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SHANDITE, $Ni_3Pb_2S_2$, IN A SERPENTINIZED METADUNITE FROM THE ISUA SUPRACRUSTAL BELT, WEST GREENLAND

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ABSTRACT

The rare sulfide mineral shandite, $Ni_3Pb_2S_2$, has been identified in a metadunite from the Isua Supracrustal Belt, West Greenland. It forms a thin (*ca.* 10 µm) continuous rim on heazlewoodite, Ni_3S_2, which, in addition, contains patches of Co-rich pentlandite, $Co_{7.0}Ni_{1.5}Fe_{0.5}S_8$. Mg-, Ni-rich magnetite is associated with these sulfide aggregates as well. The shandite is interpreted to have formed during prograde metamorphism of serpentinite from a Fe–Ni–Co(–Pb?) "pentlandite" precursor phase, by a continuous reaction that involved desulfidation and oxidation of iron, possibly of the form: pentlandite (Fe,Ni-rich, Co-poor) + H_2O → pentlandite (Fe,Ni-poor, Co-rich) + heazlewoodite + shandite + magnetite + H_2S, where the water is supplied by the breakdown of serpentine. The Pb needed to form shandite may have been present in the precursor phase, or was extracted from the environment during reaction. Shandite is difficult to distinguish optically from heazlewoodite. Other ultramafic metamorphic rocks containing sulfides with a high metal/sulfur ratio should be examined for its presence, especially those with awaruite.

Keywords: shandite, heazlewoodite, pentlandite, magnetite, olivine, serpentinite, dunite, metamorphism, Isua, Greenland.

SOMMAIRE

On a trouvé la shandite, sulfure rare de composition $Ni_3Pb_2S_2$, dans une métadunite de la ceinture Isua de roches supracrustales, dans le Groënland occidental. Elle forme un liséré d'environ 10 µm autour des grains de heazlewoodite Ni_3S_2 qui contiennent, en plus, des taches de pentlandite cobaltifère $Co_{7.0}Ni_{1.5}Fe_{0.5}S_8$. Une magnétite riche en magnésium et en nickel leur est associée. On attribue la shandite à un événement de métamorphisme prograde, qui aurait affecté une "pentlandite" Fe–Ni–Co (–Pb?) primaire dans une serpentinite selon une réaction continue impliquant à la fois désulfurisation et oxydation du fer: pentlandite (riche en Fe et Ni, pauvre en Co) + H_2O → pentlandite (pauvre en Fe et Ni, riche en Co) + heazlewoodite + shandite + magnétite + H_2S. L'eau serait le résultat de la déstabilisation de la serpentine. Le plomb nécessaire pour la shandite pourrait avoir été présent dans le précurseur, ou extrait du milieu pendant la réaction. On ne parvient à distinguer la shandite de la heazlewoodite qu'avec difficulté. D'autres roches ultramafiques contenant des sulfures à rapport élevé de métal à soufre, et, tout particulièrement, de l'awaruïte, pourraient aussi contenir de la shandite.

(Traduit par la Rédaction)

Mots-clés: shandite, pentlandite, magnétite, olivine, serpentinite, dunite, métamorphisme, Isua, Groënland.

INTRODUCTION

The purpose of this note is to document an occurrence of the extremely rare sulfide mineral *shandite*, $Ni_3Pb_2S_2$, which has been identified during a systematic investigation of ultramafic metamorphic rocks from the 3800-Ma Isua Supracrustal Belt, West Greenland. The shandite is found in serpentinized "metadunite" where it forms a delicate rim on composite grains of heazlewoodite–pentlandite. This metadunite is of additional interest because it contains intergrowths of titanian chondrodite and clinohumite, which are considered elsewhere (Dymek *et al.* 1983). In the present paper, I report the petrography and chemistry of the sulfide assemblage, and discuss its origin in light of relevant experimental data and other evidence bearing on the metamorphic history of the Isua belt.

GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

The Isua Supracrustals outcrop in an arcuate belt about 25 km across situated approximately 150 km northeast of Godthåb, the administrative centre of Greenland. The supracrustal rocks comprise a diverse suite of clastic to chemical metasediments interlayered with mafic metavolcanic rocks (Allaart 1976, Nutman *et al.* 1984). Ultramafic rocks form concordant layers or lenses within and at the margins of the above sequence, and attain a few km in strike length. They were involved in the deformation and metamorphism that affected the rest of the supracrustal sequence.

The ultramafic rocks have bulk compositions ranging from dunite to harzburgite, and contain a metamorphic mineralogy consisting of olivine + chlorite + (Cr) magnetite ± tremolite ± magnesiocummingtonite or anthophyllite ± magnesite ± dolomite (Brothers & Dymek 1983). This assemblage is indicative of middle-amphibolite-facies conditions (*cf.* Evans 1977), for which we have estimated temperatures of about 600°C (Dymek *et al.* in press). This estimate is consistent with values of 550°C calculated from garnet–biotite geothermometry on metapelites at Isua (Boak & Dymek 1982). At one locality, however, the ultramafic rocks contain relict orthopyroxene + green spinel, an assemblage that indicates higher-grade conditions of uncertain affinity (T near 700°C, based on olivine–spinel thermometry).

All samples have been variably retrograded to talc–magnesite schist or antigorite serpentinite; in many cases, the retrograde assemblages have completely obliterated earlier assemblages. Traces of sulfides (pentlandite, Ni-pyrrhotite, pyrite and possible thiospinel compositions) are found in most of the ultramafic rocks, irrespective of their lithologic type.

The sample analyzed for this study (IW809–4) is a serpentinite with the bulk composition of a dunite. It consists of a few percent relict olivine (Fo_{97}; 0.4–0.6 wt.% NiO), magnesite (X_{Mg} 0.95), titanian humites (X_{Mg} 0.97), magnetite (see below) and sulfide in a "matrix" of platy to elongate serpentine (antigorite) charged with extremely fine-grained magnetite dust. This platy serpentine is pseudomorphic after the olivine, and former grain-boundaries are clearly recognizable (Fig. 1A). The

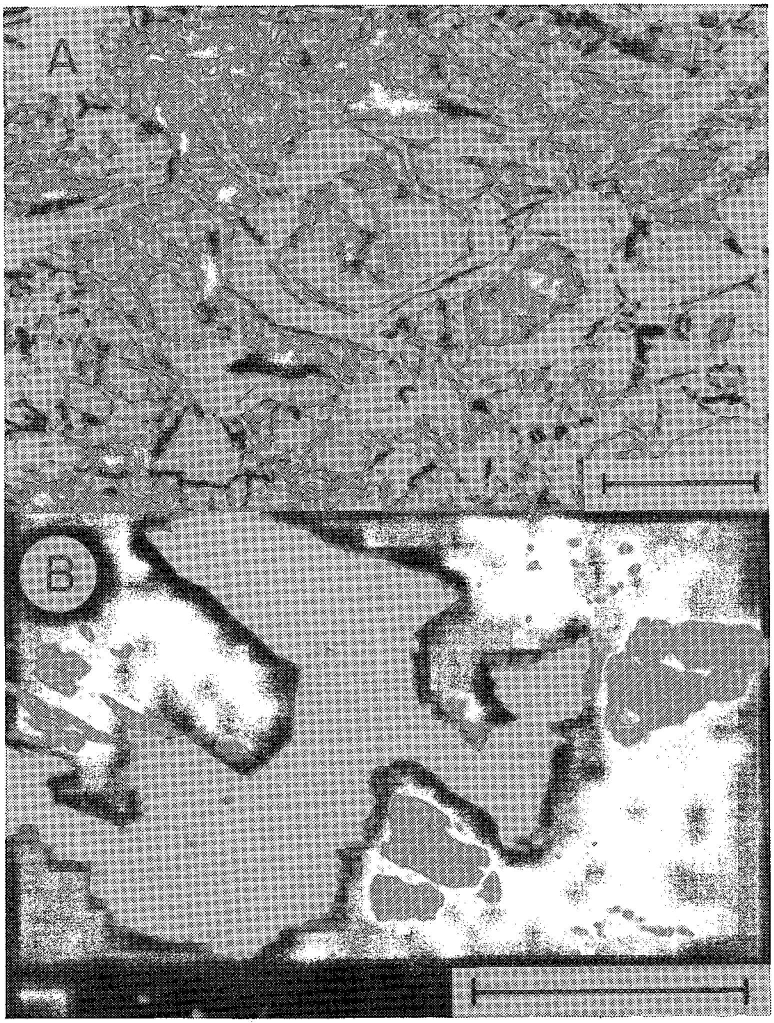

FIG. 1. A. Rounded, relict olivine grain consisting of optically continuous polygonal subareas separated from each other by serpentine and fine-grained magnetite (transmitted, plane-polarized light; bar scale 0.5 mm). B. Sulfide aggregate (bright white) with adjacent blocky magnetite (medium grey) intergrown with olivine, Ti-humite and serpentine (dark); jagged edges of sulfide represent boundaries with serpentine. Under different conditions of illumination, it is possible to see the Co-pentlandite patches in the heazlewoodite but not the shandite rims (reflected light, oil immersion; bar scale 0.1 mm).

elongate serpentine cross-cuts all other phases, and formed late in the history of the sample. The metadunite itself most probably evolved from an altered protolith such as serpentinite or talc–magnesite rock, as indicated by the highly magnesian compositions of the silicates. This early serpentinite was then metamorphosed to conditions where olivine, magnesite, Ti-humites and the sulfides formed, which were followed by events(s) of late serpentinization.

The composition of the blocky magnetite is relevant to the evolution of the metadunite, and to the genesis of the sulfide assemblage as well. This magnetite is characterized by low Cr (less than 0.2 wt. % Cr_2O_3), has essentially no detectable Al, V or Ti, but has unusually high contents of Mg (2–3 wt. % MgO) and Ni (0.8–1.2 wt. % NiO). These are among the highest values known for a relatively pure Fe^{3+}-spinel phase (*cf.* Haggerty 1975). The high X_{Mg} is in line with the overall highly magnesian compositions of the silicates, whereas the elevated Ni-content could reflect the fractionation of that element into the magnetite during serpentinization of an originally Ni-rich olivine. However, the composition of the magnetite is more likely related to the occurrence of Ni-rich sulfides, as discussed later.

Sulfide Petrography and Chemistry

Sulfides occur as somewhat amoeboid grains, up to 500 μm across, that are intergrown with olivine, Ti-humites, magnetite and elongate serpentine (Fig. 1B). Each sulfide grain comprises aggregates of three distinct, apparently homogeneous phases, which are Ni-, Co- and Pb-rich, respectively, as indicated in the back-scattered electron and X-ray images illustrated in Figure 2. Representative microprobe data on each sulfide are listed in Table 1.

The most abundant sulfide is the Ni-rich phase heazlewoodite, whose composition is close to stoichiometric Ni_3S_2. It contains only small amounts of other metals (in the present case, principally Fe, Co and Pb), which is a characteristic shared by other reported compositions of heazle-

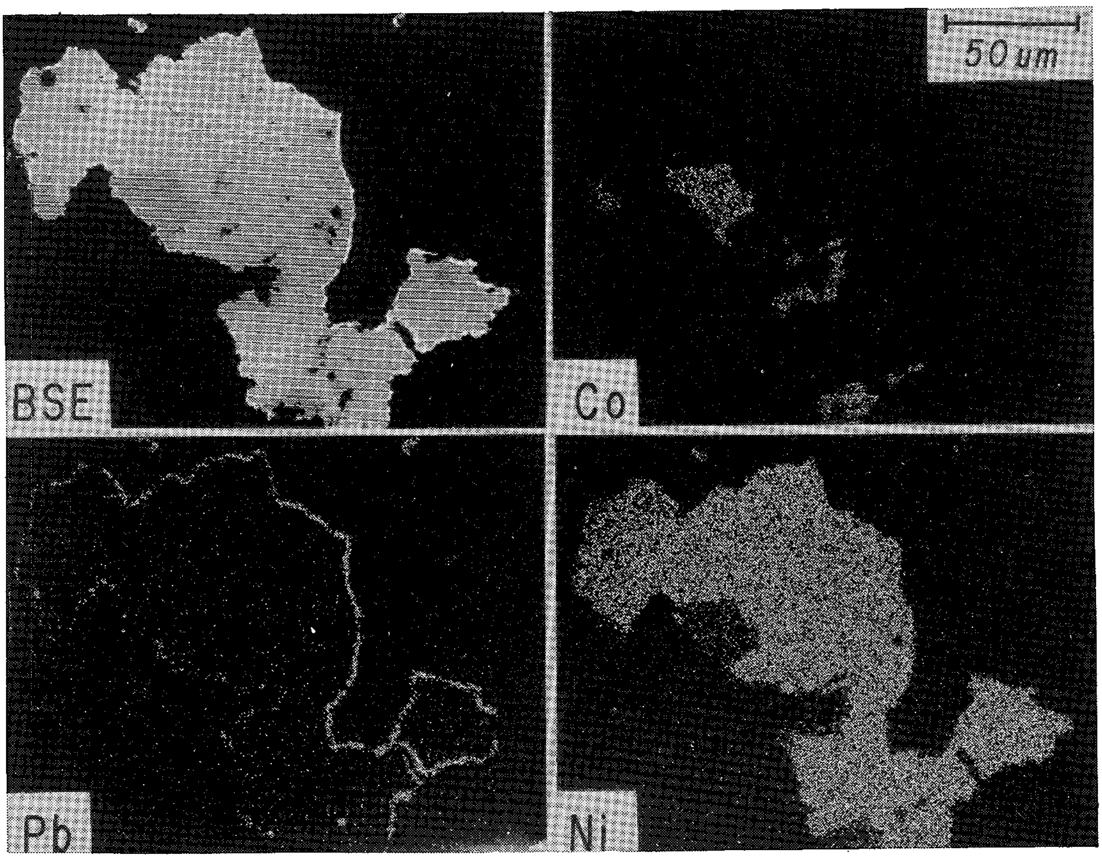

FIG. 2. Back-scattered electron (BSE) and X-ray images on sulfide aggregate. Co-, Ni- and Pb-rich regions correspond to pentlandite, heazlewoodite and shandite, respectively; note how the latter appears as a thin, continuous grain-boundary rim.

TABLE 1. COMPOSITION OF THE SULFIDES

	Weight %			Atom %		
	1.	2.	3.	1.	2.	3.
Mn	0.02	0.02	0.08	0.0	0.0	0.0
Fe	0.10	3.38	0.43	0.1	2.8	0.7
Co	0.48	52.65	0.14	0.4	41.3	0.2
Ni	72.70	11.58	28.40	59.5	9.1	44.2
Cu	0.00	0.00	0.00	0.0	0.0	0.0
Zn	0.03	0.00	0.01	0.0	0.0	0.0
Pb	0.14	0.26	61.64	0.0	0.1	27.3
Bi	-	-	0.00	-	-	0.0
S	26.47	32.35	9.58	40.0	46.8	27.5
Sum	99.95	100.24	100.29			

Approximate chemical formulae: (1) Heazlewoodite: Ni_3S_2, (2) Pentlandite: $Co_{7.0}Ni_{1.5}Fe_{0.5}S_8$, (3) Shandite: $Ni_3Pb_2S_2$.

woodite (*e.g.*, Misra & Fleet 1973). Dispersed throughout the heazlewoodite are patches of Co-rich pentlandite containing considerable Ni and Fe in solid solution. Its chemical formula corresponds to $Co_{7.0}Ni_{1.5}Fe_{0.5}S_8$, which is similar to compositions of Finnish and Canadian examples of cobalt pentlandite reported in Riley (1977; *cf.* Kuovo *et al.* 1959). The heazlewoodite–pentlandite intergrowths are in all cases surrounded by a thin continuous rim (less than 10 μm wide) of the extremely rare Pb-Ni sulfide shandite. It contains only a small amount of Fe and Co in solid solution, and has a composition close to stoichiometric $Ni_3Pb_2S_2$.

Discussion

Conditions of formation for the Isua sulfides

The overall textures of the sulfide aggregates indicate that they evolved from a precursor Ni–Co–Pb–Fe phase, possibly a Ni-rich pentlandite. This putative pentlandite could have formed during the prograde metamorphism of serpentinite (*i.e.*, along with olivine and magnesite), or from "magmatic" sulfides of uncertain type; the following discussion presumes its former presence.

Vassjoki *et al.* (1974) have determined experimentally that Co-free pentlandite having approximately equal amounts of Ni and Fe breaks down to Ni-bearing pyrrhotite and "heazlewoodite" at 610°C, and that the presence of Co increases the field of stability of pentlandite to higher temperature (although the effects of variable Fe/Ni values remain unknown). Kullerud (1963) noted that pentlandite with 51.7% Co (similar to the composition of the Isua sample) is stable to temperatures in excess of 825°C. Kullerud also showed heazlewoodite by itself to be unstable above 550°C, where it inverts to a non-quenchable high-temperature phase of variable stoichiometry.

The fact that Ni-rich magnetite invariably is associated with the sulfides in the Isua samples (*cf.* Fig. 1B), and that the sulfides are notably Fe-poor, suggests that oxidation of iron played an important role in the development of the present sulfide assemblage. Accordingly, the Isua intergrowth could have developed from a continuous reaction like the following: pentlandite (Fe,Ni-rich, Co-poor) + $H_2O \rightarrow$ pentlandite (Fe,Ni-poor, Co-rich) + heazlewoodite + shandite + magnetite + H_2S, where the water was supplied by the breakdown of serpentine. In this scenario, the shandite represents a grain-boundary precipitate stabilized in preference to the expected Ni-pyrrhotite phase owing to the presence of Pb and deficiency in S. The source of the Pb is unclear; it may have been present in trace quantities in the precursor phase, or extracted from the environment during metamorphism.

The experimental work mentioned above indicates that this proposed reaction could have occurred at temperatures in excess of 550°C, which is the preferred temperature for main-stage regional metamorphism at Isua (Boak & Dymek 1982). However, those experimental results apply strictly to the situation where the fluid was very sulfur-rich, whereas in the present case, any metamorphic fluid was certainly dominated by H_2O and CO_2. Thus the breakdown of pentlandite would be shifted to lower temperatures, possibly within the P–T region indicated for Isua metamorphism.

Other occurrences and suggestions

Shandite was originally identified and named by Ramdohr (1950), who observed it in serpentinized ultramafic rocks at Trial Harbor, Tasmania, where it occurs with heazlewoodite and the Ni–Fe alloy awaruite (awaruite has been looked for but not found in the Isua sample). Ramdohr characterized this "shandite" optically and by X-ray methods, and suggested that it represents the Pb-analogue to the Ni–Bi sulfide parkerite, $Ni_3Bi_2S_2$. Peacock & McAndrew (1950) independently confirmed the similarity in crystal structure between synthetic $Ni_3Pb_2S_2$ and the "shandite" provided to them by Ramdohr. Other investigators have provided refinements to the crystal structure of synthetic shandite (Brower *et al.* 1974, Clauss *et al.* 1978), but only one other report of its natural occurrence has been located (Nickel *et al.* 1979); these authors did not include compositional information. Thus the composition of shandite listed in Table 1 appears to be the first reported in the literature. Among other findings, the present result confirms the existence of virtually pure end-member $Ni_3Pb_2S_2$, as the Isua shandite contains no detectable Bi.

The fact that the only three known occurrences of shandite are in serpentinized ultramafic rocks suggests that a restricted set of compositional or P–T circumstances lead to its formation. The relatively high Pb-content of the Isua metadunite (13 ppm, as determined by X-ray fluorescence analysis) would appear to be an important contributing factor.

However, this rarity in nature may be more apparent than real. Although Ramdohr noted differences in reflection anisotropy between heazlewoodite and shandite in the type material, these phases are virtually indistinguishable in incident light in the Isua samples, even with the use of oil-immersion methods (no etching was carried out). Hence, the occurrence of shandite as a thin rim on heazlewoodite could be overlooked easily; in fact, the widespread presence of shandite in the Isua sample became evident only upon the use of back-scattered electron imaging. Consequently, other sulfide parageneses with a high metal/sulfur ratio should be examined for the presence of shandite.

Acknowledgements

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