

Middle Archean ocean ridge hydrothermal metamorphism and alteration recorded in the Cleaverville area, Pilbara Craton, Western Australia

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ABSTRACT A hydrothermally metamorphosed greenstone complex, capped by bedded cherts and banded iron formations (BIFs), is exposed in the Cleaverville area, Pilbara Craton, Western Australia. It has been interpreted as an accretionary complex characterized by both a duplex structure and an oceanic plate stratigraphy, and is shown to represent a 3.2 Ga upper oceanic crust. Three metamorphic zones are identified in the basaltic greenstones. The metamorphic grade increases from sub-greenschist facies (zones A and B) to greenschist facies (zone C) under low-pressure conditions. The boundaries between three mineral zones are subparallel to the bedding plane of overlying chert/BIF, and metamorphic temperature increases stratigraphically downward. The zones correspond to the thermal structure of ocean-floor metamorphism, at a mid-ocean ridge. The uppermost greenstone in the study area is more pervasively altered and carbonatized than the modern upper oceanic crust. This indicates the enrichment of CO₂ in the metamorphic fluid by which widespread formation of carbonate occurred, compared with a narrow stability region of Ca-Al silicates. It is, therefore, suggested that the Archean hydrothermal alteration played a more important role in fixation of CO₂ than present-day ocean-ridge hydrothermal alteration, as an interaction between sea water and oceanic crust.

Key words: Archean; greenstone; high X_{CO_2} ; low-pressure metamorphism; ocean-floor metamorphism.

INTRODUCTION

Since the discovery of sea-floor hydrothermal vents at the Galapagos spreading centre in 1977 (Corliss *et al.*, 1979), it is well known that hydrothermal alteration of oceanic crust is an important process affecting the surface environment and solid Earth (German *et al.*, 2004; Wilcock *et al.*, 2004). Chemical interaction between sea water and oceanic crust, and secondary minerals in modern hydrothermal systems have been well documented from many drill cores (e.g. Alt *et al.*, 1995; Elderfield *et al.*, 1999; Wheat *et al.*, 2000) and on-land ophiolites (e.g. Nehlig & Juteau, 1988; Pflumio, 1991; Gillis & Banerjee, 2000). Hydrothermal metamorphism is classified into axial and off-axis settings (Lister, 1982). The former is caused by a magmatic heat source at mid-oceanic ridge, and is characterized by low-pressure metamorphic facies series of zeolite-greenschist-amphibolite facies with depth. The high thermal gradient leads to the extensive exchange of heat and elements between sea water and oceanic crust (e.g. Elderfield *et al.*, 2004). On the other hand, off-axis or ridge-flank alteration results mainly from cooling of the underlying lithosphere (e.g. Alt, 1995; Wheat *et al.*, 2000). This is characterized by the presence of carbonate, quartz, zeolite and prehnite

veins with depth, and the geothermal gradient reaches about 50 °C km⁻¹. Temperatures are generally < 150 °C and commonly a few tens of degrees celsius. Many carbonate minerals occur along the veins and are formed at the off-axis hydrothermal alteration (Coggon *et al.*, 2004). Therefore, off-axis hydrothermal alteration is also important for fixing CO₂ in the oceanic crust from the ocean (Staudigel *et al.*, 1989; Alt & Teagle, 1999).

Recently, many Archean greenstone belts have been reinvestigated based on modern geological concepts, and their tectonic settings re-interpreted as vestiges of Archean ocean floors; e.g. 3.8 Ga Isua supracrustal belt (Komiya *et al.*, 1999), 3.5 Ga North Pole and Marble Bar greenstone belts (Maruyama *et al.*, 1991; Kitajima *et al.*, 2001a; Komiya *et al.*, 2002; Kato & Nakamura, 2003), 3.5 Ga Barberton Greenstone Belt (de Wit *et al.*, 1992), 3.2 Ga Cleaverville Greenstone Belt (Maruyama *et al.*, 1991; Ohta *et al.*, 1996) and 2.7 Ga Abitibi Greenstone Belt (Kimura *et al.*, 1993). The petrological and geochemical studies of the greenstones, derived from Archean mid-oceanic ridge magmatism, showed that the Archean oceanic crust was also basaltic but was about 15 km thick, much thicker than the modern equivalent (Ohta *et al.*, 1996; Komiya *et al.*, 2002, 2004; Komiya, 2004). On the

other hand, vestiges of Archean hydrothermal alteration of oceanic crust were also found in some greenstone belts with different ages: 3.8 Ga Isua supracrustal belt (Appel *et al.*, 2001), 3.5 Ga North Pole and Marble Bar greenstone belts (Kitajima *et al.*, 2001a; Kato & Nakamura, 2003; Terabayashi *et al.*, 2003; Nakamura & Kato, 2004), 3.5 Ga Barberton greenstone belt (Cloete, 1999), 3.2 Ga Cleaverville greenstone belt (Kiyokawa *et al.*, 2006), and 2.7 Ga Abitibi greenstone belt (Weiershäuser & Spooner, 2005). There are two kinds of studies of Archean hydrothermal metamorphism: investigations of (i) petrology and geochemistry of greenstones (Cloete, 1999; Appel *et al.*, 2001; Kitajima *et al.*, 2001a; Terabayashi *et al.*, 2003; Nakamura & Kato, 2004), and (ii) chemistry and microthermometry of hydrothermal fluids (de Ronde *et al.*, 1994, 1997; Cloete, 1999; Appel *et al.*, 2001; Kitajima *et al.*, 2001b; Foriel *et al.*, 2004; Weiershäuser & Spooner, 2005). The petrology of the greenstones shows pervasive metasomatism by carbonatization, silicification and chloritization, and sericitization of greenstones is distinct from the modern equivalents (de Wit *et al.*, 1982; Kitajima *et al.*, 2001a; Nakamura & Kato, 2002; Terabayashi *et al.*, 2003). Especially, recent studies focused on the widespread carbonate metasomatism of the greenstones, and show that the CO₂ concentrations of the hydrothermal fluids were much higher, by ~30 times in the Middle Archean than at present, on the basis of secondary mineral assemblages of greenstones and thermodynamic calculations (Kitajima *et al.*, 2001a). This estimate is consistent with much higher atmospheric CO₂ levels in the Archean so that the high CO₂ greenhouse effect compensated for the faint solar luminosity of the young sun (Kasting, 1993). Nakamura & Kato (2004) suggested that hydrothermal carbonatization of the Early Archean oceanic crust at mid-ocean ridges played an important role as a sink of surface CO₂ based on the CO₂ concentration fixed as carbonate minerals in the greenstones. However, these studies are restricted to only one 3.5 Ga greenstone belt, the North Pole-Marble Bar area, Pilbara. This study presents another example of Archean ocean-floor hydrothermal alteration in the 3.2 Ga Cleaverville greenstone belt in Pilbara, and discusses carbonatization of oceanic crust caused by widespread circulation of hydrothermal fluids with high partial pressure of CO₂.

GEOLOGICAL SETTING

The Pilbara Craton is exposed over an area of 18 300 km² in the northern part of Western Australia, and comprises granite-greenstone belts and subsequent volcano-sedimentary basins. The Pilbara granite-greenstone terrane is subdivided into three major tectono-stratigraphic terranes according to their lithostratigraphies and structures, with West and East Pilbara terranes (WP and EP) separated by the Mallina

Basin (e.g. Hickman, 2001). Moreover, the greenstone belts in the WP are divided into three domains, the Karratha, Cleaverville and Sholl domains (Hickman, 2001). The Cleaverville area is located in northern coast of West Pilbara, and is underlain by basaltic greenstones of the Regal Formation and sedimentary rocks of the Cleaverville Formation (Hickman, 2001). The upper part of the Cleaverville greenstone belt is composed mainly of sedimentary rocks of bedded chert, banded iron formation (BIF), and clastic rocks of sandstone, mudstone and conglomerate, whereas the lower part comprises basaltic greenstones with volcanic structures of pillow lava, pillow breccia and sheeted flows (Fig. 1). The total thickness is over 3500 m. They strike NE–SW and dip sharply to the NW. The way-up, generally speaking, is also to the NW, obtained by structures of sedimentary rocks and pillow lava. There are two types of faults in the area; primary layer-parallel thrusts with NE trends, and secondary high-angle normal faults (Fig. 1). Duplex structures are ubiquitous in the upper part, and the deformational structure indicates top-to-the-SW reverse displacement. The thrust-bounded subunits consist of basaltic greenstone, chert and clastic sedimentary rocks in ascending order. The rocks were later intruded by dolerite dykes. The southern part of the greenstone belt is tectonically in contact with sedimentary rock units of the Nickol River Formation (Hickman, 2002). The depositional age of the Cleaverville Formation is constrained by the U–Pb age of zircon in the tuff in the formation, which is dated at 3195 ± 15 Ma (Kiyokawa *et al.*, 2002).

The basaltic greenstones in the Cleaverville area are derived from pillow lava, hyaloclastite, reworked hyaloclastite and massive sheet flows. The pillows range from 30 cm to 1 m across, and extend at least several metres as tubes in some cases (Fig. 2a,b). They have a dark-coloured chilled margin without any traces of vesicles. Most pillows are close-packed with minor amounts of matrix. The matrix is composed of altered glassy materials, mostly altered into chlorite and a minor amount of epidote and calcite. Vesicles within the pillows are filled by quartz, chlorite, epidote and calcite. Carbonatization is developed throughout the area, but is most intense just below the chert/BIF sequence. However, structures of pillow lavas, vesicles and amygdulites are well preserved even in strongly altered greenstones.

The tectonic setting of the Cleaverville greenstone belt is still controversial, but generally interpreted as an accretionary complex that originates from upper oceanic crust formed at a mid-ocean ridge. Ohta *et al.* (1996) found duplex structures in the upper part, and reconstructed original lithostratigraphy within each horse of the duplex structure. They showed that the reconstructed lithostratigraphy is composed of greenstone, chert/BIF and clastic rocks in ascending order, that the greenstone and chert/BIF contain no detrital materials, and that the lithostratigraphy is similar to

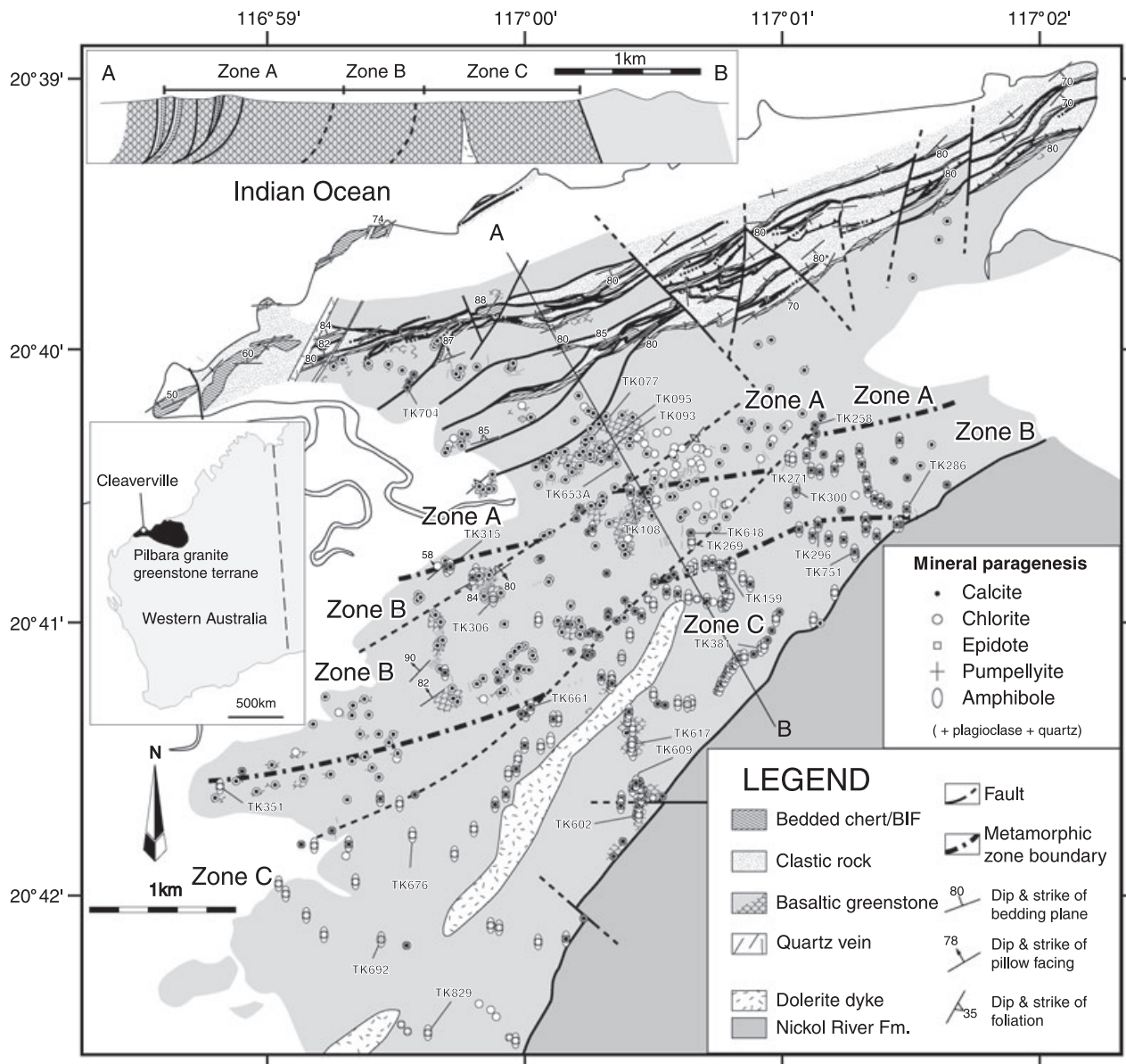


Fig. 1. Geological map of the Cleaverville area and the distribution of secondary mineral assemblages.

oceanic plate stratigraphy in the Phanerozoic accretionary complexes (Matsuda & Isozaki, 1991). They suggested that the Cleaverville greenstone belt is an accretionary complex based on the presence of duplex structures and an oceanic plate stratigraphy, and proposed that the depositional environment changed from basaltic volcanism at a mid-oceanic ridge, through depositions of chert/BIF in an open sea to deposition of terrigenous sediments at a trench (Maruyama *et al.*, 1991; Ohta *et al.*, 1996).

Kiyokawa and colleagues interpreted the tectono-sedimentary environment of the Dixon Island Formation, a NE extension of the Cleaverville greenstone belt, as oceanic sea-floor of an immature island arc, based on basaltic and rhyolitic bimodal volcanism, a

cyclic volcano-sedimentary sequence, the absence of detrital material, and imbricated top-to-the-north thrusting events (Kiyokawa & Taira, 1998; Kiyokawa *et al.*, 2002, 2006). However, the absence of detrital material and imbricated top-to-the-north thrusting events are consistent with oceanic plate stratigraphy and duplex structure respectively. Ohta *et al.* (1996) considered that the cyclic volcano-sedimentary sequence was tectonic because of the presence of the layer-parallel thrusts between basaltic piles and terrigenous sedimentary rocks (Fig. 1). In addition, Kato *et al.* (1998) analysed rare earth elements (REE) of sedimentary chert, BIF and clastic rocks, and showed that the positive europium anomaly of these sedimentary rocks gradually decreases upward and the light

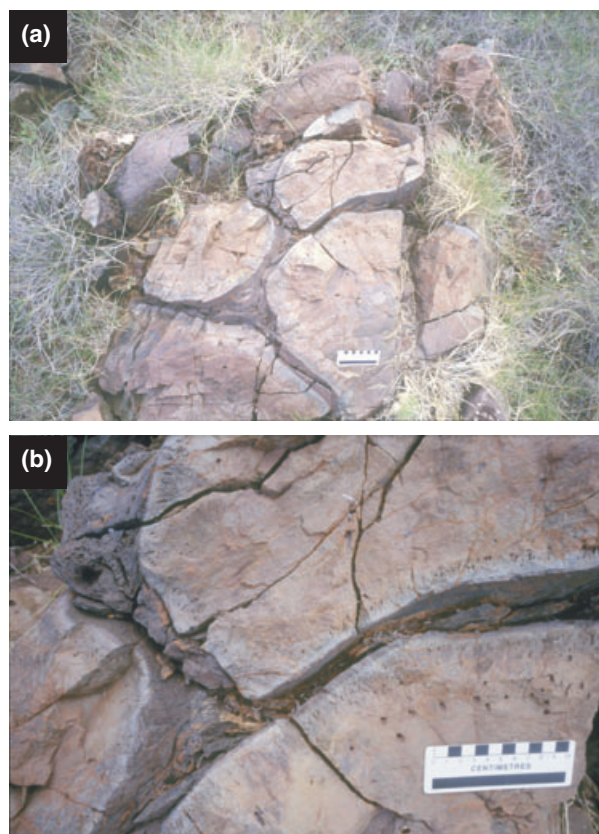


Fig. 2. (a) Basaltic greenstones with pillow structure showing dark-coloured chilled margin, and are close-packed with minor amounts of matrices. (b) Vesicles are concentrated in the margin of pillow but absent in the chilled margin. The size and the number of vesicles become larger and decrease toward inside of pillow, respectively. There are no vesicles in the core of pillow.

REE become enriched as well. They interpreted that the lower part of sedimentary rocks was deposited from sea water with hydrothermal affinity near a mid-oceanic ridge, and that the upper part formed from sea water with continental affinity. The evidence is consistent with the change of depositional environment of sedimentary rocks from mid-oceanic ridge to subduction zone (Kato *et al.*, 1998). In addition, the whole-rock composition of the greenstones is similar to modern MORB (Ohta *et al.*, 1996; Sun & Hickman, 1999), which is also consistent with the accretionary complex model.

MINERAL ISOGRADS OF THE CLEAVERVILLE AREA

Observations of ~1000 thin sections show that a metamorphic aureole was restricted within less than a few tens of metres from the contact with the dolerite dykes. Therefore, samples that underwent the contact metamorphism are also excluded from the following descriptions.

The greenstones in the Cleaverville area underwent various extents of carbonatization but less carbon-

atized greenstones retain index secondary minerals such as chlorite (Chl), epidote (Ep), albite (Ab), oligoclase (Olg), calcite (Cc), Ca-amphibole, pumpellyite (Pmp), hematite (Ht) and quartz (Qz). Under such low-grade metamorphism, original igneous textures and minerals are ubiquitously preserved, and fine-grained samples have intergranular, intersertal or hyaloophitic textures, whereas coarse-grained samples form ophitic textures. The original igneous minerals in groundmass of fine-grained volcanic rocks are partly or completely replaced by secondary minerals such as chlorite, epidote, quartz, sericite and calcite. However, many igneous clinopyroxene are well preserved in some coarse-grained samples in the lower part of the greenstones (Fig. 3a,c). Olivine phenocrysts are completely replaced by aggregates of quartz, chlorite, epidote and calcite. Plagioclase is replaced by epidote, albite, sericite and calcite. Veins such as carbonate, prehnite and quartz are also present but they are excluded from the following description because the cross-cutting relation indicates they were formed during later processes.

We subdivided the Cleaverville area into three zones, from zone A to C, based on the mineral isograds in less carbonatized greenstones (Fig. 1). The mineral parageneses in zones A, B and C are shown in Fig. 4. Zone A is characterized by the assemblage of Chl + Ab + Qz + Cc ± Ep ± Pmp ± Ht (Fig. 3b) but Ca-Al silicates such as pumpellyite and epidote are extremely rare. Zone B is defined by the first appearance of actinolite (Act) in the greenstone; the typical mineral assemblage is Chl + Ep + Act + Qz + Ab ± Pmp ± Cc. Zone C is defined by the emergence of calcic plagioclase of oligoclase composition; the mineral assemblage is Chl + Ep + Act ± Pmp + Ab + Olg + Qz ± Cc (Fig. 3c). Although they were shifted by secondary layer-parallel faults in some places, the boundaries of the metamorphic zonation among zones A to C are almost parallel to the lithological boundaries in the upper part of the Cleaverville area (Fig. 1).

Carbonate minerals are ubiquitous throughout the area, but the modal amount decreases from zone A to C. They show intimate textural association with other secondary minerals (Fig. 3b,c), indicating that carbonate minerals coincide with other secondary minerals. Relict igneous clinopyroxene tends to be preserved in coarse-grained rocks (Fig. 3a), which increase stratigraphically downward. Moreover, even fine-grained rocks in the stratigraphic lower part preserve igneous clinopyroxene (Fig. 3c). This indicates that the extent of the recrystallization decreases stratigraphically downward.

MINERAL CHEMISTRY

Chemical compositions of minerals were analysed with an electron probe (JEOL-JXA-8800M) at Tokyo Institute of Technology. All analyses were

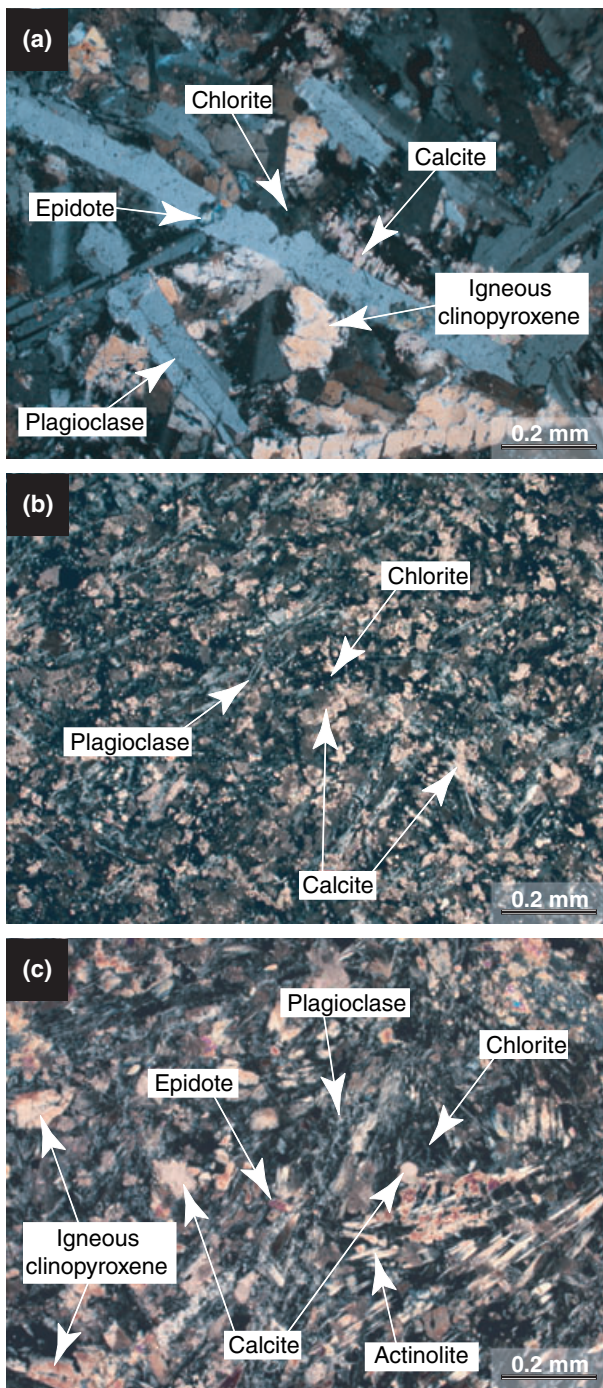


Fig. 3. (a) Relict igneous clinopyroxene in a coarse-grained basaltic greenstone in zone C. (b) Photomicrographs of a greenstone in zone A. The greenstones contain a lot of calcite coexisting with chlorite and albite. (c) Photomicrograph of a greenstone in zone C. The greenstones have small amount of calcite coexisting with chlorite, epidote, and actinolite, but preserve igneous clinopyroxene.

performed with an accelerating voltage of 15 kV, 12 nA beam current and a counting time of 10–40 s.

Metamorphic Zones	Zone A	Zone B	Zone C
Secondary minerals			
Epidote	-----		
Pumpellyite	-----	-----	-----
Ca-amphibole		-----	
Albite			
Ca-plagioclase			
Chlorite			
Rutile	-----		
Titanite	-----		
Quartz			
Calcite			-----

Fig. 4. Summary of mineral parageneses of metabasites in the Cleaverville greenstone. Solid lines show major phases, and dashed lines show minor phases.

Plagioclase

Secondary plagioclase is ubiquitous in zones A, B and C, whereas the igneous calcic plagioclase is completely replaced by secondary sodic plagioclase, sericite, carbonates or rare epidote. The anorthite (An) content of the plagioclase from zone A to C is shown in Fig. 5a,b.

In zones A and B, all plagioclase is albite, but in zone B have higher An than those in zone A. The An content ranges from 0.3% to 5.8% in zone A and from 0.2% to 9.2% in zone B. In zone C, albite and oligoclase with the peristerite gap coexist in some samples. For example, plagioclase in TK661 has a bimodal composition of 0.7–6.2 and 15.3–18.9 An (Fig. 5a). In contrast, TK692 contains one phase of plagioclase without the peristerite gap; An content ranges from 1.5 to 15.6. In summary, the An content of plagioclase increases from zone A to C and two phases of plagioclase with the peristerite gap are present in upper part of zone C, and the peristerite gap disappears in lower part of zone C (Fig. 5a,b).

Calcic amphibole

Colourless to pale-green and fine-needle-like Ca-amphibole occurs in zones B and C. The amphibole partially replaces the rim of relict clinopyroxene. Chemical compositions of Ca-amphibole in zones B and C are plotted on the amphibole classification diagram (Fig. 6a,b). The Fe^{3+} content of amphibole was estimated from the stoichiometry based on a formula of 23 oxygen (Terabayashi, 1993).

The Si content of amphibole in zone B ranges from 7.70 to 8.00 and the X_{Mg} [$\text{Mg}/(\text{Mg} + \text{Fe})$] ranges from 0.60 to 0.73 (Fig. 6a). The amphibole in zone C ranges from 7.60 to 8.00 in Si content and from 0.49 to 0.76 in X_{Mg} . Based on the Ca-amphibole discrimination diagram of Leake *et al.* (1997), amphibole in zones B and C is actinolite except for one spot analysis of ferroactinolite in zone C (Fig. 6a). Ca-amphibole in zone C is slightly enriched in edenite and tschermakite

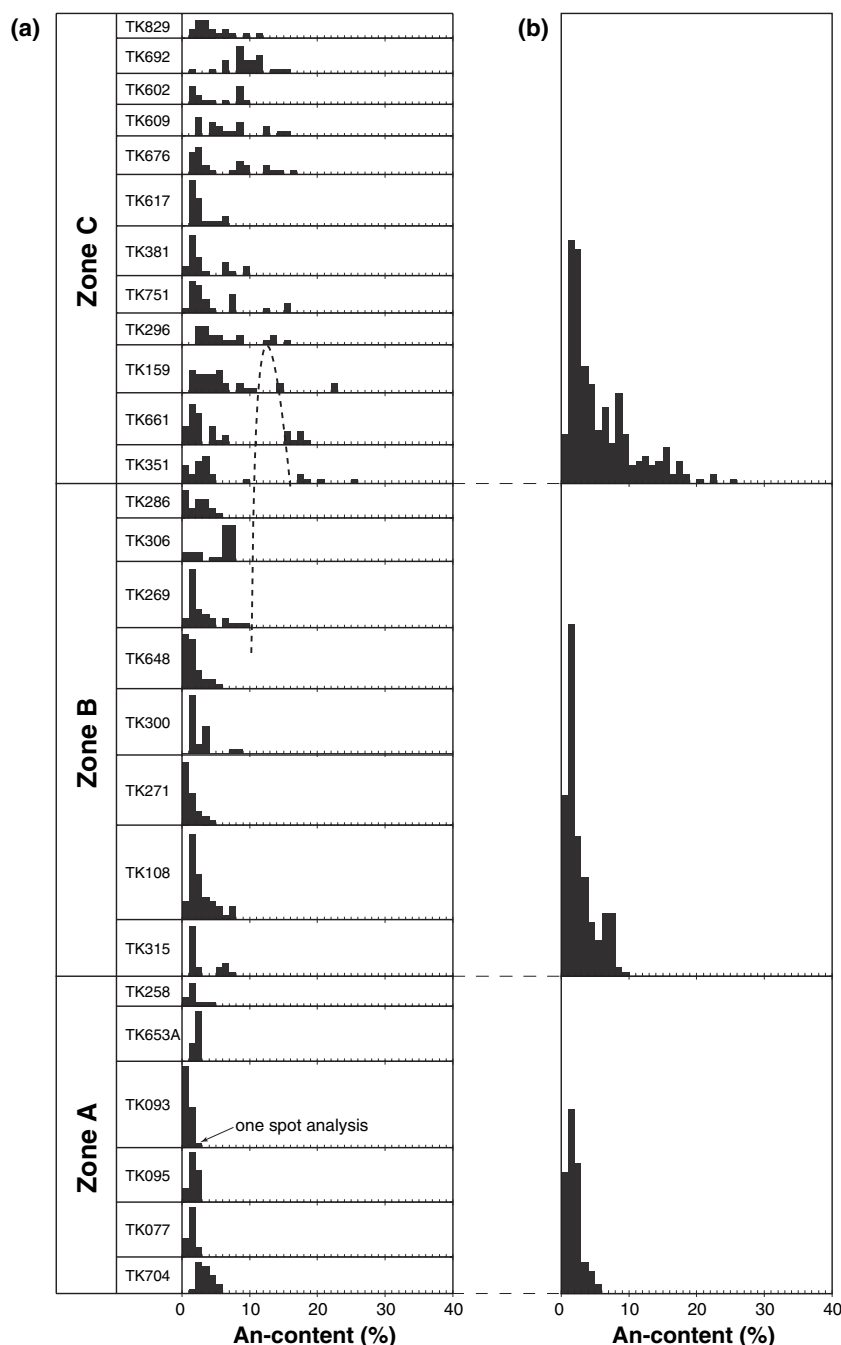


Fig. 5. Frequency diagrams of An content of plagioclase (a) in samples (b) from zones A to C.

component relative to that in zone C on the Hallimond diagram (Hallimond, 1943) (Fig. 6b).

Epidote

Epidote is one of the most common Ca-Al silicates in the greenstones of the Cleaverville area. However, the distribution and modal amount strongly depend on the metamorphic zone: it is common in zones B and C but is rare in zone A. It occurs as granular aggregates in the groundmass of igneous textures, and replaces

plagioclase accompanied with chlorite in few places. The variation of $X_{\text{Fe}^{3+}} [\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})]$ of epidote, assuming no ferrous iron and a formula of 12.5 oxygen, is illustrated in Fig. 7.

In zones A and B, $X_{\text{Fe}^{3+}}$ in epidote shows a correlation with mineral assemblage. Epidote in pumpellyite-bearing samples has lower $X_{\text{Fe}^{3+}}$ than that in pumpellyite-free samples, except for TK269 that has strongly zoned epidote. For example, in zone A, $X_{\text{Fe}^{3+}}$ of epidote in pumpellyite-free samples of TK093 and TK258 ranges from 0.27 to 0.31, but in pumpellyite-

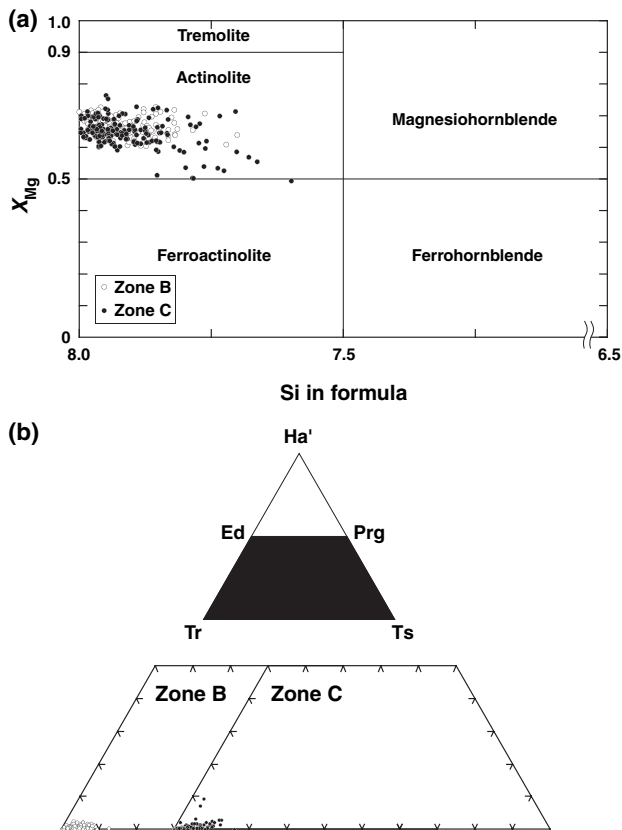


Fig. 6. (a) Chemical composition of Ca-amphibole from zone B and C (Leake *et al.*, 1997). (b) Compositional variation of Ca-amphibolites in greenstones from zones B and C, shown on quadrilateral diagram (Hallimond, 1943).

bearing sample (TK704) it has lower $X_{Fe^{3+}}$ ranging from 0.11 to 0.19. On the other hand, the $X_{Fe^{3+}}$ ratio in epidote from zone C systematically decreases stratigraphically downward (except for the lowermost part of zone C). In zones B and C, some coarser-grained epidote clearly shows chemical zoning; the rim has a lower $X_{Fe^{3+}}$ ratio than the core. For example, $X_{Fe^{3+}}$ of zoned epidote in TK751 from zone C ranges from 0.26 to 0.30 in the core and from 0.21 to 0.24 in the rim, and homogeneous epidote has $X_{Fe^{3+}}$ ratios ranging from 0.21 to 0.24. In summary, $X_{Fe^{3+}}$ of epidote correlates with the mineral assemblage (zones A and B) and stratigraphic depth (zone C).

Pumpellyite

Green pumpellyite is a minor phase in greenstones from zone A to C, and occurs as aggregates of small grains in the groundmass. Compositional variations of the pumpellyite are shown in Al-Fe*-Mg diagrams (Coombs *et al.*, 1976) (Fig. 8). The variation of $X_{Fe^{3+}}$ is presented in Fig. 7.

In zone A, only TK704 contains pumpellyite with relatively homogeneous composition (Fig. 8). On the other hand, pumpellyite in zones B and C has large

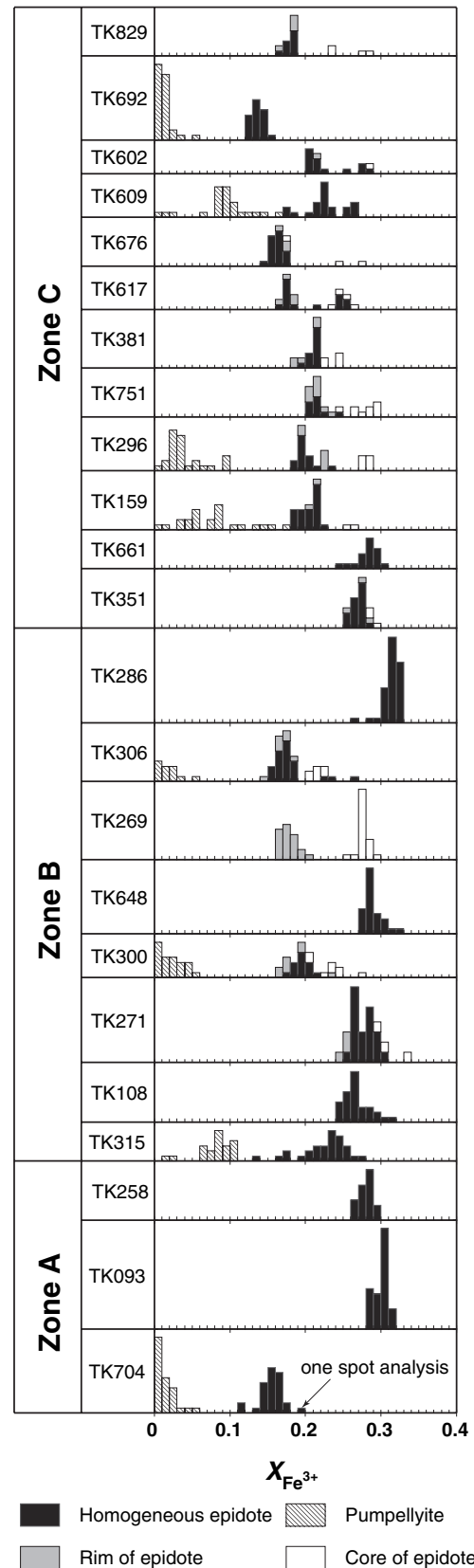


Fig. 7. Frequency diagrams of $X_{Fe^{3+}}$ of epidote and pumpellyite in each sample from zone A to C.

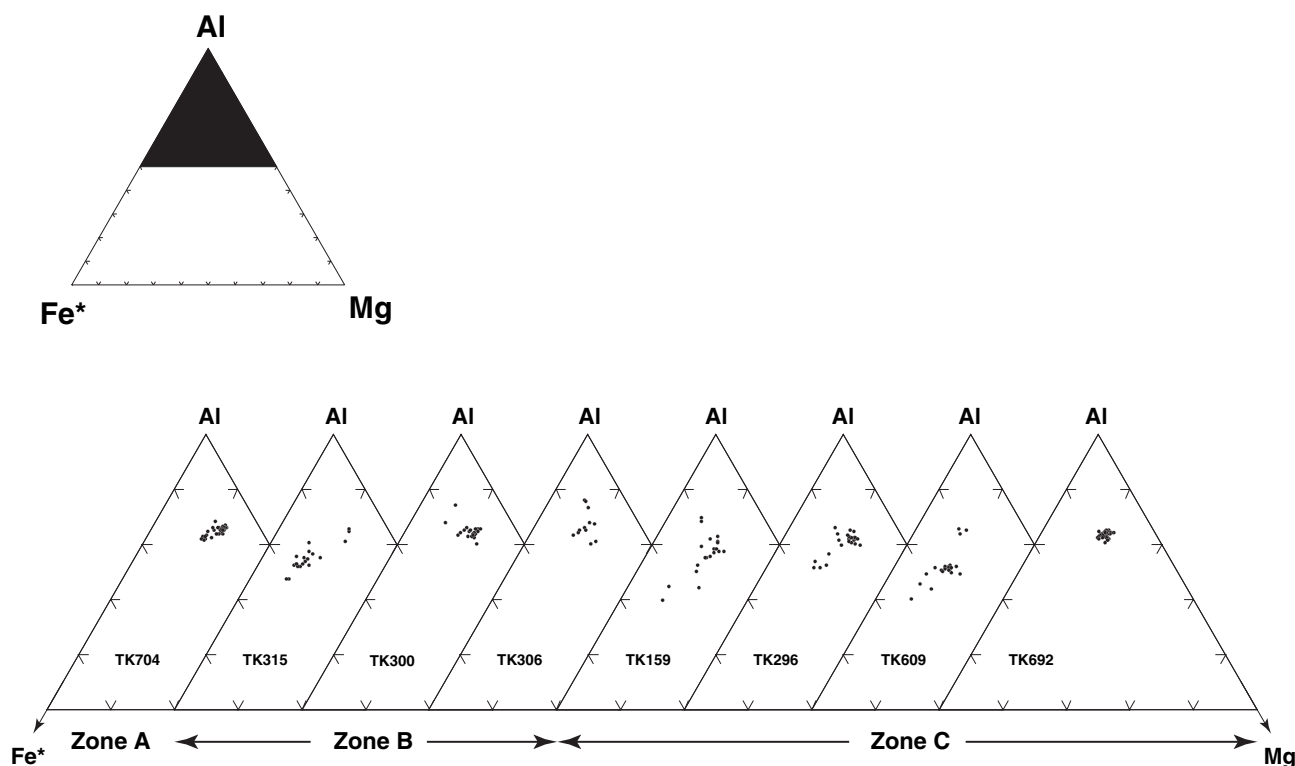


Fig. 8. Chemical composition of pumpellyite from zone A to C, plotted on Al-Fe*-Mg diagram. Fe* is total iron.

compositional variation of total iron. In zones A and B, pumpellyite coexists with epidote that has a relatively low $X_{\text{Fe}^{3+}}$ ratio (Fig. 7). The $X_{\text{Fe}^{3+}}$ [$\text{Fe}^{3+}/(\text{Fe}^{3+} + \text{Al})$] of the pumpellyite is calculated using the ideal formula $\text{Ca}_4(\text{Mg}, \text{Fe}^{2+})(\text{Al}, \text{Fe}^{3+})_5\text{Si}_6\text{O}_{21}(\text{OH})_7$ (Nakajima *et al.*, 1977).

Chlorite

Chlorite replaces igneous olivine, clinopyroxene, plagioclase and interstitial glass. It ubiquitously occurs in all zones but the modal amount decreases from zone A to C. The chlorite has large compositional variations within even a single metamorphic zone (Fig. 9a–c), but is relatively homogeneous in terms of the X_{Fe} [$\text{FeO}/(\text{FeO} + \text{MgO})$] ratio in each sample. Chlorite in zone A has larger compositional variation than that in zones B and C; the X_{Fe} ranges from 0.40 to 0.62, and the Si content ranges from 5.20 to 5.99 on the basis of 28 oxygen in the formula. The X_{Fe} and Si content of chlorite in zone B are in the range from 0.39 to 0.55 and from 5.34 to 6.03, respectively. Chlorite in zone C has slightly higher X_{Fe} ratio than that in zone B; X_{Fe} ranges from 0.42 to 0.58, and Si content from 5.37 to 6.13. As a whole, chlorite in the Cleaverville area mostly overlaps chlorite from DSDP/ODP Hole 504 B, some chlorite in zone A has clearly higher X_{Fe} ratio than those from DSDP/ODP Hole 504B (Fig. 9d). No systematic change of chlorite composition from zone A

to C was observed, but the X_{Fe} ratio of chlorite is closely related to the mineral assemblages, especially appearance of pumpellyite within a single zone.

DISCUSSION

Metamorphic temperature and progressive metamorphism of the Cleaverville area

Effect of the FeO/MgO ratio on the mineral paragenesis

Mineral paragenesis generally depends not only on the metamorphic grade but also the effective bulk compositions. Beiersdorfer & Day (1995) summarized the literature and discussed the systematic correspondence between effective bulk composition and metamorphic mineral assemblage in low-grade metamorphic rocks. They concluded that the appearance of pumpellyite in low-grade metamorphic rock strongly depends on the whole-rock FeO/MgO ratio.

In order to check whether the difference of mineral assemblages in a metamorphic zone of the Cleaverville area is caused by whole-rock composition, epidote projections for the considered minerals from zone A to C onto $\text{Al}^*\text{-FeO-MgO}$ plane are shown in Fig. 10. Average values of analytical results are plotted on the diagram. In all Zones, $\text{Mg}^\#$ [$100 \times \text{MgO}/(\text{FeO} + \text{MgO})$] of chlorite ranges from 44.7 to 58.8. In zone A, TK704 with the lowest $\text{Mg}^\#$ (44.7) of chlorite has a

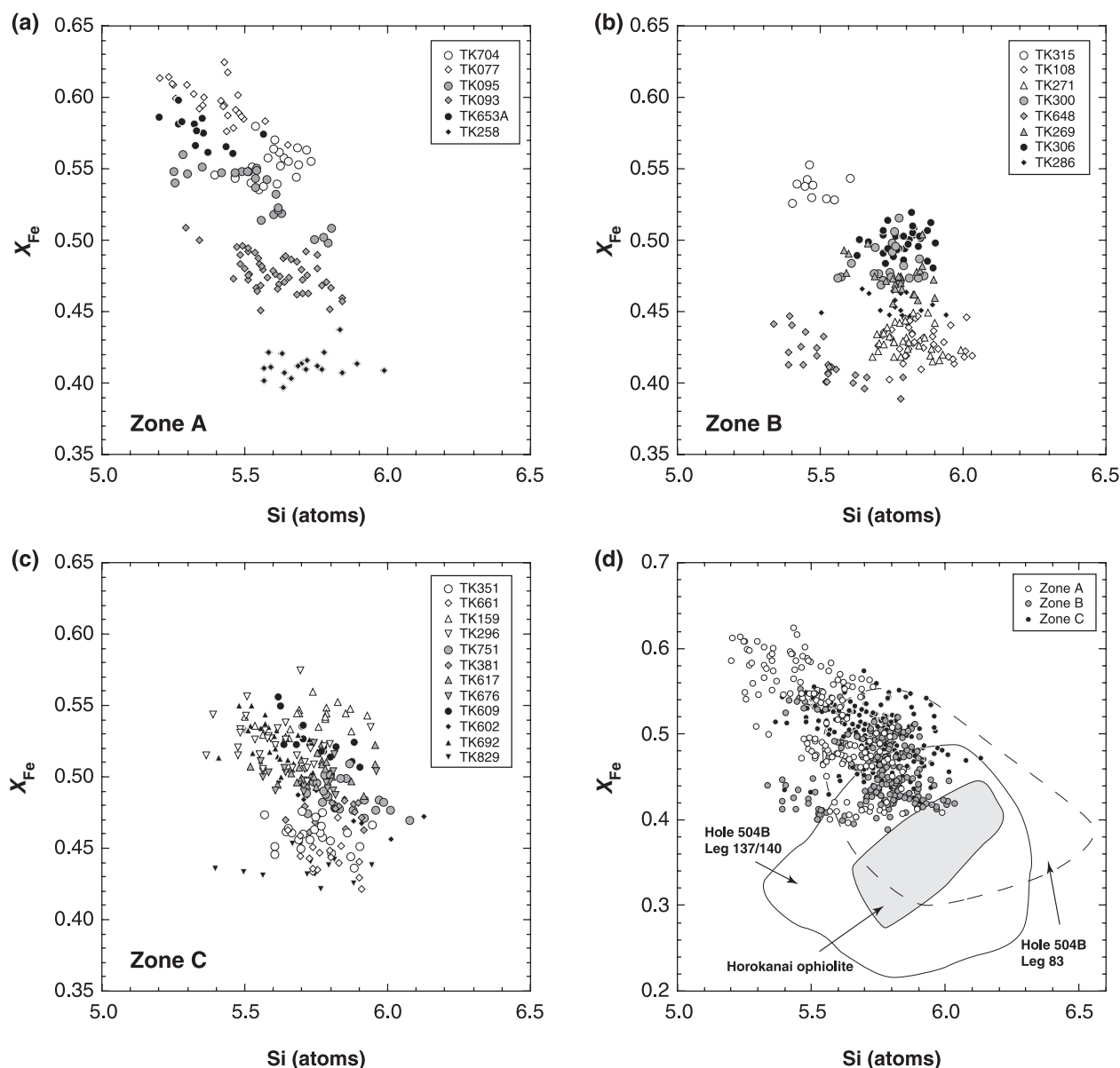


Fig. 9. (a–c) Chemical composition of chlorite from zone A to C (Hey, 1954). (d) Comparison of chlorite in metabasites from the Cleaverville area with those of DSDP/ODP Hole 504B (Alt *et al.*, 1985; Laverne *et al.*, 1995) and Horokanai ophiolite (Ishizuka, 1985). The rocks of Hole 504B Legs 83 are from the pillow/dyke complex transition and upper dyke complex section, and those of Leg 137/140 are from lower dyke complex section.

pumpellyite-bearing assemblage, whereas TK093 and TK258 with high $Mg^{\#}$ (52.3 and 58.8, respectively) of chlorite have pumpellyite-free assemblages (Fig. 10a). In zone B, TK315, 306 and 300 with the lower $Mg^{\#}$ (46.3 to 51.7) of chlorite have pumpellyite-bearing assemblages, whereas TK269, 286, 271 and 108 with higher $Mg^{\#}$ (52.6 to 57.1) of chlorite have pumpellyite-free assemblages (Fig. 10b). TK648 has the highest $Mg^{\#}$ (58.5) and AF* value (0.23) of chlorite in zone B ($Mg^{\#}$; 46.3–58.5, AF*; 0.19–0.23), and does not contain actinolite. In zone C, TK159, 296, 609 and 692

have pumpellyite-bearing assemblages, and their $Mg^{\#}$ of chlorite ranges from 45.9 to 47.5, lower than that in samples with pumpellyite-free assemblages (Fig. 10c).

Mineral assemblages of samples with chlorite $Mg^{\#}$ from 50 to 55 systematically change from Chl + Ep + Qz + Ab to Chl ± Pmp + Act + Ep + Qz + Ab to Chl + Act + Ep + Qz + Ab ± Olg from zone A to C. Furthermore, mineral assemblages of samples with chlorite $Mg^{\#}$ from 55 to 60 change from Chl + Ep + Qz + Ab to Chl ± Act + Ep + Qz + Ab to Chl + Act + Ep + Qz + Ab ±

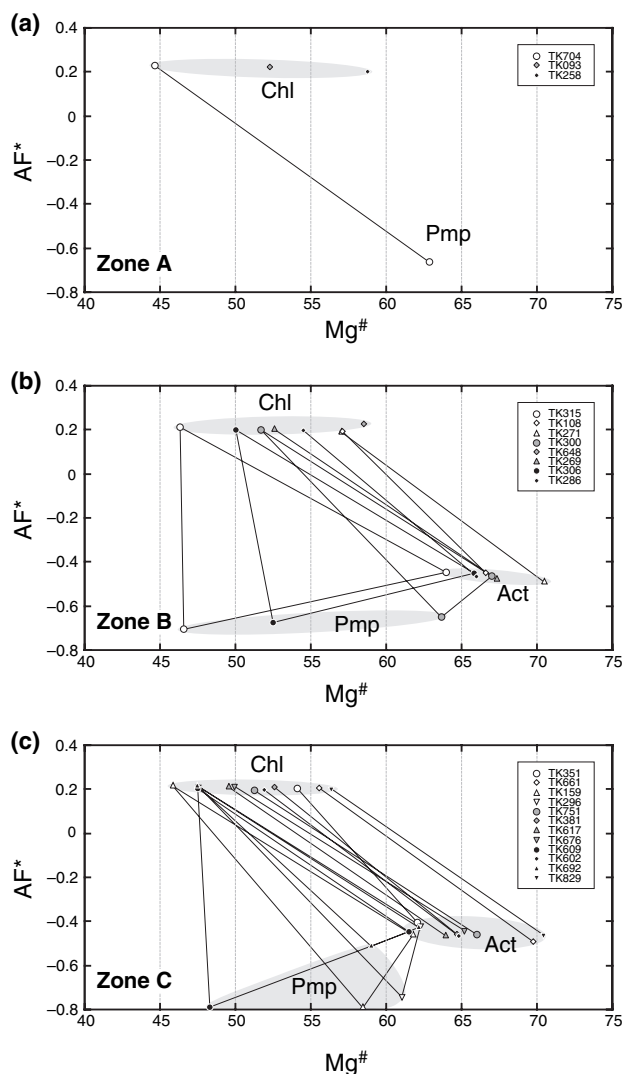


Fig. 10. (a-c) Epidote projections of metabasite mineral paragenesis from zone A to C in the Cleaverville area onto A*FM plane. Excess phases are quartz, albite and H₂O fluid. AF* is $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 - 0.75\text{CaO} - \text{Na}_2\text{O})/(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 - 0.75\text{CaO} - \text{Na}_2\text{O} + \text{FeO} + \text{MgO})$.

Olg from zone A to C. This indicates that the difference in mineral assemblages in the same metamorphic zone reflects the difference of FeO/MgO ratio of the whole rock. In other words, changes of mineral assemblages from zone A to C at a given Mg# of chlorite suggest the increase of metamorphic grade from zone A to C.

In summary, the mineral paragenesis of greenstones in the Cleaverville area is strongly influenced by the bulk-rock FeO/MgO ratio. Within a metamorphic zone, higher bulk FeO/MgO ratio leads to a pumpellyite-bearing assemblage. Therefore, it is necessary to remove the effect of the bulk composition on the mineral assemblage in order to estimate the metamorphic grade of the greenstone on the basis of the mineral assemblage.

Mineral compositions

While compositions of some major minerals change from zone A to C as described above, here compositional changes of the secondary minerals are related to the metamorphic grade in the Cleaverville area. Generally speaking, the An content of plagioclase increases with metamorphic grade and there are two plagioclase under the low-pressure condition (e.g. Maruyama *et al.*, 1982). In the Cleaverville area, the An content of plagioclase increases from zone A to C, and there is a peristerite gap in zone C (Fig. 5a,b). Compositional changes of plagioclase were reported from the Horokanai ophiolite in Japan (Ishizuka, 1985) and Karmutsen metabasites of the contact metamorphic aureole in Vancouver Island, Canada (Terabayashi, 1993), indicating that the increase of An content of plagioclase in the metabasite represents the increase of metamorphic grade (Ishizuka, 1985; Terabayashi, 1993). Therefore, the increase of An content of plagioclase in the Cleaverville area indicates that the metamorphic grade increases from zone A to C under low-pressure condition.

It is well known that Ca-amphibole changes generally from actinolite to hornblende with increasing metamorphic grade, and that actinolite becomes enriched in pargasite component with metamorphic temperature under the greenschist facies (e.g. Maruyama *et al.*, 1983; Terabayashi, 1993). Actinolite is the only amphibole in the Cleaverville area, but those in zone C are slightly enriched in edenite and tschermakite components compared with those in zone B (Fig. 6b). This is consistent with an increase of metamorphic grade from zone B to C.

Some epidote in zones B and C has chemical zonation, with decrease in $X_{\text{Fe}^{3+}}$ from core to rim, documenting prograde metamorphism (e.g. Ishizuka, 1985). Epidote coexisting with pumpellyite has lower $X_{\text{Fe}^{3+}}$ than those without pumpellyite in zone B (Fig. 7a). This suggests that the occurrence of pumpellyite and low $X_{\text{Fe}^{3+}}$ of epidote in a sample of zone B reflects the low $X_{\text{Fe}^{3+}}$ of the bulk composition.

Although chlorite in the Cleaverville area mostly overlaps chlorite from DSDP/ODP Hole 504 B, some chlorite in zone A has clearly higher X_{Fe} ratio than those from DSDP/ODP Hole 504B (Fig. 9d). Because X_{Fe} ratio of chlorite strongly reflects not only the mineral assemblage or metamorphic grade but also the X_{Fe} ratio of whole-rock composition (e.g. Hayashi *et al.*, 2000), the FeO enrichment of chlorite in the Cleaverville area may be due to hydrothermal alteration.

Metamorphic reaction and condition

Mineral assemblages and mineral compositions systematically change from zone A to C, and here metamorphic reactions that define the boundaries are

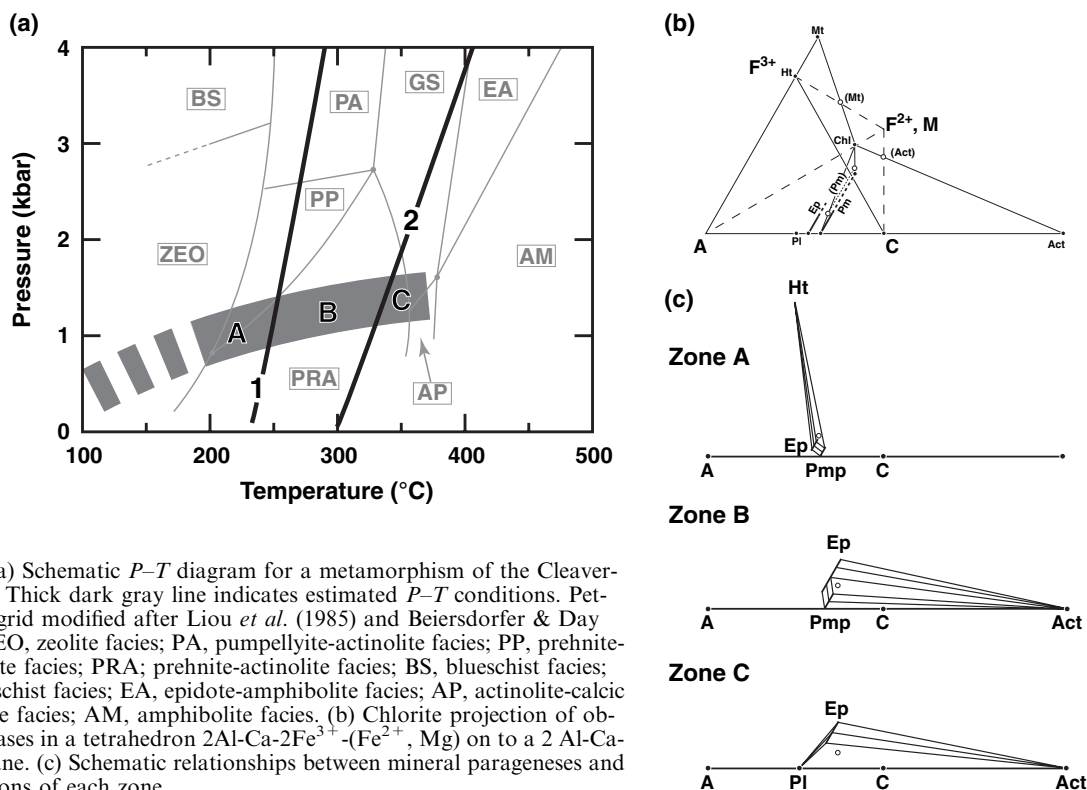
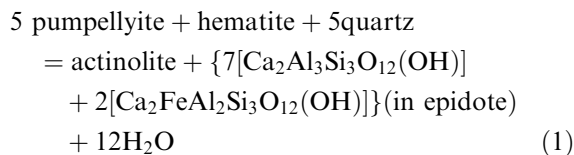


Fig. 11. (a) Schematic P - T diagram for a metamorphism of the Cleaver-ville area. Thick dark gray line indicates estimated P - T conditions. Petrological grid modified after Liou *et al.* (1985) and Beiersdorfer & Day (1995). ZEO, zeolite facies; PA, pumpellyite-actinolite facies; PP, prehnite-pumpellyite facies; PRA, prehnite-actinolite facies; BS, blueschist facies; GS greenschist facies; EA, epidote-amphibolite facies; AP, actinolite-calcic plagioclase facies; AM, amphibolite facies. (b) Chlorite projection of observed phases in a tetrahedron $2\text{Al-Ca-}2\text{Fe}^{3+}$ -(Fe^{2+} , Mg) on to a $2\text{Al-Ca-}2\text{Fe}^{3+}$ plane. (c) Schematic relationships between mineral parageneses and compositions of each zone.

investigated. The P - T conditions of the following reactions were calculated with THERMOCALC 3.25 (Holland & Powell, 1998; and its update). A model $\text{CaO-MgO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system, in the presence of excess quartz and H_2O , and Fe^{3+} -free pumpellyite are assumed.

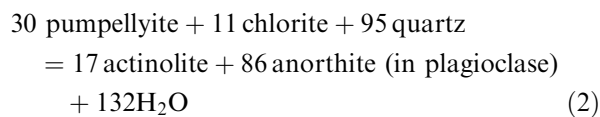
The diagnostic mineral assemblage changes from $\text{Chl} + \text{Ep} \pm \text{Pmp} + \text{Qz} + \text{Ab} \pm \text{Ht}$ in zone A to $\text{Chl} + \text{Ep} \pm \text{Pmp} + \text{Act} + \text{Qz} + \text{Ab}$ in zone B. The boundary between zones A and B is defined by the occurrence of actinolite in metabasites. This is written as the following reaction;



This reaction has a steep Clapeyron-slope on a P - T diagram (Fig. 11a). It represents the change from a hematite-pumpellyite tie line to an epidote-actinolite tie line in the system (Fig. 11b,c). The occurrence of epidote, pumpellyite and actinolite depends on $X_{\text{Fe}^{3+}}$ ratio and Ca/Al ratio of the whole-rock composition. Thus a metabasite with higher $X_{\text{Fe}^{3+}}$ ratio has the assemblage $\text{Chl} + \text{Ep} \pm \text{Act}$, whereas a metabasite with lower $X_{\text{Fe}^{3+}}$ ratio contains the assemblage $\text{Chl} + \text{Ep} + \text{Pmp} \pm \text{Act}$ (Fig. 11c). This fact is

consistent with the petrographic observation that epidote with lower $X_{\text{Fe}^{3+}}$ value coexists with pumpellyite, whereas epidote with higher $X_{\text{Fe}^{3+}}$ value does not coexist with pumpellyite in zone B (Fig. 7).

The reaction between zones B and C, defined by the appearance of oligoclase in the metabasite, can be attributed to the following reaction:



This reaction means decomposition of pumpellyite to form anorthite and actinolite (Fig. 11c). The assemblage of $\text{Chl} + \text{Ep} + \text{Pmp} + \text{Act} + \text{Olg}$ in zone C indicates that it was formed on the reaction line (2). However, this assemblage is widely present in zone C, which is not consistent with the reaction (2). This may be attributed to the assumption of an FeO-free model system. The addition of FeO into the system makes reaction (2) a continuous reaction, and results in a wide temperature range depending on the variation of FeO/MgO ratio as well as $X_{\text{Fe}^{3+}}$ ratio of the bulk rock. In zone C, pumpellyite is present only in FeO-rich samples (Fig. 10). This suggests that reaction (2) shifts towards the higher-temperature side with increasing FeO/MgO ratio of the bulk rock.

Moreover, pumpellyite in zones A and B also coexists with relatively aluminous epidote (Fig. 7), indicating that the disappearance of pumpellyite is controlled by two factors. One is the whole-rock composition (the increase of $X_{\text{Fe}^{3+}}$ and decrease of FeO/MgO ratio), and another is temperature leading the decomposition of pumpellyite. This suggests that low $X_{\text{Fe}^{3+}}$ and high FeO/MgO ratio of the whole rock tend to stabilize the pumpellyite-bearing assemblage at constant P – T .

The transition from greenschist to amphibolite facies is subdivided into a higher-pressure albite-epidote-amphibolite subfacies and a lower-pressure actinolite-calcic plagioclase subfacies (e.g. Miyashiro, 1973; Maruyama *et al.*, 1983). Therefore, the first appearance of calcic plagioclase precedes hornblende with increasing temperature at low-pressure condition (e.g. Maruyama *et al.*, 1983). On the other hand, a calcic plagioclase-bearing assemblage without hornblende is also reported from the prehnite-actinolite facies of low-pressure contact metamorphism (Terabayashi, 1993) and on-land ophiolites (Liou & Ernst, 1979; Ishizuka, 1985; Shibuya *et al.*, 2006). In the Cleaverville area, the assemblage of Olg + Act + Ep + Chl in zone C indicates low-pressure conditions.

Between the zeolite and greenschist facies, the pumpellyite + actinolite assemblage is stable at relatively high-pressure conditions, whereas prehnite + pumpellyite and prehnite + actinolite assemblages occur at lower-pressure conditions. However, the occurrence of prehnite- and pumpellyite-bearing assemblages strongly depends on bulk composition (Frey *et al.*, 1991), and an increase of whole-rock FeO/MgO ratio stabilizes the pumpellyite-bearing assemblage (e.g. Beiersdorfer & Day, 1995). This is consistent with the restricted occurrence of pumpellyite-bearing assemblages in the metabasites with high FeO/MgO ratio (Fig. 10). Thermodynamic calculations by Frey *et al.* (1991) suggested that pumpellyite-bearing assemblages can be formed at a low-pressure condition (<1 kbar) according to variation of bulk-rock composition. In the Vema fracture zone (Atlantic Ocean), abundant pumpellyite occurs in altered basalts that have strongly modified bulk composition because of hydrothermal alteration, and the estimated metamorphic condition is ~250 °C and <1 kbar (Mevel, 1981). This indicates that pumpellyite can occur in spite of low-pressure condition. These support the low-pressure condition in the Cleaverville area.

Ca-Al silicates such as prehnite, pumpellyite and epidote are generally unstable under high PCO_2 conditions, and decompose to the chlorite-calcite assemblage. In the Cleaverville area, many carbonatized samples with a chlorite + calcite assemblage are present, suggesting that the metamorphic fluid had relatively high CO_2 content. On the other hand, prehnite, pumpellyite and epidote have different resistance to CO_2 -rich fluid at a given P – T condition (Seki, 1973). With increasing CO_2 content in the metamorphic fluid, prehnite, pumpellyite and epidote decom-

pose in this sequence (Liou *et al.*, 1987). Epidote has the strongest resistance to CO_2 -rich fluid among these Ca-Al silicates. This is one of the most feasible reasons for the ubiquitous occurrence of epidote, rare occurrence of pumpellyite and absence of prehnite in the Cleaverville area.

Hydrothermal metamorphism and alteration of the Cleaverville area

The estimated metamorphic grades of the Cleaverville area range from subgreenschist facies (zones A and B) to greenschist facies (zone C). The metamorphic facies series are indicated to be a low-pressure type. The boundaries between the three zones are parallel to the bedding plane of overlying chert/BIF, and the metamorphic temperature increases stratigraphically downward. This progressive metamorphism is broadly consistent with the thermal structure of mid-ocean ridges, and suggests that the primary hydrothermal metamorphism at mid-ocean ridge is well preserved in the Cleaverville area.

On the other hand, metamorphism of the Cleaverville area is characterized by carbonatization. The carbonate minerals show intimate textural association with other secondary minerals (Fig. 3), indicating that the carbonate minerals coincide with other secondary minerals. Most of samples from zone A include carbonate minerals, whereas most samples from the lower part of zone C do not contain carbonate minerals. Although there are some lateral variations, the proportion of carbonate-bearing samples decreases from zone A to C. This is consistent with the increase of metamorphic temperature from zone A to C because the carbonate minerals generally become unstable with increasing temperature. These geological observations suggest that the carbonatization coincided with metamorphism in the Cleaverville area. It is, therefore, suggested that the hydrothermal carbonatization occurred at a mid-ocean ridge.

Comparison with modern ophiolite and sea-floor rocks

Parageneses and compositions of secondary minerals that were formed by ocean ridge hydrothermal alteration have been reported from modern oceanic crust such as DSDP/ODP Hole 504B (e.g. Alt *et al.*, 1985, 1996) and IODP Hole 1256D (Expedition 312 Scientists, 2006; Wilson *et al.*, 2006), the 6 Ma Taitao ophiolite (Shibuya *et al.*, 2006), and 3.5 Ga North Pole greenstone belt (Kitajima *et al.*, 2001a). The geological and hydrothermal characteristics of alteration in the Cleaverville greenstones are compared with modern ocean crust in Fig. 12. A relatively thick volcanic section in the Cleaverville area is explained by the higher Archean potential mantle temperature than present (Ohta *et al.*, 1996). The North Pole section presented in the Fig. 12 is an example of relatively thin volcanic sequence among the North Pole greenstone belt.

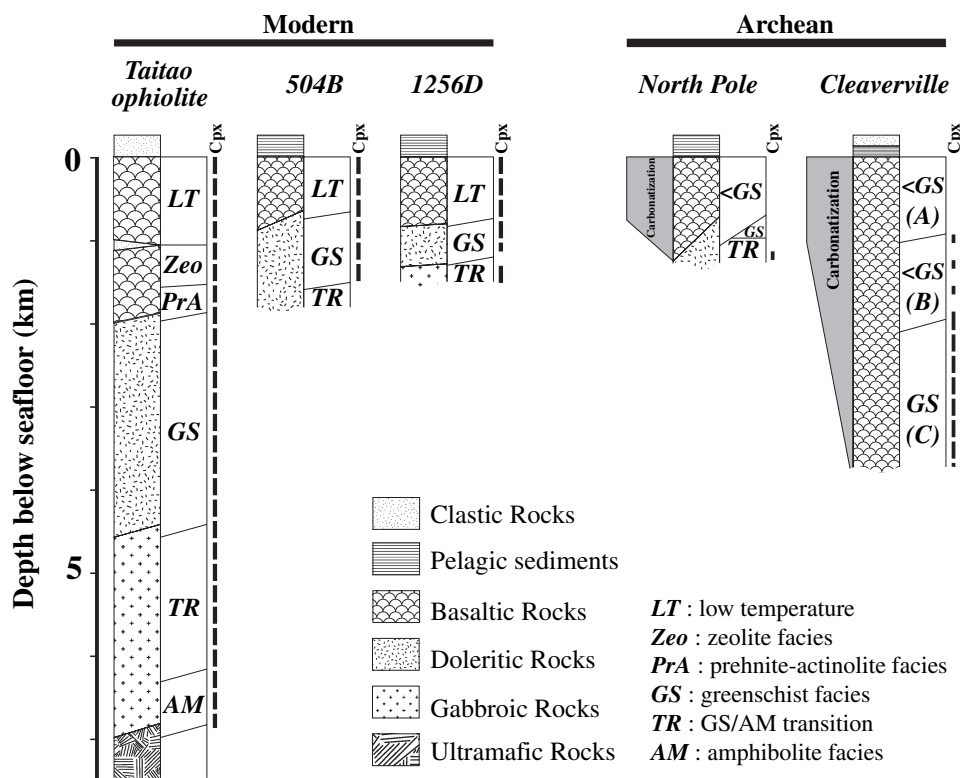


Fig. 12. Comparison of metamorphic facies and alterations in the Cleaverville area with those from DSDP/ODP Hole 504 B, Hole 1256D, 6 Ma Taitao ophiolite and 3.5 Ga North Pole greenstone belt. Preservation of igneous clinopyroxene is marked by broken line. In this paper, TR is defined by the presence of both actinolite and hornblende in the metabasites.

Thermal structure

At modern mid-oceanic ridges such as DSDP/ODP Hole 504 B, and the 6 Ma Taitao ophiolite, the metamorphic grade increases with depth. The metamorphic grade of Holes 504 B and 1256 D increases discontinuously from low-temperature (less than typical zeolite facies) to greenschist/amphibolite facies transition (locally amphibolite facies), and that of the Taitao ophiolite ranges from low temperature to amphibolite facies, respectively. Between the Taitao ophiolite, Hole 504 B and 1256 D, there is a difference in thickness of basaltic rocks and underlying doleritic rocks, but the metamorphic grade shows good correlation with lithology. For example, low-temperature and zeolite facies correspond to the volcanic sequence whereas greenschist facies is restricted to the underlying doleritic rocks. In the 3.5 Ga North Pole area, metamorphic grade increases from subgreenschist facies to greenschist/amphibolite facies transition stratigraphically downward, and shows a relatively higher temperature signature in the doleritic rocks than those of modern oceanic crust and ophiolite (Kitajima *et al.*, 2001a). In the Cleaverville area, a relatively thick basaltic sequence (> 3.5 km thick) is present and the metamorphic grade increases continuously from subgreenschist (zeolite or prehnite-

pumpellyite) facies to greenschist facies stratigraphically downward. The increase of metamorphic grade with depth is consistent with modern ophiolite and oceanic crust. However, the metamorphic temperature of the basaltic sequence in the Cleaverville area is more continuous and slightly higher than modern mid-ocean ridges. These signatures of alterations in the Cleaverville area may be due to sediment cover of chert or BIF (Fig. 1). The chert/BIFs in the Cleaverville area are suggested to have been deposited from seawater with hydrothermal affinity near the mid-ocean ridge on the basis of their REE composition (Kato *et al.*, 1998), which kept the underlying greenstones at high temperature. This is consistent with modern terrigenous sediment-covered oceanic crust that maintains the volcanic sequence at higher temperature than uncovered ridge (e.g. Davis *et al.*, 1997).

Occurrence of pumpellyite

Pumpellyite is a minor phase in the Cleaverville area but the occurrence clearly contrasts with the extreme rarity of pumpellyite in modern oceanic crust. However, pumpellyite was reported from the Vema fracture zone (Mid-Atlantic Ridge; Mevel, 1981), the La Palma seamount (Schiffman & Staudigel, 1994,

1995) and ophiolites (e.g. Liou, 1979; Ishizuka, 1985; Harper, 1995). Schiffman & Staudigel (1994) showed that the metamorphic gradient of the La Palma seamount is distinct from that of Hole 504B: the former is characterized by continuous metamorphic facies series ranging from zeolite, prehnite-pumpellyite, and greenschist facies, and the latter by stepped metamorphic gradient in which the prehnite-pumpellyite facies is absent. Therefore, one of the reasons for the lack of pumpellyite in modern oceanic crust may be the discontinuous thermal gradient (Schiffman & Staudigel, 1994; Alt, 1999). The geothermal gradient of the Cleaverville area is continuous (Fig. 11), which is suggested to be caused by sediment cover of chert/BIF, as discussed above. This continuous thermal gradient may account for the presence of pumpellyite in the Cleaverville area. On the other hand, the composition of metamorphic fluid also influences the formation of pumpellyite (Mevel, 1981; Harper, 1995). In the Cleaverville area, pumpellyite-bearing samples are suggested to have higher FeO/MgO ratio and lower $X_{\text{Fe}^{3+}}$ of bulk composition than pumpellyite-free samples. This may reflect local metasomatism by heterogeneous hydrothermal fluid.

Degree of alteration

The degree of alteration of oceanic crust is best exemplified by monitoring the degree of alteration of igneous clinopyroxene to secondary minerals (Gillis & Banerjee, 2000). In modern oceanic crust and ophiolites, porosity and permeability decrease stratigraphically downward which leads to the decrease of water/rock ratio with depth. However, igneous clinopyroxene is preserved throughout the sections of modern oceanic crust, with localized zones of complete replacement in the basal dykes (Gillis, 1995; Alt *et al.*, 1996; Gillis & Banerjee, 2000; Expedition 312 Scientists, 2006; Wilson *et al.*, 2006). The Taitao ophiolite ubiquitously preserves igneous clinopyroxene (Fig. 12; Shibuya *et al.*, 2006). In the Cleaverville area, igneous clinopyroxene is well preserved in zone C, but completely replaced by the secondary minerals in zone A. This indicates the degree of alteration in the Cleaverville area decreases stratigraphically downward which is consistent with the decrease of water/rock ratio with depth in modern oceanic crust and ophiolite. Although there are some differences of alteration degrees between oceanic crusts and ophiolites (e.g. Alt & Teagle, 2000; Gillis & Banerjee, 2000; Gao *et al.*, 2006), the absence of clinopyroxene in the uppermost part of the Cleaverville greenstone indicates that the alteration degree of the uppermost greenstone is higher than volcanic sequences of modern oceanic crust and the Taitao ophiolite. This probably reflects the higher temperature or the higher water/rock ratio of alteration, or both, compared with those of modern oceanic crust and ophiolites.

CO₂ concentration of hydrothermal fluid

Ca-Al silicates such as Ca-zeolite, prehnite and epidote are common in lower volcanic sequence and sheeted dykes of the Taitao ophiolite, and sheeted dykes of modern oceanic crust. In addition, carbonate minerals mainly occur in the low-temperature (<150 °C) volcanic sequence of modern oceanic crust (Alt *et al.*, 1985, 1996). In contrast, the uppermost part of Cleaverville greenstones has mainly chlorite-calcite assemblages, with Ca-Al silicates being extremely rare. Calcite-chlorite assemblages occur in zones B and C in spite of relatively high temperature (250–350 °C; Figs 1 & 11). In general, a metamorphic fluid with high X_{CO_2} stabilizes the carbonate-chlorite assemblage instead of Ca-Al silicates that are stable in case of low X_{CO_2} fluid, and carbonate becomes unstable with increasing temperature under constant PCO_2 condition (e.g. Liou *et al.*, 1987). This indicates that the metamorphic fluid of the Cleaverville area has relatively higher CO₂ concentration than modern hydrothermal fluids at mid-ocean ridges. In the 3.5 Ga North Pole area, carbonate-chlorite assemblages are also dominant instead of Ca-Al silicates in the uppermost part of the greenstones (Kitajima *et al.*, 2001a; Terabayashi *et al.*, 2003). Kitajima *et al.* (2001a) estimated X_{CO_2} in the Archean hydrothermal fluid based on thermodynamic calculation, as much higher X_{CO_2} (0.012–0.140) than present-day mid-ocean ridges (up to 0.005). Therefore, calcite-chlorite dominated assemblages in the Cleaverville area suggest that hydrothermal fluid had also high X_{CO_2} .

Archean ocean ridge hydrothermal alteration

The 3.2 Ga Archean uppermost oceanic crust is more pervasively altered and carbonatized than modern equivalent. These features suggest that Archean hydrothermal alteration played a more important role in fixation of CO₂ than present-day ocean-ridge hydrothermal alteration, as an interaction between seawater and oceanic crust, as proposed by Nakamura & Kato (2004). The higher degree of alteration in the 3.2 Ga upper volcanic sequence develops the more intensive chemical and heat exchanges between sea water and oceanic crust. This suggests that the 3.2 Ga sea water was more strongly controlled by the hydrothermal alteration at mid-ocean ridge than at present. The 3.2 Ga high X_{CO_2} hydrothermal fluid implies that sea water had also high CO₂ concentration because the hydrothermal fluid originates from the ambient sea water that penetrates along listric normal faults and fractures. The widespread carbonate minerals in the 3.2 Ga upper oceanic crust suggest that CO₂ in the seawater was fixed into the oceanic crust near the mid-ocean ridge. Considering the 3.5 Ga hydrothermal carbonatization of the upper oceanic crust (Kitajima *et al.*, 2001a; Terabayashi *et al.*, 2003; Nakamura & Kato, 2004) as well as that in 3.2 Ga Cleaverville area,

it is suggested that the severe carbonatization of upper oceanic crust at Archean mid-ocean ridge had continued for three billion years or more.

CONCLUSIONS

The greenstones in the 3.2 Ga Cleaverville area are divided into three mineral zones based on the parageneses and compositions of secondary minerals in the less carbonatized greenstones. The metamorphic grade increases stratigraphically downward and ranges from subgreenschist facies (zeolite facies or prehnite-pumpellyite facies) to greenschist facies. The metamorphic facies series corresponds to the low-pressure type. The boundaries between each zone are subparallel to the overlying chert/BIF. This metamorphic feature suggests that primary hydrothermal metamorphism at mid-ocean ridge is well preserved in the Cleaverville area.

Extremely carbonatized samples are widely distributed in the stratigraphic upper part, and have the assemblage of chlorite-calcite instead of Ca-Al silicates such as Ca-zeolite, prehnite, epidote that are common in the modern upper oceanic crust. This suggests that high X_{CO_2} hydrothermal fluid circulated in the upper oceanic crust near the 3.2 Ga mid-ocean ridge. Furthermore, these samples are completely altered and have no relict igneous clinopyroxene, which is well preserved throughout much of the modern oceanic crust. This suggests that the uppermost 3.2 Ga oceanic crust is more pervasively altered than that of modern equivalent.

Considering the strong carbonatization in 3.5 Ga uppermost oceanic crust (Kitajima *et al.*, 2001a; Terabayashi *et al.*, 2003; Nakamura & Kato, 2004) and in 3.2 Ga oceanic crust (this study), it is suggested that the hydrothermal carbonatization at mid-ocean ridge had continued at least from 3.5 to 3.2 Ga.

ACKNOWLEDGEMENTS

We thank S. Yamamoto, M. Igisu and D. Kurokawa for assistance in the field work, and Drs T. Ota and S. Omori for many fruitful discussions. We also thank Dr D. Robinson, Dr J.C. Alt and an anonymous referee for their thoughtful reviews that significantly improved this manuscript. We are grateful to Drs J.C. Alt and D. Robinson for correction of English expression. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology of Japan. T.S. is supported by the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

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Received 16 October 2006; revision accepted 20 May 2007.