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Interaction of calcite with iron-rich hydrothermal solution leads to anoxic oxidation of iron: implications for early earth atmosphere

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We investigated the interaction of calcite with iron(II)-rich hydrothermal solutions with a series of experiments at 150-300 °C and 40 MPa under anoxic conditions. Periodic monitoring of the fluid chemistry revealed that between 200 and 300 °C, >98% of the dissolved iron (~80 mmol/L) is depleted within 48 hours from the solution which shows a counter-enrichment of Ca ions and rapidly increasing H_2(aq) concentrations. Analysis of the solid reaction products shows the metasomatic replacement of calcite by siderite as well as an abundant formation of magnetite (seen as euhedral octahedral and dodecahedral crystals of up to 35 mm in size). Up to 10 mmol/L of H_2 is produced when magnetite forms by the reaction $3Fe^{2+} + 4H_2O \rightarrow Fe_3O_4 + H_2(aq) + 6H^+$. The release of protons triggers the dissolution of calcite and its replacement by siderite. These results agree with equilibrium geochemical reaction path model computations that predict the initial formation of magnetite followed by siderite replacement of calcite. A strong temperature-dependency of the rate and the extent of the oxidation is observed as the maximum amount of magnetite and H_2-levels are reached at 300 °C and within a few hours after the start of the experiment. Conversely, at 150 °C, the reaction is relatively slow with equilibrium attained after 180 hours and produces only a few μmol/L of H_2.

Our results show that calcite is not stable under anoxic ferruginous oceanic conditions, argued to be a dominant feature of the early earth oceans. Siderite must have played a role in the extensive CO_2-removal from the Hadean atmosphere. Oxidation of the dissolved ferrous iron by water led to H_2-production within the ocean, which contributed to keep the Hadean ocean-atmosphere system reducing and favorable to abiotic synthesis of organic compounds.