Metastable equilibrium in the C-H-O system: Graphite deposition in crustal fluids

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The presence of graphite in natural environments is governed by the redox and thermal conditions of C-H-O fluid/mineral equilibrium in hydrothermal veins and metasomatic contacts. The majority of experimental and theroetical studies on the C-H-O system are focused on deriving the thermodynamic properties of species, and on modeling phase relationships under equilibrium conditions. The distribution of C-H-O species in natural systems, however, may also be controlled by metastable equilibria that involves disequilibrium volatile concentrations and deposition of graphitic carbon with different degrees of crystallinity.

Hydothermal experiments were performed to investigate the graphite undersaturated C-H-O system at $600^{o}C$ – 1 GPa and at supercritical water conditions. Aqueous solutions were reacted in the presence of $Si_5C_{12}H_{36}$ (tetrakis(trimethylsilyl) silane) to generate C-H-O volatiles (e.g. CO_2, CH_4, H_2) in a piston cylinder apparatus. Phase equilibrium relationships were placed along a continuum from highly reducing (iron-wustite) to highly oxidizing (Pt/PtO_2) redox gradient that rendered $CH_{4(aq)}$ and $CO_{2(aq)}$ as dominant species.

Time-series measurements of the dissolved volatile concentrations and mass balance constraints indicate the formation of a metastable non-volatile carbon phase, that attained significant concentrations (up to 0.62 of total carbon) especially during methane oxidation to $CO_{2(aq)}$. The intermediate occurrence of this phase is short-lived and is linked to the precipitation of amorphous graphitic carbon. Indeed, Raman spectroscopic measurements performed on the solid reaction products revealed the presence of poorly-ordered graphite under all the redox conditions investigated. However, the thermometric empirical expressions using the distribution and the shape (FWHH) of the G and D bands in the Raman spectra of graphite failed to accurately estimate the experimental temperature. Thus, the existing Raman geothermometers appear inadequate to address graphite formation under metastable equilibrium conditions and to account for kinetic effects that could greatly affect the degree of crystallinity.

Formation of poorly ordered graphite suggests that the disordered structure of the mineral is more readily deposited than crystalline graphite, and thus it may attain a broader thermodynamic stability field. Exposing this metastable graphitic carbon to high temperatures and pressures could function as a precursor and substrate for the deposition of the well-ordered phase. Such metastable graphite, therefore, may provide an intermediate state that facilitates subduction of carbonaceous material other than crystalline carbonate minerals. This might also have important implications for the formation mechanisms and the carbon isotope systematics of deep seated carbonaceous fluids and minerals such as diamonds.

Steep Rock carbonate platform: an early marine oxygen oasis

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Limestones of Mesoarchean-Neoarchean (~2.8 Ga) age at Steep Rock Lake, Ontario, Canada, are up to 500 m thick and at least 35 km in extent. We suggest that this early example of a thick and relatively well-preserved carbonate platform represents an ‘oxygen oasis’ that formed in shallow-water adjacent to deeper-water iron oxide and iron carbonate sediments. Anoxic Archean seawater rich in dissolved iron and bicarbonate is expected to have precipitated iron carbonate minerals such as siderite, which is common in banded iron formation (BIF). Dominance of Ca-carbonates over Fe-carbonates at Steep Rock is consistent with relatively low levels of ferrous iron in a suboxic/oxic shallow-water zone above a chemocline. The most likely source of dissolved O_2 to sustain these conditions is oxygenic photosynthesis by cyanobacteria.

Our rare earth element (REE) analyses confirm that oxygen was present in the seawater from which the Ca-carbonate minerals at Steep Rock precipitated. A distinct negative cerium anomaly is present in the limestone and absent in the laterally and vertically adjacent iron formations. Cerium is the only REE with a 4+ valence state, in which it forms an insoluble oxide and is removed from solution. The negative anomaly indicates that seawater at Steep Rock locally encountered sufficient oxygen to remove cerium. Direct evidence for the source of the oxygen is lacking, but two features are consistent with a cyanobacterial origin. First, stromatolites are common in the Steep Rock limestone and cyanobacteria could have been included in their microbial communities. Second, black shales in the basinal iron formation contain up to 30 weight percent organic carbon suggesting the presence of phytoplankton and this community also could have included cyanobacteria.

We conclude that the Archean origin of marine carbonate platforms was closely linked to the transient development of shallow-water ‘oxygen oases’ at the margins of otherwise anoxic iron-rich seas, and that these were present locally in the mid-Archean, as exemplified at Steep Rock.