

## Mineralogy and geochemistry of an Archaean chert: In quest of N-sites

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The nitrogen breakdown product of organic matter (OM) is preserved in ancient metasediments and can be used as biomarker. Archaean cherts show multiple N components. In order to provide a correct interpretation of their N isotopic signature, N-bearing phases should be identified. Therefore, SEM-EDX, EPMA (WDS) and nuclear reaction analyses were carried out on the hydrothermal chert PB 458 (Marble Bar, Pilbara, Australia). The  $\delta^{15}\text{N}$  in this chert vary from  $-5$  to  $9\text{‰}$  (Pinti et al. 2001). We identified two redox-environments: (1) Low  $f\text{O}_2$  and high  $f\text{S}_2$  are indicated by the presence of silicified euhedral dark ghost phenocrystals in a cryptocrystalline quartz matrix. They are rich in Fe, Al, K, Ca, Mg, Cu, Ti, Zn and host euhedral Fe-sulfides. (2) The redox-front (2 mm wide), changing to high  $f\text{O}_2$  and low  $f\text{S}_2$  conditions, is marked by the precipitation of Fe- and Fe-Mn oxide (BI) and coarse-grained quartz bands of stromatolite-like structure. The Fe–Mn-oxides of worm-like textures are probably pseudomorph after euhedral quartz. Arsenic is incorporated in Fe-oxides, whereas Fe-Mn oxides contain traces of Ca, Al, K, Au-Pd, Cu-Ni-Zn; Cr-Ni alloys (1–2  $\mu\text{m}$ ); Y-REE phosphates (2  $\mu\text{m}$ ) and Mg-Fe-spinel occur in interstitial quartz. Precipitation of cryptocrystalline quartz continued under high  $f\text{O}_2$ , but lower metal activity. The matrix rarely hosts orthoclase ( $< 10\mu\text{m}$ ), Ti-V oxides, Ba-mica, Ca-Mg carbonates and barite ( $< 1\mu\text{m}$ ). Secondary mm-wide quartz veins with Fe-Mn oxides, biotite and clay minerals crosscut the chert. Nitrogen and C occur in Fe-Mn oxides (C: 214–2380 ppm, N: 107–150 ppm, N/C: 0.06–0.5), and in K-Al-silicates related to the quartz veins (C: 1790–4190 ppm, N: 710–2130 ppm, N/C: 0.4–0.5). The N/C ratio is 10 to 100 times higher than the N/C-ratio of the whole rock, suggesting that additional C might be adsorbed on mineral surfaces or included in quartz as OM. The occurrence of N and C in Mn-Fe-oxides of the BI of PB458 might indicate microbial activity during Fe-Mn oxide precipitation, while secondary K-Al silicates incorporated remobilized  $\text{NH}_4^+$  by replacing  $\text{K}^+$ .

### Reference:

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## “Microbial plumes” as inferred from the increase of stable carbon isotope composition of methane originated from submarine hydrothermal activity

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Spatial distributions of neutrally buoyant hydrothermal plumes were traced using dissolved methane ( $\text{CH}_4$ ) and its stable carbon isotope ratio ( $\delta^{13}\text{C}_{\text{PDB}}$ ) at the following hydrothermal active areas: i) No.4 Yonaguni Knoll of southern Okinawa Trough, northwestern Pacific ( $24^\circ 50' - 54' \text{N}$ ,  $122^\circ 41' - 44' \text{E}$ ), and ii) Gulf of Aden, south of the Arabian Peninsula ( $12^\circ - 13^\circ \text{N}$ ,  $45.5^\circ - 49^\circ \text{E}$ ). At the former area, CTD hydrocasts were performed at five stations, one is nearly close ( $\sim 0.4$  mile) to a known black smoker chimney site and the others locate within 3 miles from the chimney site. Seawater samples were kept in sealed glass vials with  $\text{HgCl}_2$  for the measurement of  $\text{CH}_4$  and its  $\delta^{13}\text{C}$  with a CF-IRMS system at Hokkaido University. We detected triple layered  $\text{CH}_4$  plumes, the centers of which were at depths of  $\sim 800$  m,  $\sim 1,050$  m and  $\sim 1,200$  m. The  $\text{CH}_4$  concentrations and the  $\delta^{13}\text{C}$  values for the 1,200 m plume ranged between 1,026 nM and 10 nM, and between  $-22.4\text{‰}$  and  $+40.4\text{‰}$  (the heaviest values yet reported for oceanic  $\text{CH}_4$ ), respectively, indicating active microbial  $\text{CH}_4$  oxidation to cause the  $\delta^{13}\text{C}$  increase (fractionation factor of  $\sim 1.010$ ) of residual  $\text{CH}_4$  as the plume ages. As for the 800 m plume, it was found that the  $\text{CH}_4$  oxidation or the  $\delta^{13}\text{C}$  increase still occurs after the  $\text{CH}_4$  concentration reached at the background level ( $\sim 1$  nM) or less. In this case, we can recognize the hydrothermal plume from the  $\delta^{13}\text{C}$  anomaly, accompanied by little (or negative)  $\text{CH}_4$  anomaly. Such a “microbial plume” or  $\delta^{13}\text{C}$  plume was also observed in the Gulf of Aden.