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Sulphide minerals in Early Archean chemical sedimentary rocks of the eastern Pilbara district, Western Australia

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With 6 Figures

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Summary

The occurrence and paragenesis of sulphide minerals in chemical sedimentary rocks from the McPhee and the Towers Formations of the Warrawoona Group, eastern Pilbara Craton were examined, in order to evaluate the Archean sedimentary environment. The chemical sedimentary facies of both formations are comprised of chert or chert-carbonate units, which are highly depleted in detrital materials. The cherty rocks are mostly composed of microcrystalline quartz, containing significant types of syndepositional (or diagenetic) sulphide minerals. In particular, the cherty rocks in the Towers Formation (North Pole Chert, Marble Bar Chert) include primary sulphide minerals, such as pyrite, chalcopyrite, sphalerite, monoclinic pyrrhotite, pentlandite, gersdorffite and millerite. This assemblage and the measured FeS content (8.4–10.4 mol%) of sphalerite associated with the Fe-sulphide minerals suggest that the cherty rocks were formed under reducing conditions at temperatures below 200 °C (about 150 °C), and also that the metamorphic temperature of the rocks was less than $\sim$325 °C. Furthermore, the virtual absence of detrital materials and the minor element compositions imply that the cherty rocks of the eastern Pilbara Block were formed by rapid precipitation from reducing hydrothermal solutions.

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Zusammenfassung

Sulfide in chemischen Sedimentgesteinen des älteren Archaikums im östlichen Pilbara Block, Westaustralien

Das Auftreten und die Paragenese von Sulfiden in chemischen Sedimentgesteinen der McPhee und der Towers Formation der Warrawoona Gruppe, östlicher Pilbara Block, wurden untersucht, um das sedimentäre Milieu im Archaikum besser abschätzen zu können. Die chemisch-sedimentäre Fazies beider Formationen besteht aus Chert- oder Chert-Karbonat-Einheiten, die hochgradig an detritärem Material verarmt sind. Die Cherts bestehen aus mikrokristallinem Quartz, der beträchtliche Mengen an syngenetischen bzw. syndiagenetischen Sulfiden enthält. Vor allem die Cherts der Towers Formation (North Pole Chert, Marble Bar Chert) führen Pyrit, Kupferkies, Zinkblende, monoklinen Magnetkies, Pentlandit, Gersdorffit und Millerit als primäre Sulfide. Diese Vergesellschaftung und die gemessenen FeS-Gehalte der mit den Fe-Sulfiden assoziierten Zinkblende (8.4–10.4 Mol%), weisen darauf hin, daß die Cherts unter reduzierenden Bedingungen bei Temperaturen unter 200 °C entstanden sind und daß die Matamorphosetemperatur 325 °C nicht überschritten hat. Das Fehlen detritärer Sedimentkomponenten und die Spurenelementzusammensetzungen lassen darauf schließen, daß die Cherts im östlichen Pilbara Block durch rasche Ausfällung aus reduzierenden hydrothermalen Lösungen entstanden sind.

Introduction

Sulphide minerals in sedimentary rocks, except diagenetic iron sulphides, have not been practically utilized in evaluating the sedimentary environments. In particular, few studies have been made on the sulphide mineralogy of Archean sedimentary rocks, although there have been many geochemical studies (see *Holland*, 1984; *Barley*, 1993). A few exceptional cases are the mineralogical studies of banded iron-formations (BIF) of Archean age; studies related to the early history of the Earth's surface environments (see *Morris*, 1993). However, in order to put constraints on Archean surface environments, it is necessary to comprehensively investigate the mineralogy of a variety of Archean sedimentary rocks, including sandstones, shales, cherts and carbonates, since they directly reflect the chemical environments of the ocean and the atmosphere during sedimentation. The characteristics of syndepositional and diagenetic sulphide minerals can provide some constraints on depositional conditions, particularly for chemical sedimentary rocks.

The Pilbara district is a block and basin terrane of both tectonic and economic interest (*Barley* et al., 1992; *Barley*, 1993), consisting predominantly of a granitoid-gneiss complex and a surrounding greenstone belt (*Hickman*, 1983, 1990). The greenstone belt is composed of ultramafic-mafic to felsic lavas and marine sedimentary rocks which have undergone low-grade metamorphism ranging from prehnite-pumpellyite facies to lower greenschist facies (*Barley*, 1993; *Buick* et al., 1995). Thus, the sedimentary rocks from the Pilbara district are suitable for a study of surface conditions during the Archean. The objectives of this paper are to specify the occurrence and paragenesis of sulphide minerals in Early Archean chert from the eastern Pilbara district, Western Australia, along with a discussion of their minor element and sulphur isotope chemistries.

Geological background

The Pilbara Craton belongs stratigraphically to the Pilbara Supergroup, and is subdivided into four major rock units, the Warrawoona, the Gorge Creek, the De Grey and the Whim Creek Groups (*Hickman*, 1990). General descriptions of the geology and stratigraphy of the Pilbara district are outlined by *Hickman* (1983, 1990) and *Krapez* (1993), and those of the eastern Pilbara Block are given in detail by many researchers including *Lowe* (1983), *DiMarco* and *Lowe* (1989) and *Barley* (1993). The eastern Pilbara Block is mainly composed of the dominantly volcanic Warrawoona Group and the overlying younger sediments (Gorge Creek Group). The Warrawoona Group consists mainly of basaltic to felsic lavas and volcaniclastic rocks with subordinate amounts of chemical sediments, such as chert and carbonate rocks (Figs. 1 and 2). The cherty layers are observed in the McPhee Formation (<3487 Ma; *McNaughton* et al., 1993) and the Towers Formation (~3460 Ma; *Thorpe* et al., 1992). The McPhee Formation of the Talga Talga Subgroup is ~100 m in thickness, and is comprised of carbonate-rich cherty sediments with thin units of intermediate volcanic rocks and volcanic sediments (*Thorpe* et al., 1992; *Krapez*, 1993). The Towers Formation of the Salgash Subgroup is characterized by basaltic pillow lavas and small amounts of bedded chert-barite units with a thickness of 5–25 m (*Buick* and *Dunlop*, 1990). The thick cherty

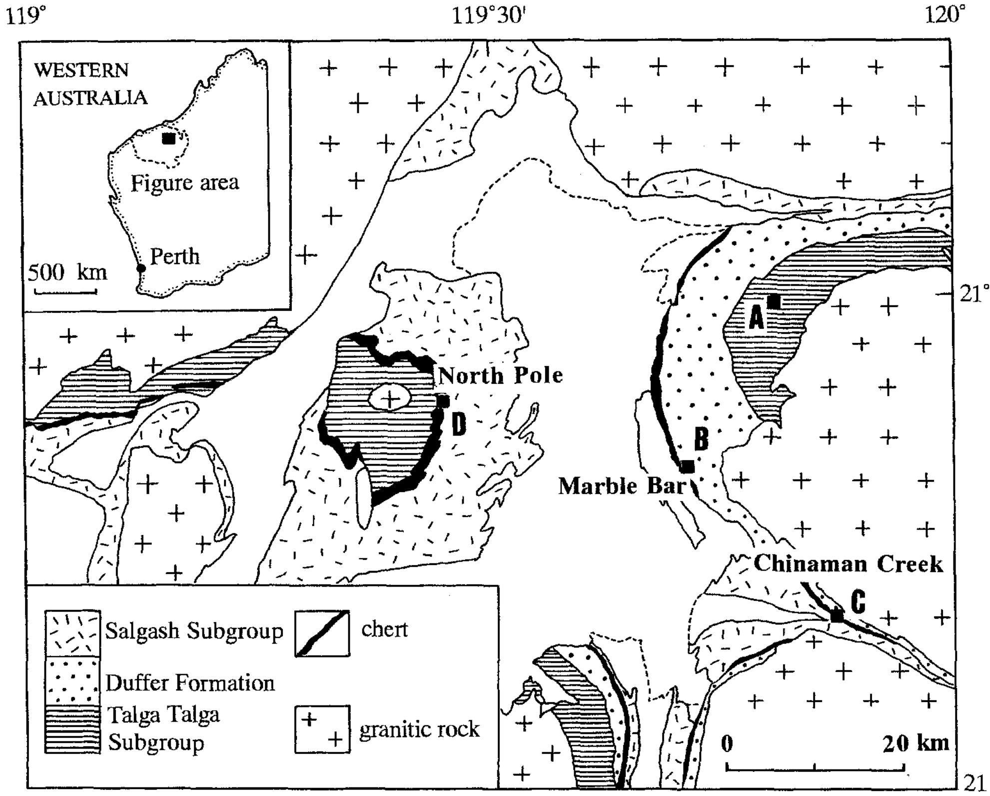
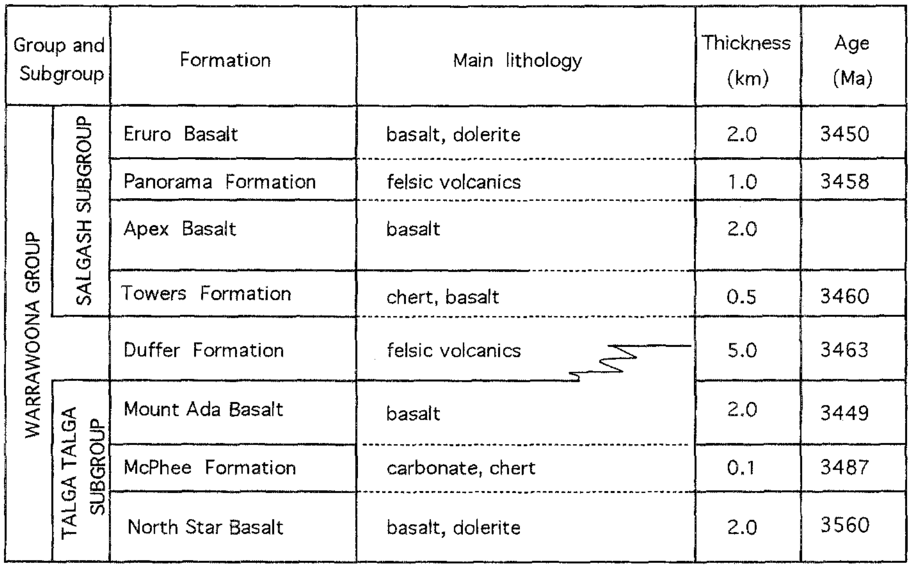


Fig. 1. Simplified geological map of the Marble Bar region, eastern Pilbara Craton (after *Thorpe* et al., 1992)



Group and Subgroup		Formation	Main lithology	Thickness (km)	Age (Ma)
WARRAWOONA GROUP	SALGASH SUBGROUP	Eruro Basalt	basalt, dolerite	2.0	3450
		Panorama Formation	felsic volcanics	1.0	3458
		Apex Basalt	basalt	2.0	
		Towers Formation	chert, basalt	0.5	3460
		Duffer Formation	felsic volcanics	5.0	3463
	TALGA TALGA SUBGROUP	Mount Ada Basalt	basalt	2.0	3449
		McPhee Formation	carbonate, chert	0.1	3487
		North Star Basalt	basalt, dolerite	2.0	3560

Fig. 2. Schematic profile showing the stratigraphy in the Warrawoona Group, compiled after *Hickman* et al. (1990) and *Krapez* (1993). The chronological data are from *Thorpe* et al. (1992) and *McNaughton* et al. (1993). In the lithology column, solid and dotted lines stand for unconformity and conformity, respectively

horizons of the Towers Formation have been given a variety of local names, such as Strelley Pool Chert (*Lowe*, 1983), Marble Bar Chert (*Hickman*, 1983) and North Pole Chert (*Buick* and *Dunlop*, 1990), and the stratigraphic relationships of these horizons have not yet been established (see *Barley*, 1993). In the present study, based on *Hickman* (1990), we consider that all the above cherty horizons belong to the Towers Formation. The North Pole area is the locality where the oldest stromatolitic cherts are found (*Lowe*, 1980, 1994; *Walter* et al., 1980). *Barley* et al., (1979) and *Barley* (1993) have suggested, based on the lithology and sedimentary structures in the Marble Bar and North Pole Cherts, that the former precipitated under a deeper-water depositional environment than the latter.

The rock specimens used in this study were collected from the carbonate-rich chert unit of the McPhee Formation (Loc. A, Fig. 1), the Marble Bar Chert (Locs. B, C, Fig. 1) and the North Pole Chert units (Loc. D, Fig. 1) of the Towers Formation; about 50 surface and core samples have been studied. Also, sulphide minerals included in a clastic sedimentary unit (Tumbiana Formation) of younger age ($\sim$2750 Ma; *Hickman* et al., 1990) were examined for comparison with those in the cherty rocks. In general, the primary sulphide minerals are better preserved in the cherty sedimentary rocks compared with the clastics (shales and sandstones).

Analytical methods

The samples were microscopically studied, using polished thin sections. For definite identification of constituent minerals, X-ray powder diffraction analysis was applied (operating conditions: 30–35 kV; 10–14 mA, Cu-Kα radiation). Moreover, qualitative and quantitative analyses of several sulphide and oxide minerals were performed by both wavelength and energy dispersive methods, using a Cameca SX-50 electron microprobe analyzer at The Pennsylvania State University and a JEOL JXA-8800M microprobe analyzer at Tohoku University. Minor element compositions for representative cherty rocks of the Towers Formation were determined using an automatic X-ray fluorescence spectrometer (Rigaku System 3080; 50 kV and 50 mA). All elements were analysed on glass beads using the calibration methods according to *Fujimaki* and *Aoki* (1987). Furthermore, mean isotopic compositions of sulphide sulphur were examined for several distinct specimens. The sulphide sulphur was extracted as Ag_2S by the method of *Sasaki* et al. (1979), using tin (II) strong phosphoric acid (*Kiba* et al., 1955). The Ag_2S obtained was then converted to SO_2 gas according to the procedure described by *Fritz* et al. (1974) and *Robinson* and *Kusakabe* (1975). All sulphur isotope analyses were carried out using a Finnigan MAT 252 mass spectrometer at Tohoku University.

Major constituents in cherty rocks

Almost all of the samples from the McPhee and Towers Formations are compact, firmly-consolidated cherty rocks. The cherts of the Towers Formation are characterized by banded or plane-laminated structure and a variety of colours, such as reddish brown, gray to black gray and greenish-gray (*Sugitani*, 1992). As described later, the reddish chert layers are relatively rich in hematite and hydroxide minerals which may be alteration products of pyrite and magnetite. Usually the cherty rocks consist of a microcrystalline mosaic of equigranular quartz ($>90 \sim 95$ volume%); such a texture of cherts is similar to that found in the ferruginous quartz (*Testusekiei*) from the Kuroko deposits, Japan. The cherty rocks of the McPhee and Towers Formations are very depleted in detrital materials, containing variable amounts of muscovite, chlorite and carbonate and trace amounts of prehnite, zircon and rutile. In the McPhee chert, muscovite is scarce, and chlorite frequently exhibits platy shapes. Radial aggregates of prehnite are observed only in a chert sample from the Towers Formation. Tiny crystals of zircon, apatite and rutile with typical prismatic habits are occasionally included in quartz.

Carbonate-rich units predominate in the McPhee Formation. Like the cherts, the carbonate-rich rocks exhibit a variety of colours; such as yellow, wine-red and greenish-gray. In the McPhee Formation, carbonate is closely associated with quartz and chlorite. X-ray powder diffraction analyses show that the carbonate unit of the McPhee Formation is comprised of dolomite, ankerite and calcite.

Sulphide minerals in cherty rocks

The results of reflected light microscopic observations are summarized in Table 1, which shows relative abundances of opaque minerals. Based on the frequency of occurrence, the relative abundance is estimated as: abundant (100–65%), major (65–35%), minor (35–10%) and trace (< 10%). In chemical sedimentary rocks, sulphide minerals may be genetically classified as: (a) post-depositional

Table 1. *A summary of opaque minerals and their relative abundance in cherty units of the McPhee and Towers Formations*

Formation	Sulphide minerals										Non-sulphides		
	Py	Sp	Cp	Po	Pn	Gd	Gn	Td	Ml	Cv	Mt	Hm	Lm
Towers F.	++	=	=	=	=	=	–	–	–	=		+	+
McPhee F.	=		=	+	+	=					++	++	++[1]
	=	=				=					=	+	+ [2]

Frequency; ++ abundant (>65%), + major (65-35%), = minor (35-10%), – trace (<10%). [1] carbonate-rich rock; [2] chert-dominant rock. *Py* pyrite, *Sp* sphalerite, *Cp* chalcopyrite, *Po* pyrrhotite, *Pn* pentlandite, *Gd* gersdorffite, *Gn* galena, *Td* tetrahedrite, *Ml* millerite, *Cv* covellite, *Mt* magnetite, *Hm* hematite, *Lm* limonite

(epigenetic), (b) detrital (exogenic), (c) diagenetic and (d) syndepositional (syngenetic). Although discrimination between these using only reflected light observations is difficult, the types of sulphide minerals found were evaluated as described below.

Firstly, we carefully checked vein-like minerals and those included in veinlets cutting sedimentary layers, and such minerals were categorized as epigenetic phases. In general, compact rounded grains were also recognized as typical allogenic detrital phases; this mode of occurrence is especially found in pyrite from Archean alluvial sediments (e.g., *Köppel* and *Saager*, 1974; *MacLean* and *Fleet*, 1989). Such pyrite is frequently found in the sandstone unit of the Tumbiana Formation (Fig. 3a), but is rarely observed in the chert units in the McPhee and Towers Formations. The textural relationships between sulphide minerals and silicate minerals are important criteria to distinguish between diagenetic and syndepositional phases. In particular, idioblastic grains are considered typical diagenetic (authigenic) products, occurring at grain boundaries of quartz and occasionally in pores and cavities of sediments. As shown in Fig. 3a, concretionary pyrite with higher porosity occurs in the sandstone unit of the Tumbiana Formation. This type, including oolitic and framboidal varieties, is generally considered as authigenic (*Köppel* and *Saager*, 1974; *MacLean* and *Fleet*, 1989). Pseudomorphous minerals are regarded to have formed as a result of secondary alteration, and so all these types would correspond to the diagenetic category. In contrast, syndepositional phases must be in concordant intergrowth with host minerals. Furthermore, we have checked microcracks and cleavages in the surrounding host minerals which may indicate effects of subsequent mineralizing solutions. The occurrence and paragenesis of the sulphide minerals present in the cherty sediments, based on the above criteria, is as follows:

Pyrite

In the Towers chert pyrite is the most conspicuous sulphide mineral, whereas it is subordinate in the carbonate-rich chert of the McPhee Formation. Usually pyrite

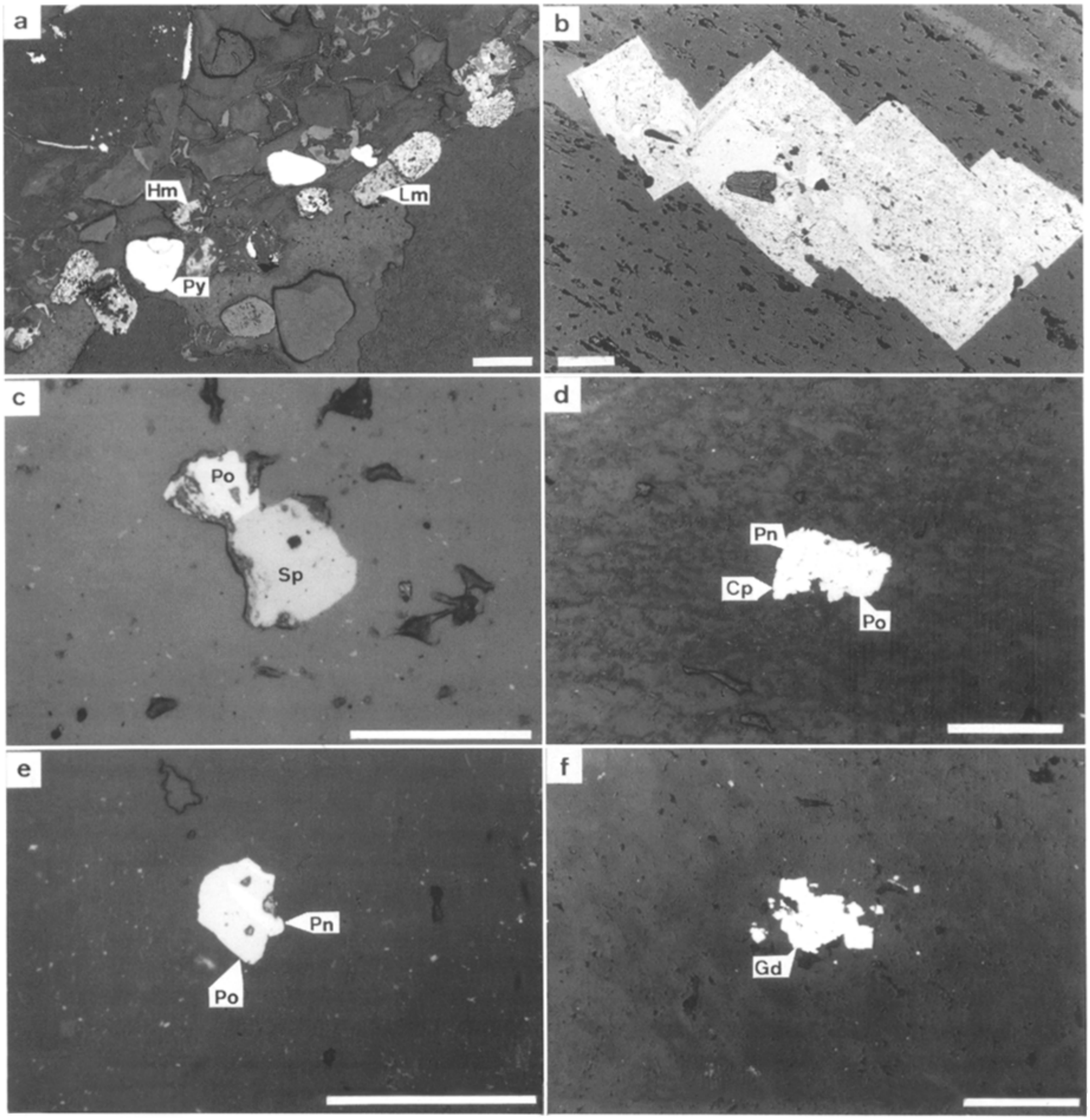


Fig. 3. Photomicrographs of same sulphide minerals and their associations in sediments from the eastern Pilbara Block, taken under reflected light. (**a**) Compact subrounded (detrial) and concretionary (diagenetic) pyrite, Tumbiana Formation; (**b**) Idiomorphic pyrite substituted by hematite and limonite, Towers Formation; (**c**) Sphalerite associated with pyrrhotite, Towers formation; (**d**) Intimate association of chalcopyrite, pyrrhotite and pentlandite, Towers Formation; (**e**) Flame-like exsolution of pentlandite in pyrrhotite, Towers Formation; (**f**) Polyhedral aggregates of gersdorffite, Towers Formation. Scale bars are 100 μm. *Py* pyrite, *Po* pyrrhotite, *Cp* chalcopyrite, *Sp* sphalerite, *Pn* pentlandite, *Lm* limonite, *Hm* hematite

occurs as irregularly-shaped granular and polyhedral grains or aggregates. The grain size of pyrite varies from <5 to ~450 µm. In general, authigenic pyrite grains are large, and occasionally exhibit an idiomorphic morphology. Such an idiomorphic pyrite observed in the Towers chert is frequently porous, and is often replaced by fine-grained aggregates of hematite (+limonite) (Fig. 3b).

Apparently diagenetic and syndepositional pyrite predominates in the cherty units. Detrial pyrite is nearly absent (<1.0%), although considerable amounts of epigenetic pyrite (~30%) are contained. EPMA analyses show that syndepositional pyrite in the Towers chert contains trace amounts of Ni, Co and Cu, and that the pyrite pseudomorph is heterogeneous in chemical compositions: i.e. Fe_2O_3, 82.8–88.3 mol%; SiO_2, 1.5–3.1 mol%; NiO, 0.9–2.0 mol%, P_2O_5, 0.2–0.4 mol%. These data reveal that the pyrite pseudomorph is composed mostly of hematite (+limonite).

Sphalerite

Subordinate amounts of sphalerite are observed in both cherts, frequently coexisting with chalcopyrite. Sphalerite occurs as irregularly-shaped grains, and displays grain sizes ranging from <5 to ~50 µm. Usually, sphalerite shows various colours from light yellow to reddish orange under transmitted light. Chemical compositions of sphalerites associated with pyrrhotite and/or pyrite in the Towers Formation (Fig. 3c) are given in Table 2, which shows that the Fe contents of sphalerite are in a narrow range of 4.2–5.2 at.% (8.4–10.4 mol%).

Table 2. *Selected microprobe data of sphalerite, pentlandite and millerite in cherty rocks from the Towers Formation*

Mineral	Fe	Zn	Cu	Ni	Co	Mn	Cd	As	Sb	S	Total
Sphalerite	6.1	61.5	0.3	–	–	0.0	0.04	–	–	33.1	101.0
	5.2	45.0	0.2	–	–	0.0	0.02	–	–	49.5	
	5.6	61.6	0.1	–	–	0.02	0.1	–	–	32.7	100.1
	4.9	45.6	0.1	–	–	0.02	0.1	–	–	49.3	
	5.0	61.6	0.2	–	–	0.03	0.03	–	–	33.3	100.1
	4.3	43.5	0.1	–	–	0.03	0.01	–	–	49.9	
	4.9	61.8	0.0	–	–	0.01	0.06	–	–	33.0	99.8
	4.2	45.8	0.0	–	–	0.01	0.03	–	–	49.9	
Pentlandite	28.6	–	0.0	38.8	0.0	–	–	0.0	0.0	32.7	100.0
	23.4	–	0.0	29.8	0.0	–	–	0.0	0.0	47.3	
Millerite	3.2	–	1.0	62.7	0.6	–	–	0.0	0.02	32.6	100.0
	2.6	–	0.7	48.9	0.5	–	–	0.0	0.01	47.3	
	2.8	–	0.3	63.3	0.4	–	–	0.04	0.0	33.1	100.0
	2.4	–	0.3	49.2	0.3	–	–	0.02	0.0	47.9	

Weight and atomic percents are in the upper and lower rows, respectively

Chalcopyrite

Frequently chalcopyrite occurs as discrete grains or fine inclusions in sphalerite. Except for the inclusion-type, the chalcopyrite is considered to be mostly syndepositional in origin. In the cherts from the Towers Formation, chalcopyrite is closely associated with pyrrhotite and pentlandite, the two minerals forming direct intergrowths (Fig. 3d). No admixtures were detected by qualitative microprobe analyses in this chalcopyrite.

Pyrrhotite

Small amounts of pyrrhotite coexisting with chalcopyrite and lamellar pentlandite are observed in the McPhee and the Towers Formations (Fig. 3e). The pyrrhotite has a composition $Fe_{46.7}Cu_{0.1}S_{53.2}$, belonging to the monoclinic type with the ideal composition nearly equal to Fe_7S_8. Although pyrrhotite occurs more frequently in the McPhee Formation than in the Towers Formations, the grain size of the pyrrhotite is generally small ($< 5\,\mu m$).

Ni-bearing sulphides

Pentlandite ($(Ni,Fe)_9S_8$), gersdorffite (NiAsS) and millerite ($Ni_{1-x}S$) are observed, and the former two minerals are found also in the younger clastic sediments of the Tumbiana Formation. Although gersdorffite is optically similar to pyrite, careful observation shows that gersdorffite has a lower hardness and lighter colour than pyrite.

Pentlandite occurs as composite grains which have mutual boundaries with pyrrhotite or as flame-like exsolution in pyrrhotite (Fig. 3e). The pentlandite in the Towers Formation, which is closely associated with pyrrhotite, is relatively Ni-rich (~ 30 at.%). No Co has been detected in the pentlandite (Table 2). Gersdorffite is found also in both formations, occurring as polyhedral crystal aggregates (Fig. 3f). Qualitative analyses show that the gersdorffite in the Towers chert contains small amounts of Fe, Co, Cu and Sb. As shown in Table 2, millerite observed only in the Towers cherts contains appreciable amounts of Fe (2.4–2.6 at.%), Cu (0.3–0.7 at.%) and Co (0.3–0.5 at.%).

Other sulphides

Trace amounts of tetrahedrite are observed only in a sample from the Towers Formation, and this contains no detectable amounts of As nor Fe. In the Towers cherts covellite occurs as a supergene product replacing chalcopyrite.

Oxide and hydroxide minerals

Hematite and limonite are observed in almost all samples, however being more abundant in the reddish cherts. As seen in Fig. 3b, the two phases occur as post-depositional secondary (diagenetic) phases replacing pyrite or magnetite. Limonite usually shows brownish to yellowish colours, exhibiting colloform and spherulitic textures in cherty sequences of the Towers Formation. Magnetite occurs as polyhedral discrete grains in the carbonate-rich chert unit of the McPhee Formation.

Minor element and sulphur isotope chemistries

The average concentrations of some minor elements contained in 20 chert specimens from the Towers Formation were determined, and compared with those of hydrothermal (inorganic) and radiolarian (biogenic) cherts (Fig. 4). The average composition of the Towers cherts is similar to those of the hydrothermal cherts accompanied by pillow basalts (Franciscan Terrane and DSDP Leg 32: *Yamamoto*, 1987) including the *Tetsusekiei* from the Kuroko deposits, Japan (*Kalogeropoulos* and *Scott*, 1983), which are represented by the stippled range in Fig. 4. As compared with the hydrothermal cherts, however, the Towers cherty rocks are rich in Ni (~150 ppm), Zn (~190 pm) and Cr (~74 ppm) and poor in Fe (~8,100 ppm) and Pb (~7.6 ppm). Such high concentrations of minor metals

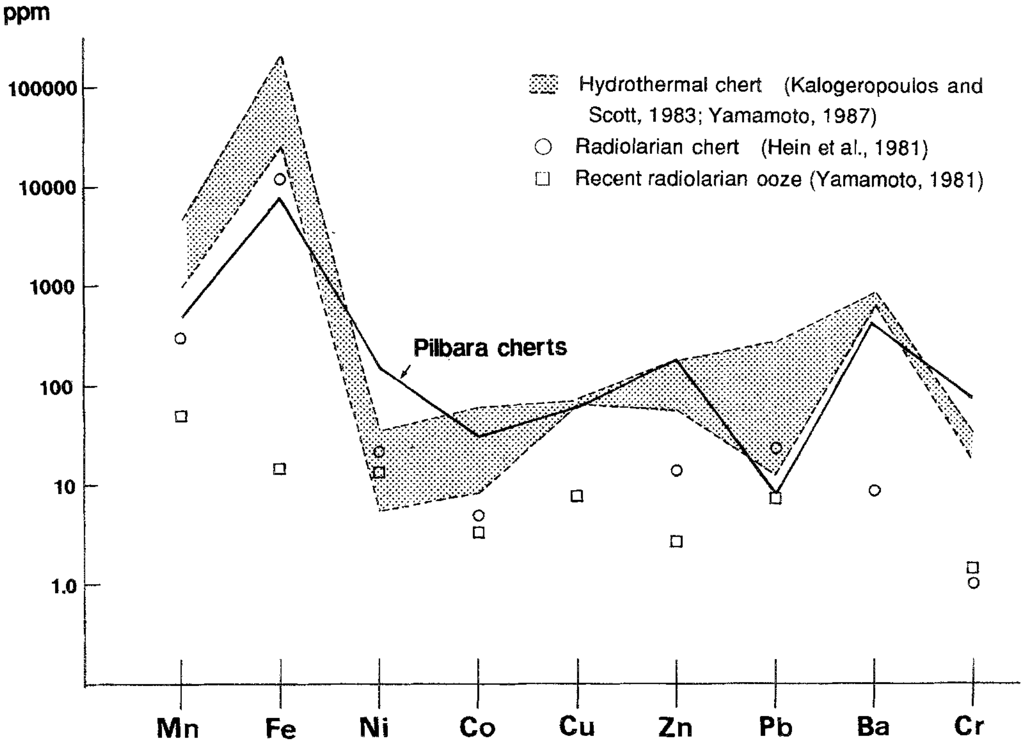


Fig. 4. Average concentrations of some minor elements contained in cherty rocks from the Towers Formation, compared with those of hydrothermal and radiolarian cherts. Reference data used are from *Hein* et al. (1981) for Cretaceous DSDP Leg 62 cherts from the Hess Rise and Mid-Pacific Mountains, *Kalogeropoulos* and *Scott* (1983) for Tetsusekiei from the Fukazawa Kuroko deposit, *Yamamoto* (1983) for recent radiolarian ooze from the central Pacific and *Yamamoto* (1987) for Franciscan Terrane and DSDP Leg 32 Cherts. See text for detailed explanations

such as Ni and Zn are also recognized in the BIFs of the Cleaverville Formation (*Ohta* et al., 1993). In contrast, the reported minor element concentrations of the Cretaceous DSDP Leg 62 radiolarian cherts from the Hess Rise and Mid-Pacific Mountains (*Hein* et al., 1981) and recent radiolarian ooze from the central Pacific (*Yamamoto*, 1983) are much lower than those of the hydrothermal cherts.

The mean isotopic compositions of sulphide sulphur were examined for three samples from the Towers cherts, which correspond to two sulphide-rich specimens with syndepositional pyrite, sphalerite and chalcopyrite and one specimen with principally diagenetic pyrite. The former and the latter are distinct in $\delta^{34}S$ (CDT) values, showing -1.7 to $+0.1$‰ and -11.8‰, respectively.

Depositional environment of the Pilbara chert

The significant amounts of sulphide minerals occurring in the cherty horizons of the Warrawoona Group, show various modes of occurrence. Most sulphide minerals are not detrital, consisting predominantly of syndepositional or diagenetic phases. In the former case, sulphide minerals are regarded to be deposited concomitantly with exhaled silica-rich solutions, so that such sulphide minerals can be used to estimate the depositional conditions of the cherty sediments. The syndepositional sulphide mineral assemblage, pyrite + chalcopyrite + pyrrhotite + pentlandite + sphalerite, is characteristically preserved in some chert samples (North Pole Chert, Marble Bar Chert) of the Towers Formation. If this assemblage was primarily in equilibrium, a constraint on the temperature of mineralization and metamorphism can be obtained; the chalcopyrite + pyrrhotite and pentlandite + pyrite assemblages suggest formation temperatures below ~325 °C (*Sugaki* et al., 1982) and below ~212 °C (*Craig*, 1973), respectively. As described earlier, however, pentlandite often occurs as flame-like exsolution in pyrrhotite, rather than as a primary precipitate. Therefore, the formation (and/or metamorphic) temperature of <212 °C would not be a good estimate. However, there is no indication of the precursor assemblage isocubanite + pyrite, suggesting that temperatures were not above ~325 °C. This is compatible with the maximum metamorphic temperatures for the Warrawoona Group rocks as estimated from the silicate mineral assemblages in metabasic rocks (*Buick* et al., 1995).

The FeS content of sphalerite in equilibrium with monoclinic pyrrhotite and pyrite is a useful criterion to judge whether monoclinic pyrrhotite has been primarily stable (*Browne* and *Lovering*, 1973; *Scott* and *Kissin*, 1973). From the compositional data of the sphalerite (8.4–10.4 mol% FeS), the monoclinic pyrrhotite is regarded as the stable phase, and so an approximate temperature range below ~254 °C (*Kissin* and *Scott*, 1982) is suggested for the sphalerite + pyrrhotite assemblage in the chert of the Towers Formation. The depositional condition of the chert containing the above assemblage are deduced using Fig. 5, where the relationship between temperature and sulphur fugacity (fs_2) is illustrated using the compositional data of sphalerite and the thermodynamic data of some univariant reactions (*Barton* and *Skinner*, 1979). As depicted by the stippled area in Fig. 5, a relatively low-fs_2 range and low temperatures below 200 °C are considered to represent conditions during chert formation. A possible range of oxygen activity (ao_2) and pH can be estimated from the primary pyrite + pyrrhotite + magnetite

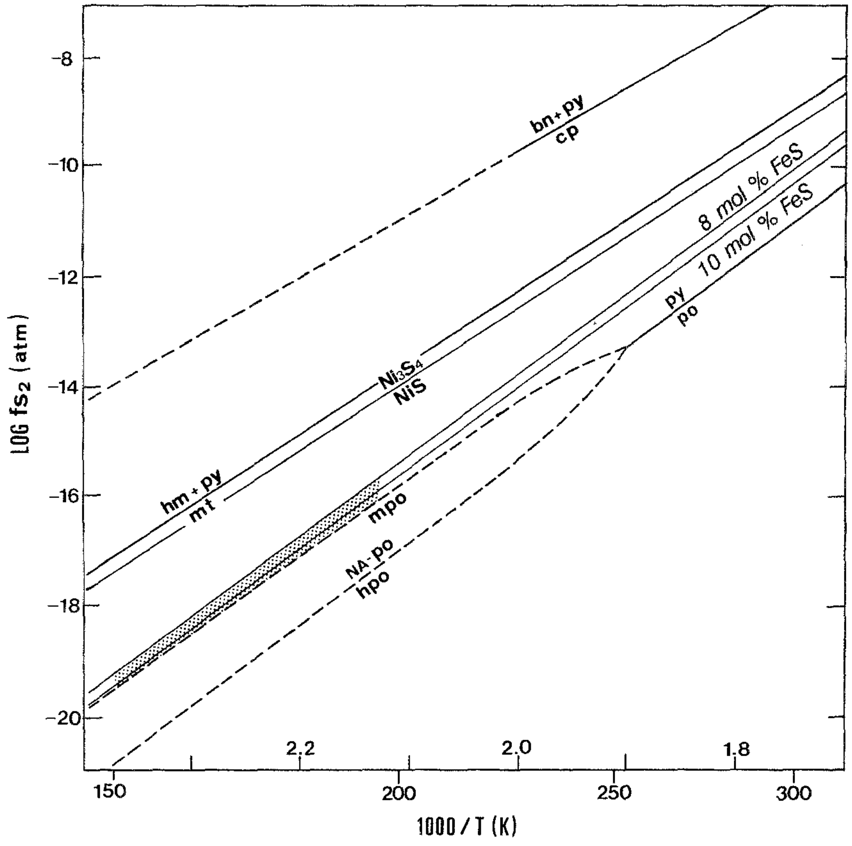


Fig. 5. Log f_{S_2}–T diagram showing the depositional condition (stippled area) for the cherty rocks of the Towers Formation (North Pole Chert, Marble Bar Chert). Data used are from *Scott* and *Kissin* (1973) and *Barton* and *Skinner* (1979). *py* pyrite, *hpo* hexagonal pyrrhotite, *mpo* monoclinic pyrrhotite, *NA-po* ordered hexagonal pyrrhotite including NA-type, *mt* magnetite, *hm* hematite, *cp* chalcopyrite, *bn* bornite

assemblage in the chemical sediments from the McPhee Formation. Reducing (log $a_{O_2} = -50.0 \sim -51.5$) and slightly alkaline ($pH = 7$–7.5) conditions are deduced (stippled field in Fig. 6) if a temperature of 150 °C is adopted. In constructing the diagram, we assumed a low level of sulphur content ($10^{-4}m$) which is typical for common geothermal fluids (*Barnes*, 1979) and a total chloride content corresponding to seawater ($0.6\,m$).

Ultramafic to mafic rocks (peridotite and tholeiitic basalt) underlie the chert unit of the McPhee Formation, or are interbedded with the cherty sediments of the Towers Formation (*Hickman*, 1990). According to *Barley* et al. (1984), these igneous rocks are moderately enriched in Ni. Hence Ni bearing fluids which leached metallic components from the igneous sequences may also have contributed to formation of the cherts. However, hydrothermal experiments (e.g., *Scott*, 1974) have shown that Ni in Ni-Fe sulphides is difficult to remobilize by hydrothermal solutions. Furthermore, studies of high-temperature seawater/basalt

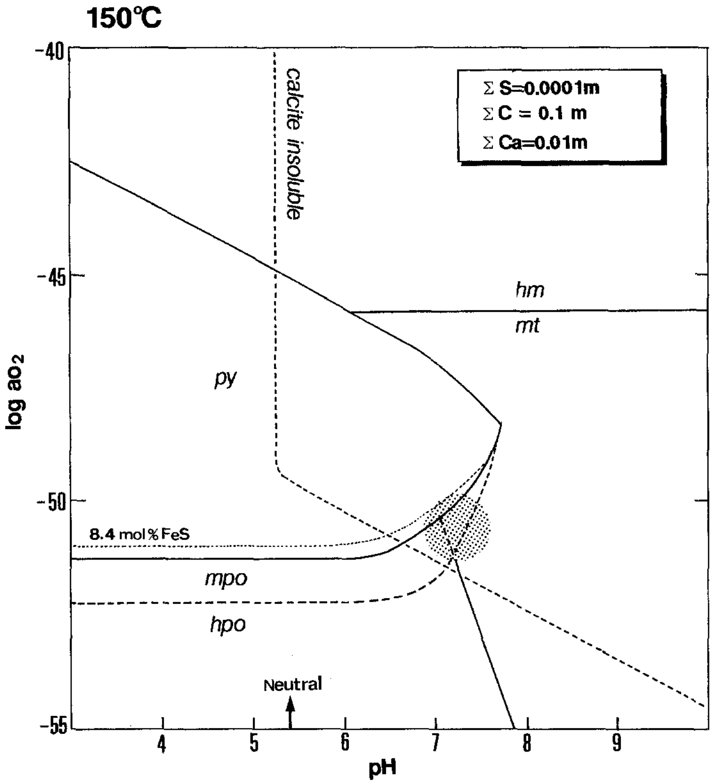


Fig. 6. Log ao_2–Ph diagram showing depositional condition (stippled area) for the chemical sediments of the McPhee Formation. Abbreviations are the same as those in Fig. 5. Thermodynamic data are from *Barton* and *Skinner* (1979)

interactions have suggested that Ni is not significantly leached from basalts during hydrothermal reactions (*Mottl* et al., 1979; *Seyfried* and *Mottl*, 1982) and that Ni is highly immobile in hydrothermal solutions (*Von Damm* et al., 1985). On the other hand, *Humphris* and *Thompson* (1978) have indicated that some mobilization of such metallic elements as Ni occurs in the hydrothermally altered basalts of the Mid-Atlantic ridge. *Lebedev* et al. (1988) have reported some Ni-bearing minerals in the modern metalliferous sediments of the Atlantis-II Deep, Red Sea. These observations suggest that Ni can be transported by hydrothermal fluids and that the Ni-bearing cherts of the eastern Pilbara Block could have formed under similar conditions as those found at active oceanic ridges.

As described earlier, the minor element chemistry of the Towers chert is similar to that of hydrothermal chert, and the "*Tetsusekiei*" also resembles the Towers chert with respect to microscopic textures. Thus, both chemical and textural features of the Towers chert are similar to those of hydrothermal cherts, suggesting that the cherty rocks of the eastern Pilbara district were precipitated from submarine hydrothermal systems. Furthermore, the mean δ^{34}S values (-1.7 to $+0.1$‰) of sulphide-rich cherts are within the range of volcanogenic sulphides in the Pilbara sedimentary rocks (*Lambert* et al., 1978), additionally supporting a model of hydrothermal origin. In contrast, the cherty rocks with principally diagenetic pyrite have a lower $\delta^{34}S$ value (−11.8‰), which is attributed to biogenic sulphur (see *Schopf*, 1993). Considering all these features, we conclude that the cherty sediments in the eastern Pilbara district represent hydrothermal sediments formed under relatively reducing conditions.

Conclusions

The mineralogy and paragenesis of primary sulphide minerals in the Early Archean cherty rocks from the eastern Pilbara Block were examined to evaluate their environment of formation. The results show the following significant characteristics:

(1) The cherty rocks from the McPhee and the Towers Formations are highly depleted in detrital materials.
(2) Both textural and chemical features of the cherts are similar to those of hydrothermal cherts, such as the "*Tetsusekiei*" from the Kuroko deposits, Japan.
(3) The chert horizons of the Towers Formation (North Pole Chert, Marble Bar Chert) preserve certain amounts of syndepositional sulphides including pyrite, chalcopyrite, pyrrhotite, pentlandite and sphalerite. The sulphide assemblage and FeS content of the sphalerite (4.2–5.2 at.%) associated with Fe-sulphide minerals (monoclinic pyrrhotite and pyrite) suggest relatively reducing conditions and formation temperatures below ~200 °C.

These features suggest a hydrothermal origin of the chert, supporting results of recent studies of the trace element and isotope chemistry of BIF-related chert (e.g. *Derry* and *Jacobsen*, 1990; *Sugitani*, 1992; *Bau* and *Möller*, 1993); they have shown that considerable components in the cherty rocks of the Pilbara district were derived from hydrothermal activity. Furthermore, *Isley* (1995) has suggested that until at least the Late Archean, hydrothermal plumes could supply a large amount of H_2S ($\sim 1.7 \times 10^{11}$ mol/year), enough to allow direct precipitation of sulphide minerals. The mineralogical aspects shown in the present study suggest not only a hydrothermal origin of these cherts but also constrain the specific chert-forming conditions. Such information will be valuable when discussing chemical environments of other Archean sedimentary provinces.

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