

Reduction of structural Fe(III) in clay minerals by mesophilic and thermophilic methanogens

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The capability of methanogens to reduce structural Fe (III) in clay mineral nontronite was studied. Mesophilic *Methanosarcina barkeri*, thermophilic *Methanothermobacter wolfei* and hyperthermophilic *Methanococcus jannaschii* were used in the experiments. Nontronite NAu-2 has a total Fe content of 23% (w/w), and almost all of the Fe is Fe (III). The NAu-2 size fraction of 0.05-0.2 μm was used in all experiments. The three methanogens were incubated with methanol, acetate, or H_2 as electron donor and structural Fe (III) in NAu-2 (0, 5, and 10 g/L) as electron acceptor. The extent of iron reduction was measured by Ferrozine assay and the 1, 10-phenanthroline method. Methane concentration, solution pH and aqueous chemistry were measured. X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM) were used to observe any mineralogical changes.

All of the three methanogens reduced structural Fe (III) in NAu-2 to Fe (II) with methanol or H_2 as electron donor. *M. barkeri* reduced Fe (III) in NAu-2, with H_2/CO_2 and methanol, but not with acetate. Using H_2 , the extent of Fe (III) reduction reached 5-10% and 7-13% as measured by Ferrozine assay and the 1, 10-phenanthroline method, respectively. For the methanol set, the extent was higher, reaching 18-23% and 25-33%, as measured by the two methods, respectively. Concentrations of Si and Al in solution markedly increased within 3 days accompanied with decreased pH, suggesting that *M. barkeri* reductively dissolved NAu-2. XRD and SEM-EDS of bioreduced materials showed that there was no biogenic illite formation but occurrence of high charge smectite or intermediate phase between smectite and illite, and silica. Methane production was almost completely inhibited by iron reduction with H_2/CO_2 as substrate which highlights the important role of iron in global methane flux. Thermophilic and hyperthermophilic methanogens were also capable of reducing structural Fe (III) in NAu-2, and the extent of Fe (III) bioreduction with H_2/CO_2 or methanol as substrate ranged from 10% to 20% at a 5g/L NAu-2 concentration. Extensive mineralogical changes also occurred as a result of bioreduction.

On the origin of pyroxene exsolution topotaxy in majoritic garnets

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The pyroxene exsolution in garnet after majorite from garnet peridotites of Otrøy and Fjörtøft Islands suggests a very deep origin (>350 km) of the rocks. Microstructures and trace element compositions of the exsolved pyroxenes and garnets indicate that these ultra-deep mantle rocks may have experienced a complex multiple stage exhumation process. The interstitial pyroxenes were exsolved during the Archean upwelling from mantle transition zone. The intracrystalline pyroxene lamellae were exsolved during the isobaric cooling after accretion to deep cratonic roots. We provide here EBSD, EMP and LA-ICPMS analyses of pyroxenes exsolved from the garnets. The EBSD analyses of more than 200 exsolved pyroxenes and host garnets reveal the following exsolution topotaxial relationship: 1) The interstitial millimeter-size orthopyroxenes have no consistent crystallographic relation with the surrounding garnets; 2) There are three different types of intracrystalline exsolutions in garnet (orthopyroxene rods (major exsolved phase), clinopyroxene rods and the rods of intergrowth of CPX and OPX). The majority (80-90%) of exsolutions have a tight topotaxial relationships with the host garnet by $\langle 001 \rangle_{\text{px}} // \langle 111 \rangle_{\text{grt}}$ and $\langle 010 \rangle_{\text{px}} // \langle 110 \rangle_{\text{grt}}$. 3) Pyroxene rods are elongated parallel to the $\langle 111 \rangle_{\text{grt}}$ or $\langle 110 \rangle_{\text{grt}}$. The elongation directions are the $\langle 001 \rangle_{\text{px}}$ in the former case. 4) The polycrystalline intergrowths of clinopyroxenes and orthopyroxenes have also a tight topotaxial relationships of $\{100\}_{\text{cpx}} // \{100\}_{\text{opx}}$, $\langle 010 \rangle_{\text{cpx}} // \langle 010 \rangle_{\text{opx}}$ and $\langle 001 \rangle_{\text{cpx}} // \langle 001 \rangle_{\text{opx}}$. The interfaces between clinopyroxenes and orthopyroxenes are most likely the $\{100\}_{\text{px}}$ planes. The $\langle 100 \rangle_{\text{cpx}}$, the elongation directions for the intergrowth pyroxene rods, are near parallel to the $\langle 111 \rangle_{\text{grt}}$. The volume ratio of Cpx/Opx varies from nearly pure Cpx to pure Opx suggesting that these exsolutions are exsolved two-pyroxene solid solutions. All exsolved clinopyroxenes show essentially no difference in major and trace element compositions as revealed by EMP and LA-ICPMS analyses. So are the exsolved orthopyroxenes and the host garnets. Based on our results and previous experimental results, we hypothesis that clinopyroxene rods were exsolved firstly from the precursor majoritic garnet, followed by solid solutions of pyroxenes and orthopyroxene rods.