Keys to ancient Fe-Si formation: low-temperature hydrothermal oxide deposits along modern oceanic ridges

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Several new hydrothermal fields were discovered on the Southwest Indian Ridge (SWIR) during 2-3 cruises of R/V *Dayang Yihao* from 2007 to 2009 (Tao et al., 2007; Chen and Li, 2009). A variety of geological samples including sulfides, basalts, sediments and Fe-Si oxides were collected using TV-guided Grabs in the vicinity of these hydrothermal fields, along with numerous bivalve and gastropod shells (Chen and Li, 2009). Of these, the hydrothermal Fe-Si oxide deposits were more pervasive than the sulfides in each of the newly discovered fields. Since these deposits are generally considered to be analogues of the banded iron formations (BIFs), Fe-Si exhalites and even umbers in ancient time, we carried out a series of investigations on these samples after the cruises, in which we described these deposits in terms of their structure, morphology and chemical composition on a fine scale.

In Fig. 1, we show modern Fe-Si oxide deposits recovered from one of the hydrothermal fields on the SWIR. Based on the mineralogical results (XRD and SAED), the light yellow area in this sample consists mainly of amorphous silica and the brown to black areas consist mainly of Si-bearing ferrihydrite.

Inspection of the structure of the precipitates by optical microscopy and scanning electron microscopy (SEM) on a fine scale showed the widespread occurrence of biogenic filaments in these samples, which represent mineralized bacteria (Fig. 2). Comparative studies with hot springs on land, and several studies of the similar samples in other hydrothermal fields, demonstrate that these bacteria are mainly neutrophilic Fe oxidizing bacteria. Based on the analysis by energy dispersive spectrometer (EDS) carried out here, all the filaments appear to be rich in Fe, Si and P and sometimes contain minor amounts of Mn.

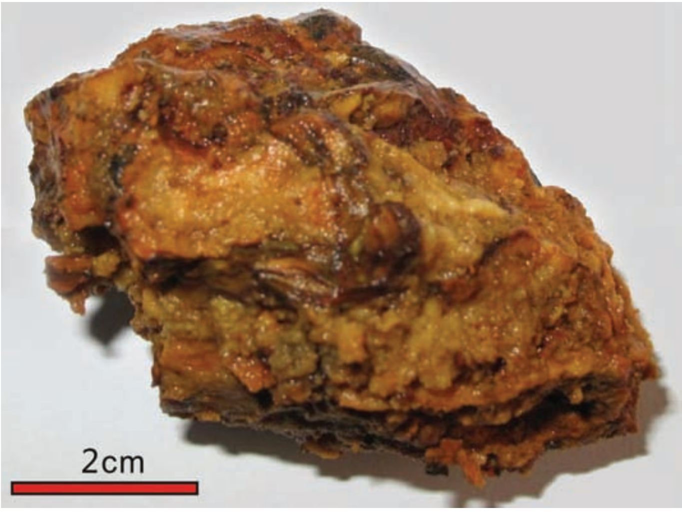

Figure 1: Hydrothermal low-temperature Fe-Si oxide deposits recovered from SWIR. Sample SL1 from 50.4678°E, 37.6587°S with water depth: 1745 m.

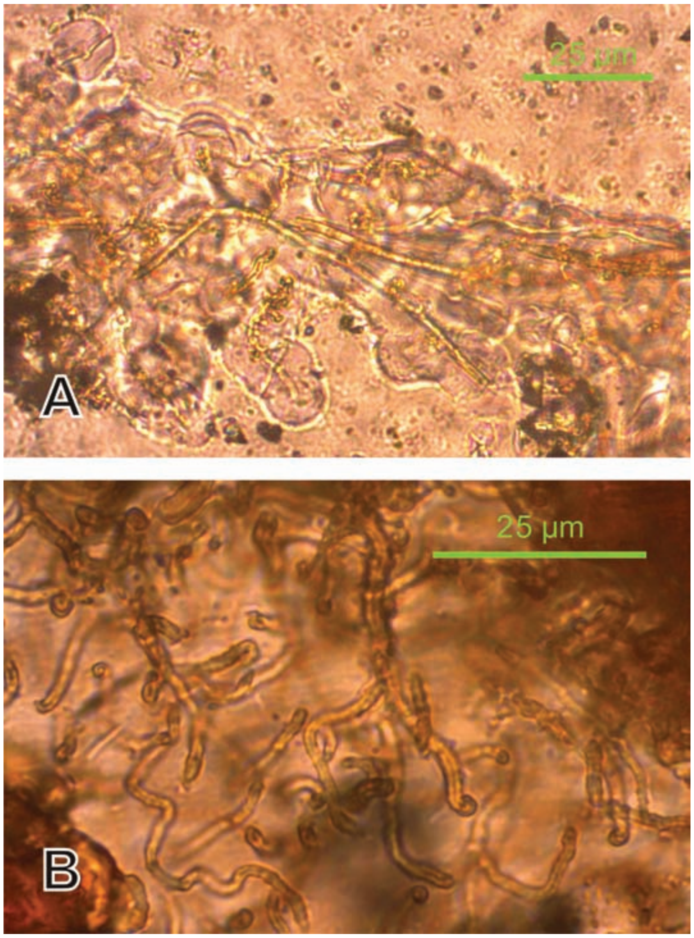

Figure 2: Mineralization of the bacteria in modern hydrothermal Fe-Si oxide deposits on SWIR. A-sample SL1 from 50.4678°E, 37.6587°S, water depth: 1745 m; B-sample SH4 from 49.6466°E, 37.7903°S, water depth: 2739m.

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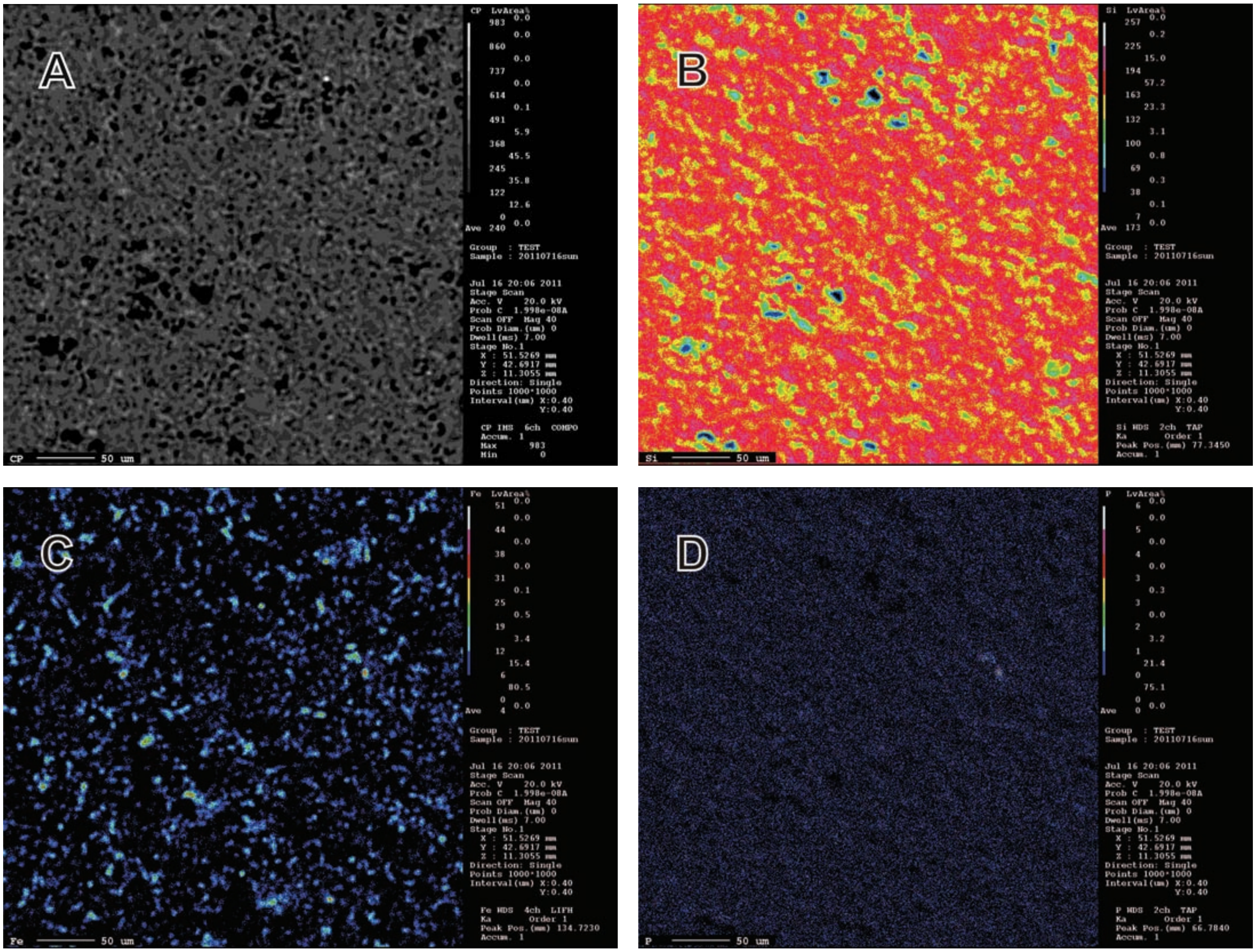

Figure 3: Elemental mapping of modern hydrothermal Fe-Si oxide deposits from the newly discovered hydrothermal fields, SWIR. Sample SH4 taken from 49.6466°E, 37.7903°S.

A common observation is that the mats have been consolidated by silicification after the formation of the Fe-rich filaments. Elemental mapping analysis of the Fe-Si oxide precipitates using an electron probe micro-analyzer (EPMA) revealed that the mats formed by mineralized filaments are not chemically homogenous and that the Fe and Si contents are decoupled (Fig. 3). The distribution of Fe is characterized by elongated rods and spheres, hinting at the presence of sheaths and stalks of Fe oxidizing bacteria, whereas the distribution of Si is characterized by a dense matrix of Fe-rich sheaths and stalks. Phosphorus shows only a faint relationship with Fe, despite the influence of the presence of abundant Si (Fig. 3).

Since the simple mixing between hydrothermal fluids and modern seawater cannot result in the saturation of these fluids with respect to silica, the presence of significant amounts of amorphous silica in the mats is considered to be the result of conductive cooling (Herzig et al., 1988). This leads to a unique structure of the filaments in which the Fe-rich core of the filament is coated by a siliceous crust. This structure is thought to be conducive to the preservation of the microfossils since the inner Fe oxides may inhibit cellular autolytic enzymes (Leduc et al., 1982; Ferris et al., 1986). At the same time, the outer siliceous crust faithfully preserves microbial shape over a relatively long period. Moreover, the stable Fe-O-Si bonds formed by the surface complexes involved in the silicification raise the temperature of segregation between the Si and Fe oxides substantially (up to 850°C, Glasauer et al., 2000 or even higher, Sun et al., under review) and thereby elevates the tolerance of the filaments to diagenetic processes or even low grade metamorphism and increases the resulting fidelity of the biosignature.

In contrast to ancient BIFs, modern low-temperature hydrothermal Fe-Si oxides always have a limited size in the immediate vicinity of hydrothermal vents with Fe-rich mats tens of cm thick covering several hundred m^2. However, this does not detract from the fact that modern hydrothermal Fe-Si oxides are the analogues or even the precursors of ancient BIFs. For example, the similarity in the composition and mineralogy of modern and ancient BIF deposits and their resemblance to the structure of modern Fe oxidizing bacteria in Precambrian BIFs (1.9-billion-year-old Gunflint iron formation; Boyce et al., 2003) together with the analogous environment in which the Fe-Si oxides precipitated (largely anoxic and rich in Fe(II) with atmospheric O_2 concentrations only a fraction of present levels; Emerson et al., 2010). Furthermore, an increasing number of studies have suggested that the iron in BIFs was probably introduced at sites along mid-ocean spreading ridges and at oceanic hotspots and sites of hydrothermal plumes (Jacobsen and Pimentel-Klose, 1988; Klein, 2005; Poulton and Canfield, 2010).

Our ongoing work has focused mainly on the relationship between modern Fe-Si oxides and their ancient BIF counterparts, especially to determine a credible biosignature for these two deposits. Since Fe-Si oxide deposits/formations probably record geobiological clues, they become important keys to reconstruct the Earth's history. So far, several similar studies have been carried out on the mid-ridges, seamounts and back-arc basins of the Pacific and Atlantic oceans, but few are based on the ultraslow-spreading ridges in the Indian Ocean, which represent 10% of the total worldwide oceanic ridges. With the recent discovery of hydrothermal deposits along the SWIR based on a series of cruises in the past 5 years to 2011, it has become clear that the SWIR will become the next focus for understanding the tectonic, biological and geochemical processes controlling the past and future evolution of the Earth.

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References

Boyce, A.J., Little, C.T.S. and Russell, M.J., 2003. A new fossil vent biota in the Ballynoe Barite Deposit, Silvermines, Ireland: evidence for intracratonic sea-floor hydrothermal activity about 352 Ma. Econ. Geol. 98, 649-56.

Chen,Y.J. and Li, J., 2009. National News: China. InterRidge News, 18, 29-30.

Emerson, D., Fleming, E.J. and McBeth, J.M., 2010. Iron-oxidizing bacteria: an environmental and genomic perspective. Annu. Rev. Microbiol., 64, 561-583.

Ferris, F.G., Beveridge, T.J., and Fyfe, W.S., 1986. Iron-silica crystallite nucleation by bacteria in a geothermal sediment. Nature, 320, 609-611.

Glasauer, S.M., Hug, P., Weidler, P.G. and Gehring, A.U., 2000. Inhibition of sintering by Si during the conversion of Si-rich ferrihydrite to hematite. Clays Clay miner., 48, 51-56.

Herzig, P.M., Becker, K.P., Stoffers, P., Bäcker, H., 1988. Hydrothermal silica chimney fields in the Galapagos Spreading Center at 86ºW. Earth. Planet. Sci. Let., 89, 261-272.

Jacobsen, S.B. and Pimentel-Klose, M.R., 1988. A Nd isotopic study of the Hamersley and Michipicoten banded iron formations: the source of REE and Fe in Archean oceans. Earth Planet. Sci. Lett. 87, 29-44.

Klein, G., 2005. Some Precambrian banded iron-formations (BIFs) from around the world: Their age, geologic setting, mineralogy, metamorphism, geochemistry, and origins. Am. Mineral., 90, 1473-1499.

Leduc, M., Kasra, R. and Van Heijenoort, J., 1982. Induction and control of the autolytic system of Escherichia coli. J. Bacteriol., 152, 26-34.

Poulton, S.W. and Canfield, D.E., 2010. Ferruginous conditions: a dominant feature of the ocean through Earth's history. Elements, 7, 107-112.

Sun, Z., Zhou, H., Glasby, G.P., Sun, Z., Yin, X. and Li, J. Mineralogical characterization and formation of Fe-Si oxyhydroxide deposits from a modern seafloor hydrothermal vent. Am. Mineral. (under review).

Tao, C., Lin, J., Guo, S., Chen, Y.J., Wu, G., Han, X., German, C.R., Yoerger, D., Zhu, J., Zhou, N., Su, X., Baker, E.T. and DY115-19 Leg 1&2 Science Party, 2007. Discovery of the first active hydrothermal vent field at the ultraslow spreading Southwest Indian Ridge: The Chinese DY115219 Cruise. InterRidge News, 16, 25-26.