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Chapter 7.3

STABLE CARBON AND SULFUR ISOTOPE GEOCHEMISTRY OF THE CA. 3490 MA DRESSER FORMATION HYDROTHERMAL DEPOSIT, PILBARA CRATON, WESTERN AUSTRALIA

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7.3-1. INTRODUCTION

The North Pole area in the Pilbara Craton of Western Australia is well known for the occurrence of the oldest (∼3.5 Ga) putative microfossils (Awramik et al., 1983; Ueno et al., 2001a) and stromatolites (Walter 1980; Hofmann et al., 1999; Van Kranendonk 2006; Allwood et al., 2006a), particularly in the chert-barite dominated sedimentary rocks of the Dresser Formation. However, a biological origin of these putative fossils has been debated (Buick et al., 1981; Buick 1990; Schopf et al., 2002; Garcia Ruiz et al., 2003; Brasier et al., 2002, 2006). Moreover, morphology-based study of prokaryotic fossils provides only limited information for the physiology of possible ancient life.

On the other hand, carbon and sulfur isotope geochemistry is useful to trace specific metabolic activities in the past, including autotrophic carbon fixation, sulfate reduction, and methanogenesis. Shen et al. (2001) reported ^{34}S-depletion of pyrite in bedded and vein barite ($\delta^{34}S_{\text{pyrite}} - \delta^{34}S_{\text{barite}} = -5$ to -21‰) in the Dresser Formation, which is interpreted as the oldest evidence for microbial sulfate reduction. The recent discovery of ^{13}C-depleted methane ($\delta^{13}C_{\text{CH4}} < -56$‰) in primary fluid inclusions of the Dresser Formation indicates that microbial methanogenesis could have been active in the Paleoarchaean (Ueno et al., 2006).

The depositional environment of the Dresser Formation has long been considered as an evaporitic, shallow marine basin (e.g., Buick, 1990; Lowe, 1983). Hence, most of the palaeontological and geochemical evidence for the putative early life forms have been interpreted from the viewpoint of a photosynthesis-based shallow marine ecosystem, which includes cyanobacteria-like microfossils (Awramik et al., 1983), stromatolites build by photosynthesizers (Walter, 1983), and sulfate-reduction in a locally sulfate-rich evaporitic basin (Shen and Buick, 2004). However, recent geological and geochemical investigations suggest that hydrothermal activity played an important role in the deposition of the chert-barite rocks of the Dresser Formation (Isozaki et al., 1997; Nijman et al., 1999; Runnegar

2001; Ueno et al., 2001a, 2004; Van Kranendonk et al., 2001b; Van Kranendonk and Pirajno, 2004; Van Kranendonk, 2006). The most striking evidence for the hydrothermal activity comes from the occurrence of a prominent swarm of silica ± barite feeder veins, which penetrated along syn-sedimentary growth faults in the footwall to bedded chert-barite rocks (Nijman et al., 1999; Ueno et al., 2001a; Van Kranendonk et al., 2001b; Van Kranendonk and Pirajno, 2004). Hence, it is plausible that the Dresser Formation represents a hydrothermally influenced volcano-sedimentary sequence deposited in a submarine volcanic caldera (Van Kranendonk, 2006, this volume).

With this new depositional setting in mind, we can now re-evaluate the link between hydrothermal activity and the palaeontological and geochemical evidence for life in the Dresser Formation. Furthermore, recent petrological studies confirm that black silica veins, which are abundant in the footwall to the Dresser Formation, commonly contain significant amounts of organic matter (e.g., Ueno et al., 2004), as reported from other Paleo- and Mesoarchaean greenstone terranes (e.g., de Wit et al., 1982; Kiyokawa et al., 2006). The origin of the organic matter in the veins is controversial, but particularly important, because the organic matter has been produced either by biological carbon fixation (Ueno et al., 2004, 2006; Brasier et al., 2006), or by pre-biotic organic synthesis (Brasier et al., 2002; Lindsay et al., 2005; McCollom and Seewald, 2006). In this paper, the mode of occurrence of the Dresser hydrothermal deposits is first briefly summarized. Then, the carbon and sulfur isotope geochemistry of the Dresser deposits is reviewed in relation to the hydrothermal activity.

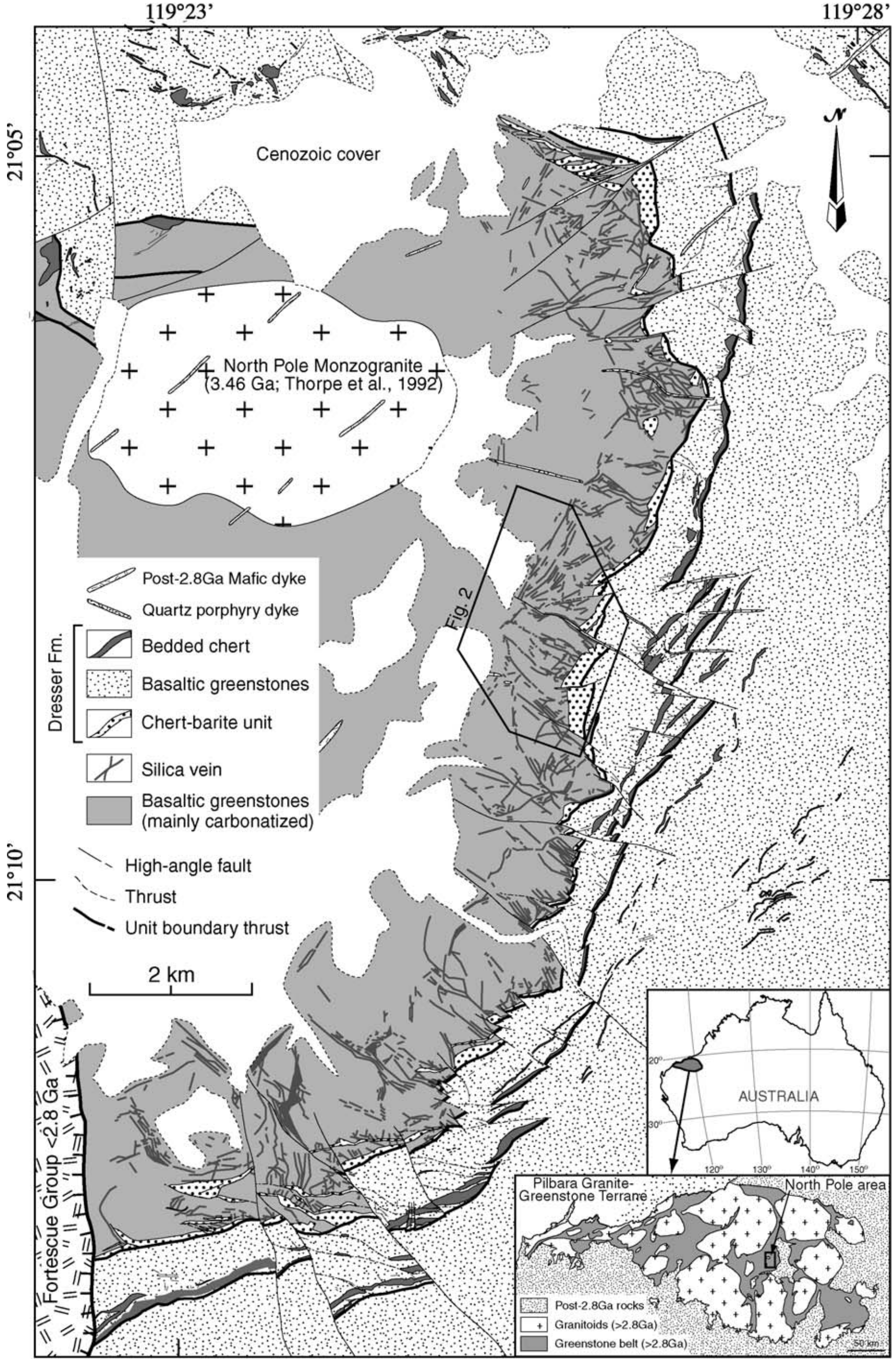
7.3-2. HYDROTHERMAL DEPOSITS IN THE NORTH POLE AREA

7.3-2.1. The Dresser Formation

The Dresser Formation is exposed in the North Pole Dome of the East Pilbara Terrane, Pilbara Craton (Fig. 7.3-1). The Dresser Formation (Van Kranendonk and Morant, 1998) consists of ca. 2-km thick basaltic greenstones intercalated with three horizons of bedded chert (Fig. 7.3-1). The lowermost chert unit is 1 to 70 m thick and is intercalated with several barite horizons of 0.1 to 5 m thickness. This barite-bearing chert unit corresponds to the "chert-barite unit" previously described by Buick and Dunlop (1990). The other two chert units are thinner (1–13 m) than the chert-barite unit, and contain only rare barite.

The precise age of the Dresser Formation has not been directly determined. Zircon U-Pb dating yields an age of 3458 ± 2 Ma for felsic volcanic rocks of the stratigraphically overlying Panorama Formation in the North Pole area (Thorpe et al., 1992a), indicating an age for the Dresser Formation of >3460 Ma. A model lead age of 3490 Ma (Thorpe et al.,

Fig. 7.3-1. Geological map of the Dresser Formation in the North Pole area, modified from Kitajima et al. (2001).


119°23'
119°28'
21°05'
21°10'
N
Cenozoic cover
North Pole Monzogranite
(3.46 Ga; Thorpe et al., 1992)
Fig. 2
Post-2.8Ga Mafic dyke
Quartz porphyry dyke
Dresser Fm.
Bedded chert
Basaltic greenstones
Chert-barite unit
Silica vein
Basaltic greenstones
(mainly carbonatized)
High-angle fault
Thrust
Unit boundary thrust
2 km
Fortescue Group <2.8 Ga
20°
30°
AUSTRALIA
120°
130°
140°
150°
Pilbara Granite-
Greenstone Terrane
North Pole area
Post-2.8Ga rocks
Granitoids (>2.8Ga)
Greenstone belt (>2.8Ga)
50 km

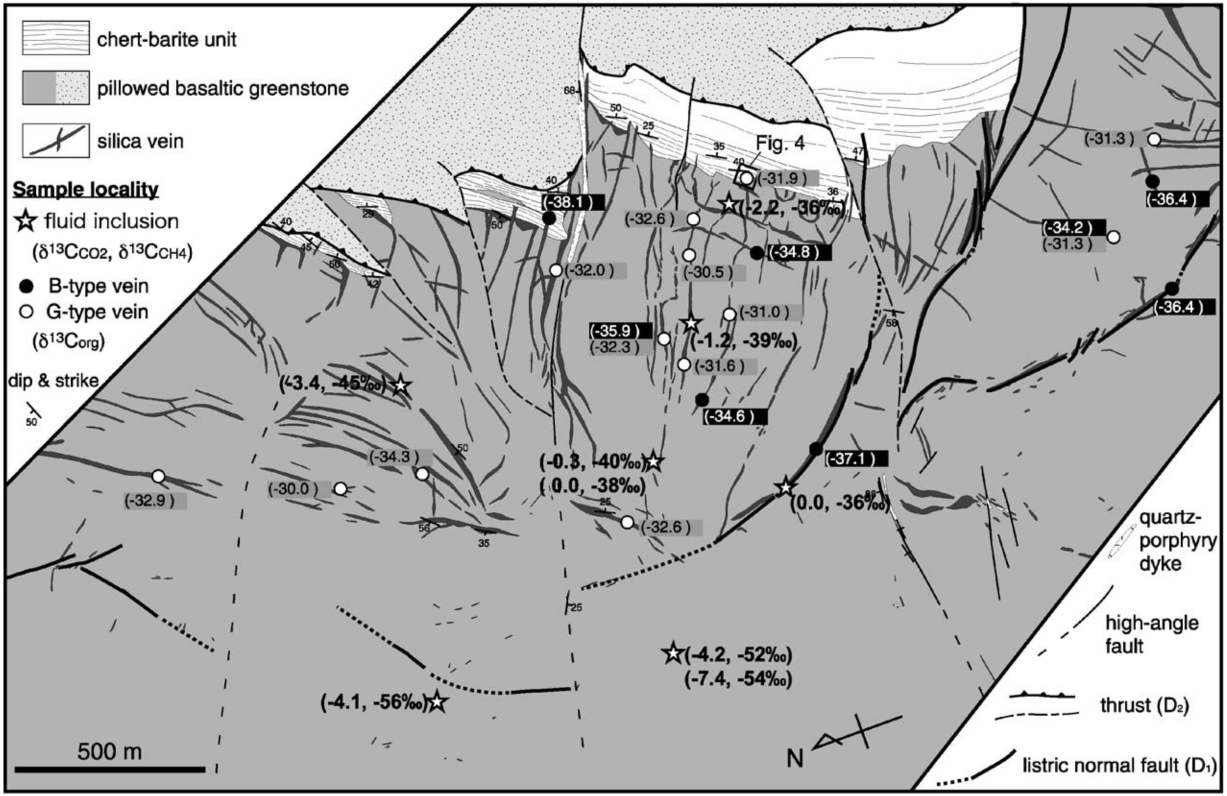


Fig. 7.3-2. Detailed geological map of part of the Dresser Formation, showing carbon isotopic values of analysed organic matter (circles), and of CO_2 and CH_4 in fluid inclusions (stars). Note that the contact between the chert-barite unit and the underlying pillowed basalt represents the sea-floor surface at the time of chert deposition, and therefore that the silica veins developed in the uppermost 1000 m of the oceanic crust. The box indicates the location of Fig. 7.3-4.

1992b) was obtained for galena from barite in the Dresser Formation, which is considered to represent the actual depositional age of the Dresser Formation.

7.3-2.2. Hydrothermal Silica Vein Swarm

In the North Pole area, numerous (>2000 identified) silica veins characteristically intruded along normal faults, which developed in pillowed basaltic volcanic rocks below the Dresser Formation (Figs. 7.3-1–7.3-4). They are 0.3–20 m wide and generally >100 m long, with the longest one over 1 km. The veins are massive and are composed mainly of fine-grained silica (<10 μm). Some silica veins show a symmetrical zonation pattern across the dike axis, and sometimes have agate at the center (Fig. 7.3-3(b)), in which the silica shows fan-shape structures grown from the margins toward the center of the veins. This suggests the precipitation of silica from a hydrothermal fluid (cf. Van Kranendonk and Pirajno, 2004).

The silica veins were previously called T-chert, which means "tectonic" chert (Hickman, 1973), chert vein (Nijman et al., 1999), chert dyke (Lindsay et al., 2005), silica dyke (Ueno et al., 2004, 2006), or silica vein (Van Kranendonk, 2006). The term "silica vein" is used in this paper, because "chert" is a term used for a chemical sedimentary rock with a distinct grain size and texture, and is thus not suitable for an intrusive rock, which has a grain size of generally microquartz. Also, the silica veins are clearly distinguished from quartz veins, which consist of white, coarse-grained quartz.

The silica veins terminate into chert beds of the Dresser Formation, but do not cut through the entire chert unit, nor into the overlying pillow basalt (Figs. 7.3-1, 7.3-2, and 7.3-4: Ueno et al., 2004; Van Kranendonk, 2006). The tops of the veins locally show a gradual transition into chert beds, forming a clear T-junction. In the field, repeated cycles of normal faulting, vein formation, and subsequent deposition of chert beds can be recognized (Fig. 7.3-4). These relationships suggest the silica veins were formed intermittently during the deposition of chert beds (Isozaki et al., 1997; Nijman et al., 1999; Ueno et al., 2001a; Van Kranendonk et al., 2001b; Van Kranendonk, 2006).

In addition, 0.1 to 2 m wide barite veins also intruded the footwall basaltic rocks, and some vein barite occurs in silica veins, as growth zones, or as discrete veins (cf. Van Kranendonk, 2006). Similar to the relationship between silica veins and bedded chert, the vein and "bedded" barite show feeder vein-deposit relationships (Nijman et al., 1999). The distribution of vein barite is laterally discontinuous and is generally restricted to the uppermost ~100 m of the pillow lava unit below the Dresser Formation, whereas silica veins occur up to about 1000 m below the formation. This distribution pattern indicates that the hydrothermal fluid circulated at least 1000 m below seafloor at the time of deposition of the Dresser Formation, but that circulation of sulfate-rich fluids was restricted to the shallower part of the system.

7.3-2.3. Organic Matter in the Silica Veins

The silica veins contain considerable amounts of organic matter (kerogen), which give the veins their black to gray color (Fig. 7.3-3). Thorough geochemical and petrological

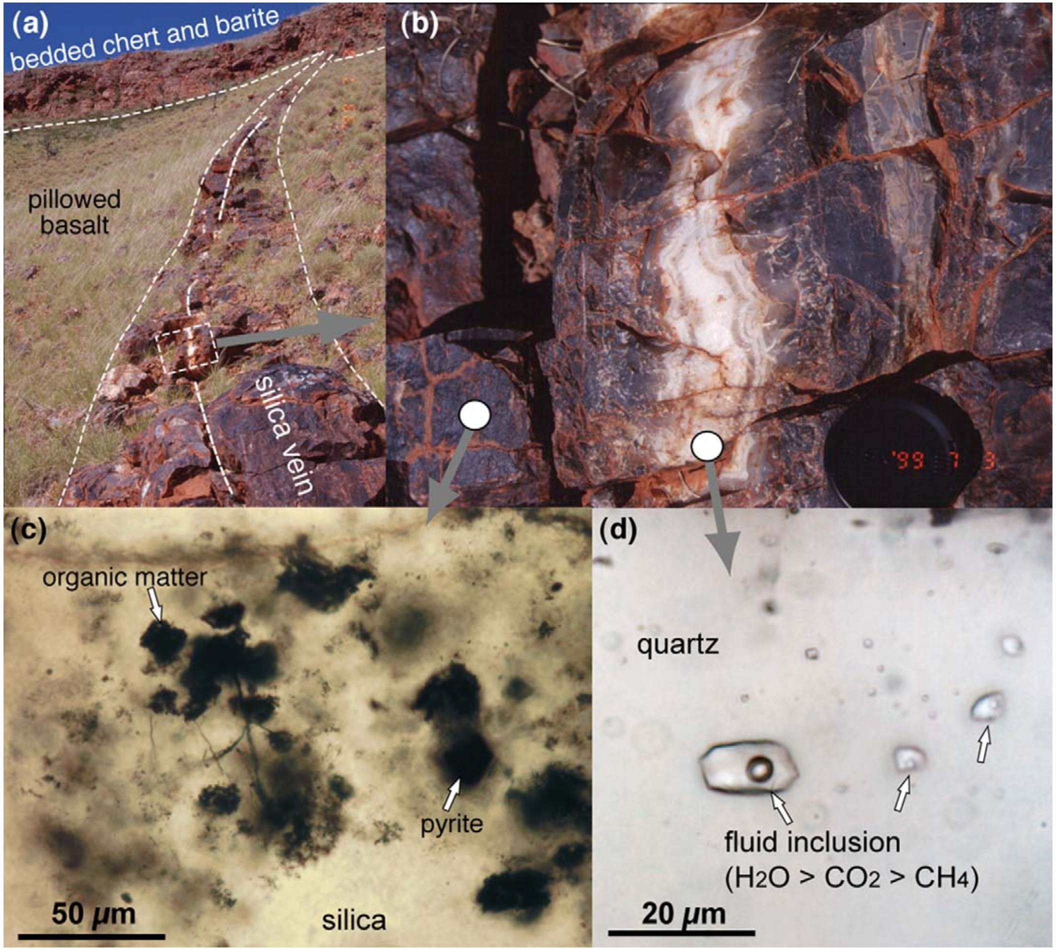

(a)
bedded chert and barite
pillowed basalt
silica vein
(b)
'99 7 3
(c)
organic matter
pyrite
silica
50 μm
(d)
quartz
fluid inclusion
(H2O > CO2 > CH4)
20 μm

Fig. 7.3-3. (a) Photograph of a 1 m wide hydrothermal silica vein leading up to bedded chert and barite. (b) Close-up view of the central part of the silica vein in (a), showing agate-textured quartz core. Width of the photo is about 30 cm. (c) Photomicrograph of a black part of the silica vein, showing irregular-shaped clots of organic matter and pyrite enclosed in a fine-grained silica matrix. (d) Photomicrograph of coarse-grained quartz developed in the central part of the vein, showing H_2O–CO_2 fluid inclusions therein.

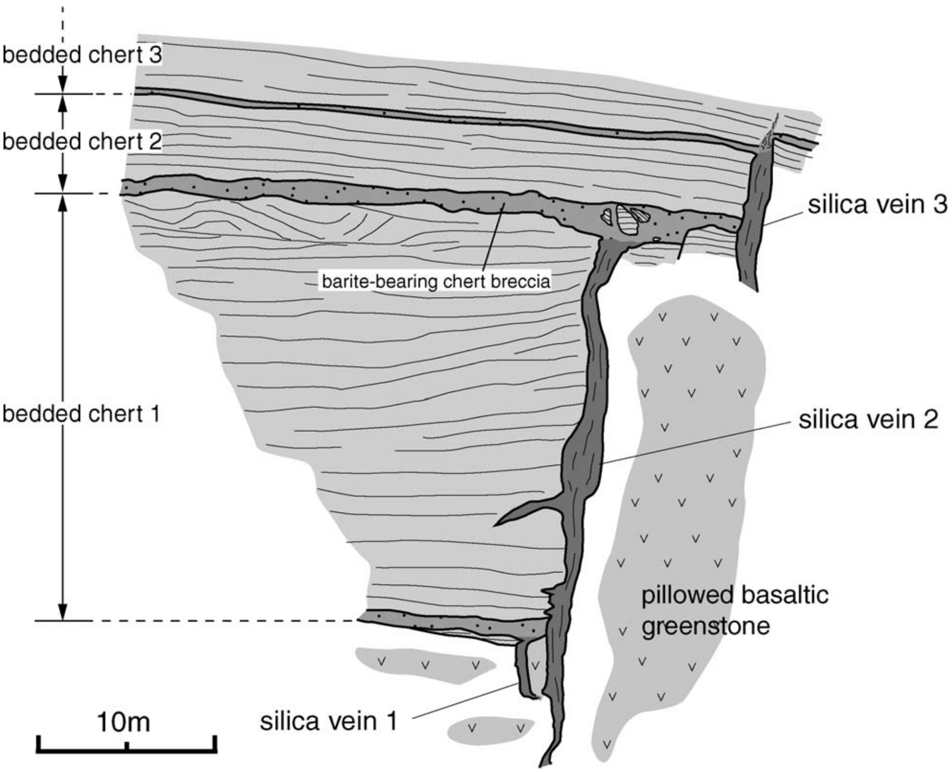


Fig. 7.3-4. Mode of occurrence of the chert-barite beds and silica veins intruding along syn-depositional growth faults (modified from Isozaki et al. (1997)). At least three stages of penetration of the silica vein and subsequent deposition of the bedded chert can be recognized in this outcrop.

investigation of more than 600 hand specimens of the silica veins has revealed that the concentration of organic carbon in the veins would have been originally >1 mg C/g (Ueno et al., 2004). Most veins have suffered post-depositional metasomatism (oxidation) and have lost about 90% of the original organic matter. However, some black silica veins possess an original mineral suite that includes pyrite, Fe-poor sphalerite, and Fe-dolomite (Ueno et al., 2004). These mineral compositions, as well as its silica- and barite-dominated mineral assemblage, suggest that the veins were deposited from relatively low temperature (100–200 °C), reducing hydrothermal fluids (Ueno et al., 2004). This temperature estimate is consistent with homogenization temperatures of fluid inclusions in vein quartz (~150 °C; Kitajima et al., 2001) and in cavity-filling quartz of pillowed basalt (90–170 °C; Foriel et al., 2004).

Consequently, this suggests that organic carbon was widely distributed in fissures that developed in the upper 1000 m of the seafloor basalt. These fissures acted as conduits for circulating hydrothermal fluids (Van Kranendonk, 2006). The estimated temperature of the fluid is low enough to permit biological activity in the sub-seafloor environment, and is suitable for thermophilic or hyperthermophilic organisms.

7.3-3. CARBON AND SULFUR ISOTOPE GEOCHEMISTRY OF THE DRESSER FORMATION

7.3-3.1. Carbon Isotopic Composition of Organic Matter in the Hydrothermal Veins

The $\delta^{13}C$ values of organic matter in the silica veins and bedded chert in the Dresser Formation are -38 to -30‰ and -31 to -29‰, respectively (Figs. 7.3-2 and 7.3-5). The isotopic variation of the organic matter does not correlate with depth below seafloor surface at that time, but rather with organic carbon concentrations. This indicates that post-depositional alteration would have reduced a considerable amount of the organic carbon in the silica veins and significantly modified its carbon isotopic composition. Hence, we have to first estimate the original isotopic composition of the organic matter before discussing its origin.

Among the silica veins, sulfide-bearing black silica veins contain higher organic carbon concentrations and show more ^{13}C-depleted isotopic compositions than gray sulfide-free silica veins, which formed by alteration of primary sulfide-bearing veins (Ueno et al., 2004). This variation would be produced by the Rayleigh distillation process with a carbon isotopic fractionation factor of 0.9985 (Fig. 7.3-5; Ueno et al., 2004). According to this model, the original organic carbon in the silica veins would have been isotopically heterogeneous (~5‰) at around -35‰, and at least some material had initial $\delta^{13}C$ values of $\leqslant -38$‰.

The inferred ^{13}C-depletion of the initial organic carbon can be explained by biological carbon fixation. The isotopic composition of carbonate carbon in the veins is -2‰ (Ueno et al., 2004). This indicates that the equilibrated dissolved CO_2 had $\delta^{13}C$ values of about -4‰ at 100 °C (Mook et al., 1974). This estimate is roughly consistent with $\delta^{13}C$ values of CO_2 entrapped in the primary fluid inclusions (-3 to -7‰; Ueno et al., 2006). Thus, the fractionation between initial organic carbon and dissolved CO_2 (i.e., δ) would have been over 34‰, for at least some of the material.

If the organic carbon was produced by autotrophic organisms, then this fractionation is too large to be associated with Rubisco ($\delta \leqslant 30$‰; e.g., House et al., 2003), the enzyme

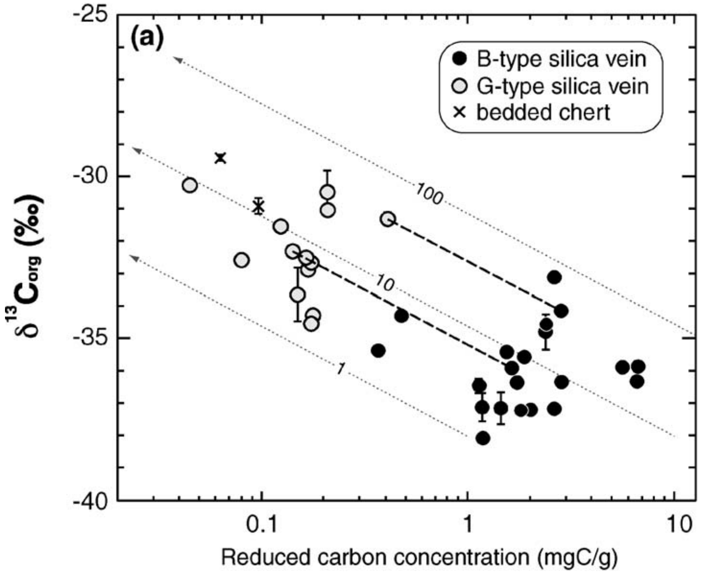


Fig. 7.3-5. Carbon isotopic compositions of organic matter, CO_2, and CH_4 in the silica veins. (a) Relationship between organic carbon concentration and carbon isotopic composition of the organic matter in the silica veins and bedded chert. Dashed lines tie the values from the same rock samples. Doted lines represent Rayleigh-fractionation trajectories with fractionation factor (□) of 0.9985. The three lines labeled 1, 10, and 100 started with an initial $\delta^{13}C$ value of −38‰, and with initial concentrations of organic carbon of 1, 10, and 100 mg C/g, respectively. (b) Relationship between $\delta^{13}C_{CH4}$ and $\delta^{13}C_{CO2}$ values of the extracted volatiles from the fluid inclusions as compared with that of fluids vented from present-day seafloor hydrothermal systems. ^{13}C-depleted CH_4 occurs preferentially in samples rich in primary fluid inclusions (Ueno et al., 2006). (c) The ranges of carbon isotopic compositions of organic matter and carbonate in the silica vein and bedded chert.

utilized by aerobic photoautotrophs. This is consistent with the newly recognized depositional model, in which phototrophs are unlikely to have been involved in the sub-seafloor hydrothermal environment. On the other hand, the large organic carbon fractionation could have been produced via the reductive acetyl-CoA pathway ($\delta \leqslant 42$‰; e.g., House et al., 2003; Londry and Des Marais, 2003), which is utilized by H_2-dependent chemoautotrophs such as methanogen, acetogen, and some sulfate-reducers. This inferred large fractionation is consistent with the reducing conditions of the sub-seafloor hydrothermal system during the Dresser Formation. In fact, such large fractionations (up to 36‰) have been demonstrated by some anaerobic and thermophilic chemoautotrophs, such as *Methanobacterium thermoautotrophicum* (Fuchs et al., 1979).

Although the geological, petrological, and geochemical characteristics of the organic matter in Dresser Formation hydrothermal veins can be fully explained by metabolic activity of autotrophic organisms in a hydrothermal environment, the data do not eliminate a possible abiological origin for the organic matter. Under hydrothermal conditions

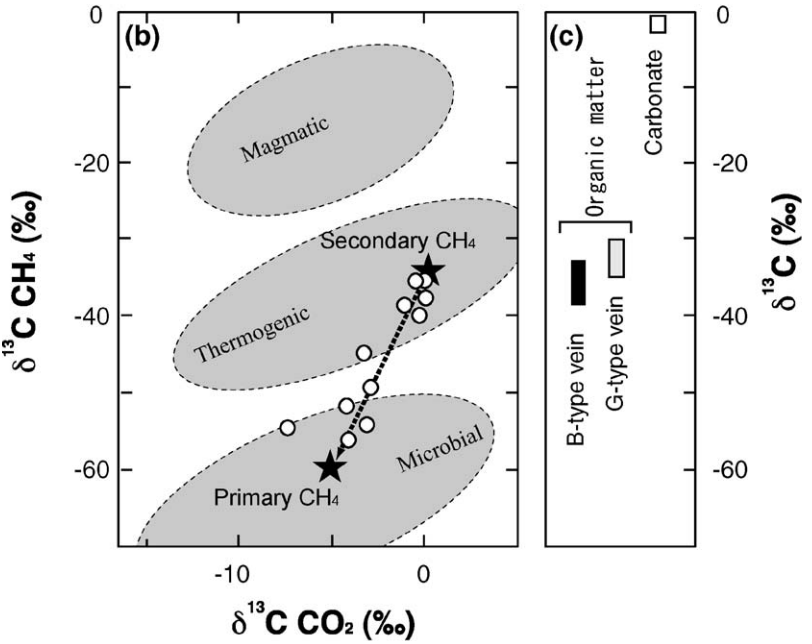


Fig. 7.3-5. (*Continued.*)

of 200–300 °C, it has been shown that abiological Fischer–Tropsch-type (FTT) reactions can produce organic matter with similarly large ^{13}C-depletions (McCollom and Seewald, 2006). However, it is questionable whether FTT synthesis took place under the conditions prevailing during silica precipitation in the Dresser Formation, because likely catalysts for FTT reactions (i.e., native metal and oxide) would not have existed under the reducing conditions exhibited by these veins. Fe-Ni alloy does not occur, despite thorough investigation of more than 300 petrographic thin sections of the silica veins (Ueno et al., 2004). Fe oxides occur only as a secondary mineral in the veins, whereas Fe-Ni sulfide (polydymite) exists as the primary mineral phase in the veins. Significantly, the presence of sulfide is known to poison industrial FTT reactions (Anderson, 1956). The apparent deficiency of an effective catalyst raises doubts as to whether FTT reactions could have produced the organic matter, under the low temperature, sulfidic conditions recorded by Dresser Formation hydrothermal veins. Note that native metal could have existed in the deeper parts of the veins than the site of silica precipitation, such that FTT reactions, if they occurred at all, may have possibly occurred under deeper and much higher temperature conditions ($\gg$200 °C). If this is the case, however, isotopic fractionation should be smaller than that observed and organic materials should increase with depths in the veins, a feature which does not occur. In the following section, this point is further discussed in relation to the isotopic compositions of methane and carbon dioxide.

7.3-3.2. Carbon Isotopic Composition of Methane in Fluid Inclusions

The hydrothermal silica veins and associated quartz veins contain fluid inclusions (Fig. 7.3-3), some of which were entrapped during the original silica precipitation. In-situ laser Raman microspectroscopy confirmed that the fluid mainly consists of H_2O and CO_2, with a minor, but detectable, amount of CH_4 and H_2S (Fig. 7.3-6).

Crushing extraction of the CO_2 and CH_4 in the fluid inclusions coupled with carbon isotope analysis revealed that the $\delta^{13}C$ values of the CO_2 and CH_4 is −7 to 0‰ and −56 to −36‰, respectively (Figs. 7.3-2 and 7.3-5: Ueno et al., 2006). Similar to the isotopic compositions of the organic matter, the $\delta^{13}C_{CH4}$ values do not correlate with the depth below the seafloor surface at that time, but with a mixing ratio of primary and secondary inclusions determined by petrographic observation (Ueno et al., 2006). This relationship indicates that the primary fluid contains ^{13}C-depleted CH_4 and CO_2 ($\delta^{13}C_{CH4} < -56‰$; $\delta^{13}C_{CO2} < -4‰$), and that a secondary fluid was more ^{13}C-enriched ($\delta^{13}C_{CH4} \approx -35‰$; $\delta^{13}C_{CO2} \approx 0‰$).

The large ^{13}C-depletion of the primary CH_4 with respect to CO_2 ($\delta^{13}C_{CO2\text{–}CH4} > 52‰$) is comparable to that exhibited by microbial methanogenesis. It is known that methanogenic microbes reduce CO_2 to produce CH_4 with a distinctively large isotope effect ($\delta^{13}C_{CO2\text{–}CH4} = 21$ to 69‰; Conrad, 2005). Although the fractionation may possibly be smaller under a high temperature environment, the large fractionation has also been observed for hyperthermophilic methanogens grown above 80 °C (Botz et al., 1996). Some methanogens can also produce CH_4 by decomposing acetate, which results in fractionations of 7–27‰ between the acetate and CH_4 (Conrad, 2005). If it is assumed that the potential substrate acetate had a $\delta^{13}C$ value similar to that of organic matter in the silica veins (≈−35‰), then the acetate fermentation process can also explain the observed fractionation of the primary methane and organic matter ($\delta^{13}C_{org\text{-}CH4} > 21‰$). Therefore, the carbon isotopic relationship among CH_4, CO_2, and organic matter is consistent with biological methane production by reduction of CO_2 and/or acetate.

The large isotopic fractionation between CO_2 and CH_4 is not to be expected from a magmatic process, which should result in much smaller isotopic fractionation due to high-temperature equilibrium (Fig. 7.3-5). Thermal decomposition of organic matter under this process may have possibly produced >20‰ fractionation between primary CH_4 and the organic matter. However, the primary fluid lacks ethane and propane, which should have been co-produced by thermogenesis. Hence, a thermogenic origin of the primary methane is controversial.

Fe-Ni alloy catalyzed FTT reactions at 200–300 °C may produce ^{13}C-depleted methane by 30–50‰, relative to CO_2 (Horita and Berndt, 1999; McCollom and Seewald, 2006). Even larger isotopic fractionation between CH_4 and CO_2 may be achieved at lower temperature below 200 °C (Horita and Berndt, 1999; McCollom and Seewald, 2006). However, as discussed in the previous section, Fe and Ni would have existed as sulfides at temperatures prevailing during the silica precipitation (100–200 °C). Hence, native metal catalysis cannot be expected to produce the methane in the veins.

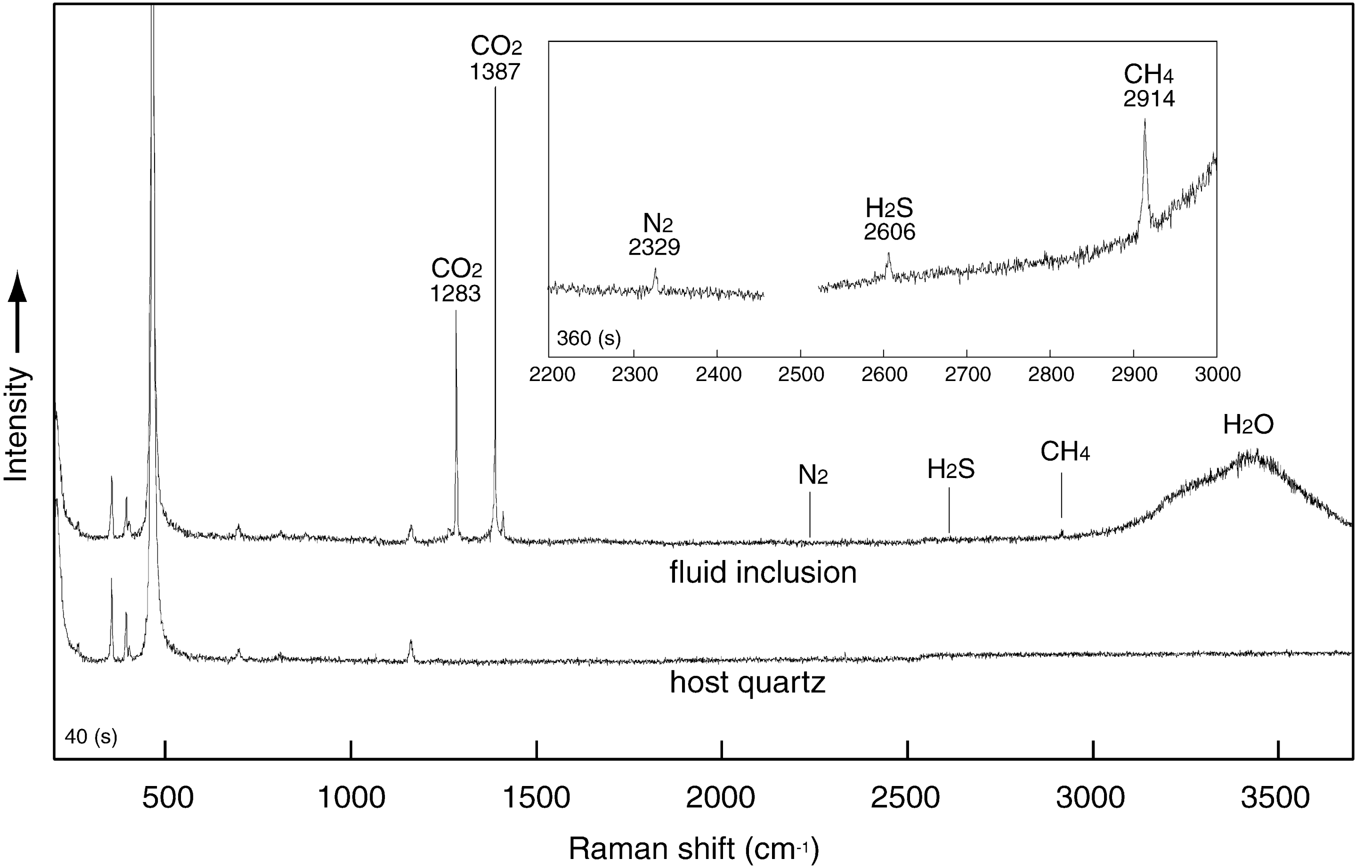


Fig. 7.3-6. Representative Raman spectra of primary fluid inclusions in the silica vein. The fluid mainly consists of H_2O (broad band around 3400 cm^{-1}) and CO_2 (two main peaks at 1283 and 1387 cm^{-1}). Inset shows the result of longer time analysis (360 seconds), indicating the presence of N_2 (2329 cm^{-1}), H_2S (2329 cm^{-1}), and CH_4 (2914 cm^{-1}) in the same fluid.

As already mentioned above, native metal could have existed in deeper parts of the hydrothermal system than the site of silica precipitation (100–200 °C). Thus, methane may have possibly been produced abiotically under much higher temperature conditions. If this was the case, isotopic fractionation between CO_2 and CH_4 should be smaller (less than 30‰ above 300 °C; Horita and Berndt, 1999). Hence deep and high temperature abiotic synthesis does not explain the observed isotopic fractionation of the primary fluid ($\delta^{13}C_{CO2} - \delta^{13}C_{CH4} > 52‰$). Even if abiotic methane in deep and high temperature regimes were introduced into the fluid inclusions, its contribution should be small in the primary fluid preserved in the veins.

Furthermore, the isotopic relationship between the methane and the organic matter in the veins is not expected from FTT reactions (Fig. 7.3-7). Recent experimental studies by

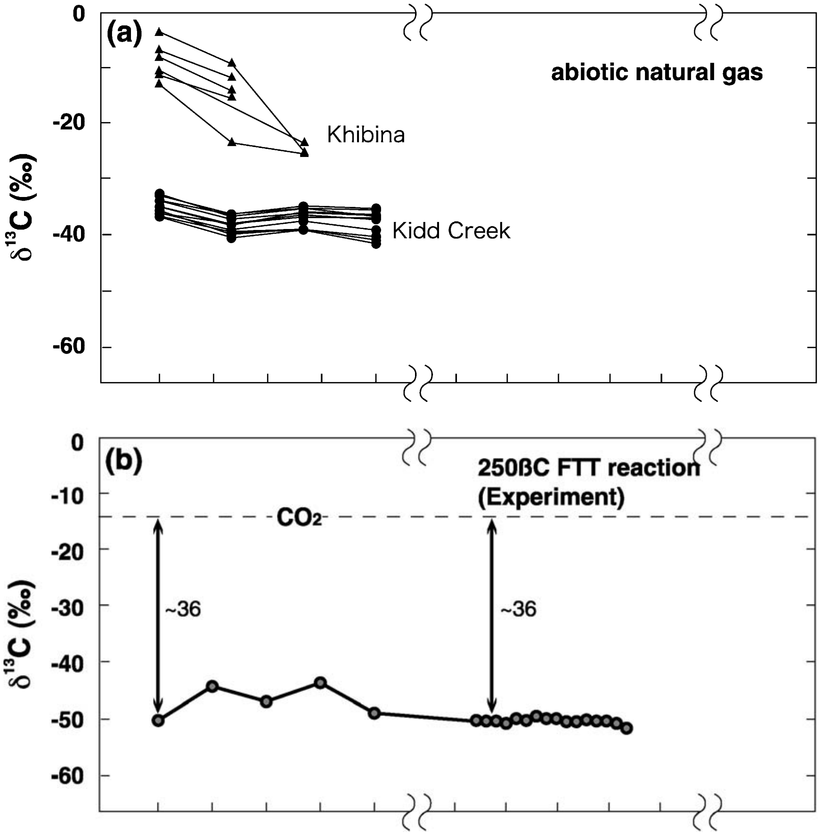


Fig. 7.3-7. Relationships between carbon number and its isotopic composition observed in: (a) abiotic hydrocarbons from Kidd Creek (Sherwood-Lollar et al., 2002) and Khibina (Potter et al., 2004) natural gas fields; (b) hydrothermal experiment (McCollom and Seewald, 2006); and (c) the Dresser hydrothermal deposit (Ueno et al., 2004, 2006).

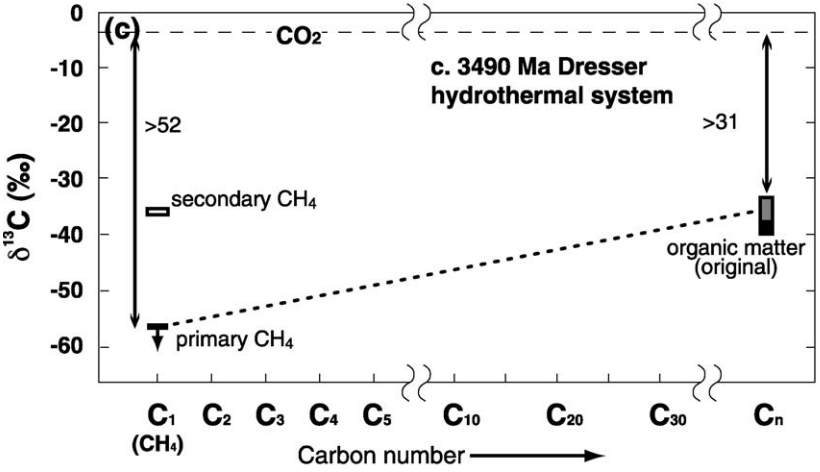


Fig. 7.3-7. (*Continued.*)

McCollom and Seewald (2006) demonstrated that Fe-metal-catalyzed FTT reactions under 250 °C hydrothermal conditions produces ^{13}C-depleted methane ($\delta^{13}C_{CO2} - \delta^{13}C_{CH4} = 36‰$) as well as C_2 to C_{28} hydrocarbons with the same degree of isotopic fractionation ($\delta^{13}C_{CO2} - \delta^{13}C_{hydrocarbons} = 36‰$). They pointed out that the organic matter in the silica veins shows similar degree of fractionation ($\delta^{13}C_{CO2} - \delta^{13}C_{org} \approx 31‰$) and thus may represent higher molecular weight organic compounds polymerized during the FTT synthesis. However, their experiments also demonstrate that significant isotopic fractionation does not occur during the polymerization step of FTT synthesis. Therefore, the observed large ^{13}C-depletion of the primary methane relative to surrounding organic matter in the veins ($\delta^{13}C_{CH4} - \delta^{13}C_{org} < -21‰$) should not result from the Fe-metal-catalyzed FTT reaction (Fig. 7.3-7(b)). In addition, slight isotopic fractionation may possibly occur during the polymerization step of some FTT reactions. It is known that abiotic hydrocarbons in several natural gas reservoirs exhibit progressive ^{13}C-depretion from C_1 to C_4 hydrocarbons (Fig. 7.3-7(a)), which may suggest that isotopically light methane selectively polymerizes into higher hydrocarbons during FTT synthesis (Sherwood-Lollar et al., 2002). This isotopic trend is opposite to that exhibited by the primary methane and organic matter in the Dresser hydrothermal veins. Hence, the inferred FTT processes can not be applied to the formation of organic matter in the Dresser Formation.

In summary, the carbon isotope geochemistry of carbonate, organic matter, methane and carbon dioxide in the Dresser hydrothermal deposits can be fully explained by biological processes including thermophilic chemoautotrophic organisms, especially methanogen. Although the organic matter and methane production by alternative abiological process is not completely dismissed, the observed isotopic relationships are incompatible with our current knowledge of abiotic organic synthesis.

7.3-3.3. Sulfur Isotopic Compositions of Pyrite in Barite Deposits

Various forms of sulfur compound occur in the Dresser Formation, and generally show δ^{34}S values close to 0‰ ($\delta^{34}S = -5$ to +5‰; Lambert et al., 1978), which seems to be derived from juvenile magmatic sulfur (Fig. 7.3-8). Exceptionally, bedded and vein barites of the formation contain more ^{34}S-depleted pyrite ($\delta^{34}S = -17$ to +5‰; Shen et al., 2001). The observed large isotopic fractionation between the pyrite and the co-existing barite (up to 21‰) is similar to those resulting from the metabolic activity of sulfate-reducing microbes and thus may represent the oldest evidence for microbial sulfate reduction (Shen et al., 2001; Shen and Buick, 2004). Also, this sulfur isotopic fractionation is exceptionally large relative to those reported from other Paleo- and Mesoarchaen deposits, such that microbial sulfate reduction may have been locally developed in sulfate-poor Archaean ocean water (e.g., Canfield, 2005).

The microbial origin of the barite-associated pyrite, however, has been debated, because abiotic reactions under hydrothermal conditions may have produced pyrite with a similar degree of isotopic fractionation (Van Kranendonk, 2006). Although initial models for the Dresser barite suggested that they were deposited as Evaporitic gypsum replaced by barite (Buick and Dunlop, 1990; Lowe 1983), recent geological and petrological investigations have demonstrated a clear hydrothermal origin of the barite (Nijman et al., 1999; Ueno et al., 2001a; Van Kranendonk, 2006) as a non-evaporitic, primary mineral confirmed by X-ray CT analyses (Runnegar, 2001). It is notable that the ^{34}S-depleted pyrite occurs not only in bedded barite, but also in vein barite. Even if the pyrites were produced by microbial sulfate reduction, the depositional environment of the ^{34}S-depleted pyrite should not be a shallow marine setting, but a submarine hydrothermal environment.

Van Kranendonk and Pirajno (2004) proposed that the pyrite and barite were deposited by hydration of magmatic SO_2, which produced both sulfate and sulfide. In this case, equi-

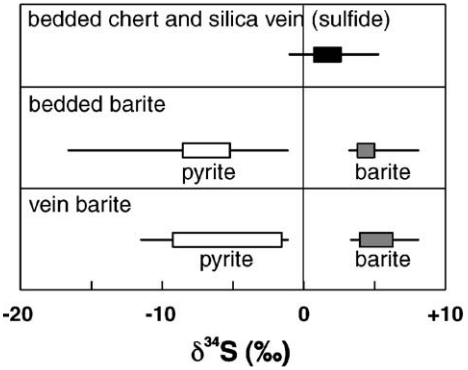


Fig. 7.3-8. Sulfur isotopic compositions of sulfide in chert and veins (black: Lambert et al., 1978; Y. Ueno et al., unpublished data) and disseminated pyrite (white) in bedded and vein barites (gray) (Shen et al., 2001; Y. Ueno et al., unpublished data). The narrow lines indicate the full ranges of observed isotopic compositions, while >70% of the data are within the broad lines.

librium isotopic fractionation between sulfate and sulfide is 22‰ at 250 °C (Ohmoto and Goldhaber, 1997), and is thus comparable to that observed in the barite-pyrite pair described by Shen et al. (2001). Alternatively, Runnegar (2001) and Runnegar et al. (2002) suggested that thermochemical reduction of seawater sulfate could have produced the barite-pyrite association. These abiotic models are roughly compatible with the $\delta^{18}O$ values of the barite ($\delta^{18}O_{SMOW} = 5$ to 10‰; Lambert et al., 1978), which would suggest about 200 °C conditions of precipitation (Runnegar et al., 2002). If this estimate is correct, the temperature is somewhat high to allow microbial activity. However, the oxygen isotope geothermometry of the barite assumes that $\delta^{18}O$ value of Archaean seawater would be the same as that of modern seawater ($\delta^{18}O_{SMOW} = 0$‰). This assumption is still untenable, because the Archaean seawater might have been more ^{18}O-depleted (Shields and Veizer, 2002; Knauth, 2005), giving a much lower temperature estimate for barite deposition. Consequently, both biological and abiological reactions could explain the observed isotopic fractionation between the barite and pyrite.

The origin of the barite-associated pyrite might be further constrained by multiple sulfur isotope analysis. Discovery of non-mass-dependent sulfur isotope fractionation in pre-2.0 Ga sedimentary rocks implies that multiple sulfur isotope ratios ($^{32}S/^{33}S/^{34}S/^{36}S$) could be a useful new tracer for the Archean biogeochemical sulfur cycle (e.g., Farquhar and Wing, 2003). Recent multiple sulfur isotope analysis revealed that the Dresser barite has non-mass dependent isotopic composition, with negative $\Delta^{33}S$ (Ueno et al., 2003; Mojzsis, this volume). This clearly suggests that the barite would have been derived from non-mass-dependently fractionated Archean seawater sulfate, but not from a magmatic source, which should be mass-dependent. The pyrites in both vein and bedded barite also show negative $\Delta^{33}S$ values, again indicating that the pyrite originated from seawater sulfate (Runnegar, 2001; Ueno et al., 2003). This means that reduction of seawater sulfate would be responsible for the ~20‰ ^{34}S-fractionation between the barite and pyrite. However, it is still ambiguous whether the pyrite was produced by thermochemical or microbial sulfate reductions.

7.3-4. CONCLUSIONS

Fig. 7.3-9 summarizes the proposed carbon and sulfur cycles in the Dresser Formation hydrothermal system. The geological and geochemical investigations suggest that the reduced forms of carbon (CH_4 and organic matter) and sulfur (e.g., pyrite) were produced in the hydrothermal system, with significantly large isotopic fractionations. This strongly indicates that low temperature reactions took place in the hydrothermal system, regardless of a biological or abiological interpretation. In principle, large isotopic discrimination could be expected under low temperature conditions, in which chemical reactions are usually prohibited due to kinetic barriers. Hence, the observed large isotopic fractionations imply catalysis that accelerated the low temperature reactions.

For carbon, large isotopic fractionations between CH_4–CO_2 and organic matter-CO_2 are best interpreted as a result of enzymatically catalyzed biological reactions, because effec-

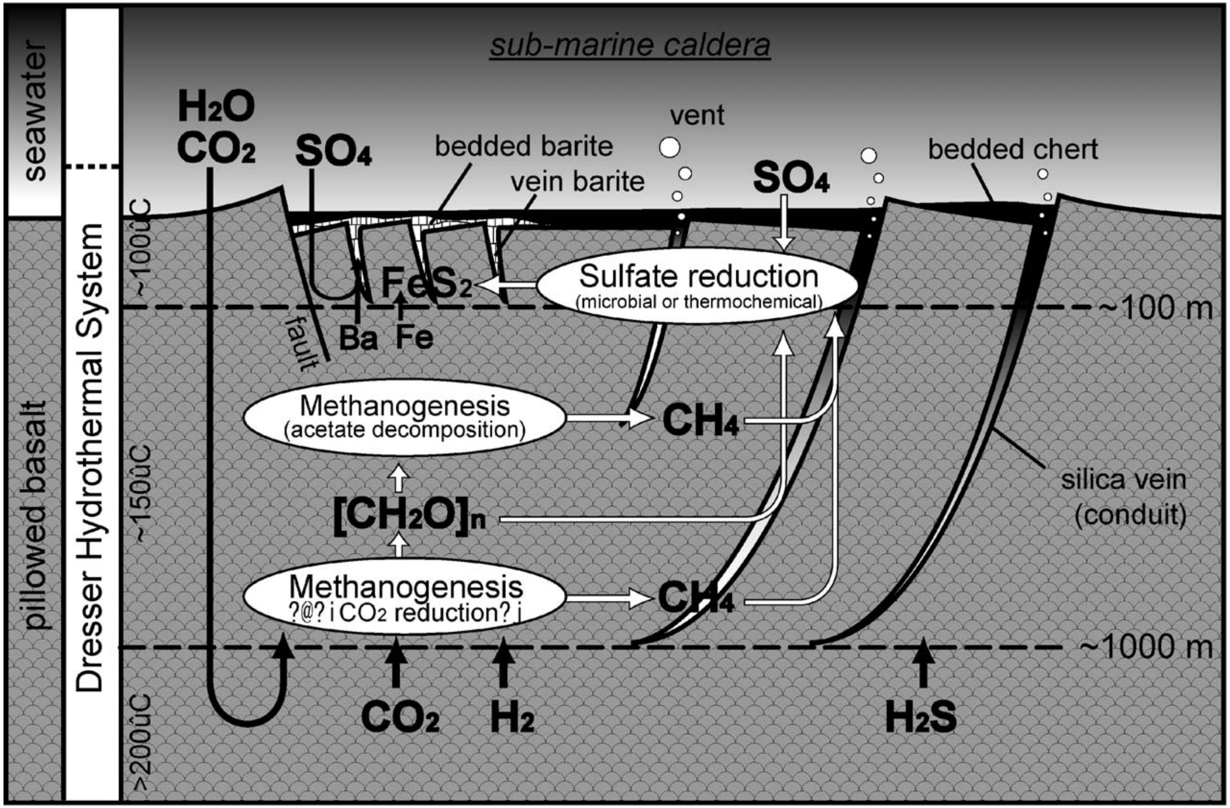


Fig. 7.3-9. A conceptual model of carbon and sulfur cycles in the Dresser hydrothermal system. See text for discussion.

tive catalysts of the FTT reactions (e.g., Fe-Ni alloy) would have been unstable in the low temperature hydrothermal environment. Hence, it is plausible that a microbial ecosystem would have existed in the Dresser hydrothermal system, including a sub-seafloor environment. Methanogens would have gained energy through the conversion of CO_2 and H_2 into CH_4 and acted as a primary producer of organic compounds, which may possibly be utilized by other heterotrophs.

For sulfur, on the other hand, both thermochemical and microbial sulfate reductions could explain the exceptionally large isotopic fractionation between barite and microscopic pyrite crystals embedded therein. Sulfide minerals occur also in bedded chert and in silica veins, but these show no such large isotopic fractionations. Hence, most sulfide minerals in the Dresser Formation seem to be derived from a volcanic source (cf. Van Kranendonk, 2006), but not from seawater sulfate. Although the origin of the barite-associated ^{34}S-depleted pyrite is still ambiguous, sulfate reduction seems to have been restricted to the shallower part of the hydrothermal system (Fig. 7.3-9). This may suggest that the redox gradient beneath the seafloor might have controlled zonation of different types of metabolisms.

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