that is, a primary uraninite grain now presumably completely changed into brannerite (Ramdohr, 1957; Schidlowski, 1966). The mackinawite particle depicted in Fig. 2 is within an assemblage of newly-formed pyrrhotite crystals. With a maximum diameter of about 0.08 mm, this grain is among the largest ever encountered in the conglomerates; normally the particles are considerably smaller. Very commonly minute flakes of this mineral have been observed as exsolution bodies within chalcopyrite. In one instance, this chalcopyrite formed exsolution blebs itself, occurring in a small nest of sphalerite; within these blebs mackinawite was found along with pyrrhotite and (locally) chalcopyrrhotite.

According to Borchert (1934), the temperatures required for the formation of mackinawite are of the order of about 225–250° C. These data were originally advanced for "valleriite" in its former sense, but refer actually to mackinawite (Ramdohr, pers. comm.). Temperatures of this order, therefore, should have been attained during metamorphism; the occurrence of newly-formed chloritoid in the Witwatersrand conglomerates is, however, likely to indicate a still higher temperature. On the other hand, it should be noted that Berner (1962) was able to synthesize mackinawite from aqueous solution at room temperature and atmospheric pressure in a strongly reducing environment.

Finally, the local occurrence of mackinawite within some of the presumed primary detrital pyrite grains of the conglomerates merits attention. The phase has been noted forming minute flakes in some of the characteristic oval inclusions mainly composed of chalcopyrite and pyrrhotite which are often contained in individual pyrite grains; with regard to these inclusions the presence of "valleriite" had already been recorded by Ramdohr (1958b). In these cases mackinawite has obviously entered the conglomerates as a component of constituents regarded by us as allogenic.

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APPLICATION OF PLASTIC PEEL TECHNIQUES TO THE STUDY OF SILICATE ROCKS

DANIEL S. BARKER, *Department of Geology, The University of Texas, Austin, Texas.*

The plastic peel techniques described by McCrone (1963), Stewart and Taylor (1965) and Frank (1965) provide easily and cheaply prepared supplements to thin sections for studies of carbonate rocks. A sheet of plastic, placed on the rock surface, is softened by a solvent which then evaporates; the plastic conforms in minute detail to surface irregularities such as grain boundaries, cleavages and etch pits. The plastic is peeled off and bears a reverse replica of the microtopography of the rock surface.

The plastic peel method can be applied to silicate rocks. Dollar (1942) and Bissell (1957) strongly endorsed this application; igneous and metamorphic petrologists generally have ignored the technique. This note is