Chemical equilibria involving aqueous carbon compounds in submarine hydrothermal systems

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Aqueous carbon compounds in submarine hydrothermal fluids contribute to global carbon cycles and influence metabolic strategies used by chemosynthetic communities that inhabit vent ecosystems. Understanding their origin represents a critical step in linking chemical, physical and biological processes in hydrothermal environments. Thermodynamic assessments of aqueous carbon compounds in submarine hot-springs typically indicate that a state of total thermodynamic equilibrium has not been achieved. The absence of total equilibrium, however, does not preclude attainment of metastable equilibrium between individual reactive carbon species, provided suitable reaction pathways exist. Laboratory experiments have been critical in identifying reactions that rapidly equilibrate and kinetic barriers that preclude total equilbrium under hydrothermal conditions. For example, metastable *n*-alkanes and their corresponding alkenes rapidly equilibrate in response to prevailing redox conditions at elevated temperatures and pressures. These reversible reactions facilitate exchange of carbon-bound hydrogen with water and the attainment of hydrogen isotopic equilibrium. Other experiments have demonstrated that kinetic barriers retard equilibration of CO_2 and CH_4 on short time scales, while equilibration between CO_2 and intermediate oxidation state species such as CO, formic acid, and methanol occurs rapidly. In contrast, despite a strong thermodynamic drive, CO_2 reduction to methanethiol (CH_3SH) appears kinetically inhibited, but oxidation of CH_4 may represent a possible source in hydrothermal systems.

Because the relative abundances of aqueous species controlled by thermodynamic equilibrium are independent of time and are controlled by temperature, pressure, and the composition of the chemical system, their concentrations in natural environments can be used to constrain physical and chemical conditions in subsurface environments during the evolution of submarine hydrothermal fluids. Recent field programs to ultramafic-, basalt- and sediment-hosted hydrothermal systems have provided new information on the abundance of aqueous carbon compounds in ridge-crest vent fluids. These data will be assessed in the context of thermodynamic and kinetic models to constrain their sources and sinks during alteration of the oceanic lithosphere.

Mineralogy of “digested” wall-rock xenoliths in transitional coherent kimberlites of Tuzo pipe (Gahcho Kué Kimberlite Field, NWT, Canada)

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Root zones of kimberlite pipes may contain a series of coherent and fragmental magmatic rocks, with coherent kimberlite usually occurring at greater depth than the fragmental variety. The interface between these rock types is marked by transitional textured kimberlite, which has both features typical for coherent as well as fragmental rocks. One of the attributes that change from coherent to fragmental kimberlite is the decreasing degree of metasomatization of country rock fragments. Xenoliths may be completely or almost completely “digested” in coherent kimberlites, while they are relatively fresh in fragmental rocks of the same pipe.

At Tuzo pipe the dominant xenolith lithology is granite. The fragments have a normal granitic mineral assemblage of K-feldspar, plagioclase, quartz, biotite and apatite. While granite xenoliths are rather fresh in the fragmental kimberlite, the accessory fragments become increasingly metasomatized as the kimberlite changes towards depth into a more coherent variety. This process of digestion is more apparent in small, mm-sized granite particles than in larger ones. Proof for clast digestion is their remnant and increasingly fluidal shape, relict mineralogy and a totally dissimilar new mineralogical assemblage in strongly recrystallized xenoliths. Electron microprobe analysis from rim to core identifies apatite, clinopyroxene, fluor-phlogopite, and amphibole (zoned fluor-richterite with arfvedsonite rims, arfvedsonite). Some large amphibole crystals grow towards the core, where they are bordered by an unidentified fine-fibrous silicate. Carbonate and serpentine minerals occur as a further interstitial assemblage.

We interpret the pronounced recrystallization of silicate xenoliths in the coherent kimberlites as being related to the higher heat and heat capacity of the coherent magma compared to fragmental kimberlites. Aggressive F, Cl and OH bearing fluids combined with released Na and K contributed to the recystallization of the xenoliths.