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Nitrogen in the deep biosphere: Mineralogical controls on aqueous ammonium

D.A.C. MANNING

School of Civil Engineering & Geosciences, University of Newcastle, Newcastle upon Tyne, UK, NE1 7RU (david.manning@ncl.ac.uk)

Nitrogen, as aqueous ammonium, is readily available in the deep subsurface as a potential microbial nutrient. The ammonium contents of minewaters and oilfield waters (UK, Western Canada) are 10 - 1000 mg/L, increasing with overall salinity [1]. Samples from a wide variety of locations that are completely unrelated geologically, and from sanitary landfills, show systematic variation that is consistent with a mineralogical control on dissolved ammonium. A plot of log aK^+/H^+ vs. log Na^+/H^+ discriminates four or more populations and indicates multiple controls on Na and K (e.g. micas and feldspars). In contrast, a plot of log aNH_4^+/H^+ vs log aK^+/aH^+ gives two populations, suggesting that the dominant mineralogical control on dissolved ammonium is either smectite or illite-muscovite-tobelite (i.e. clays and micas).

This study demonstrates that ammonium is abundant in the deep biosphere, representing a geographically and geologically dispersed sample base known to include waters from biodegraded oilfields. Ammonium derived from the decomposition of organic-N compounds participates in aqueous exchange reactions with micas and clays, which represent a mineralogical reservoir for NH_4^+ analogous to their role as sources of K^+ in terrestrial soils.
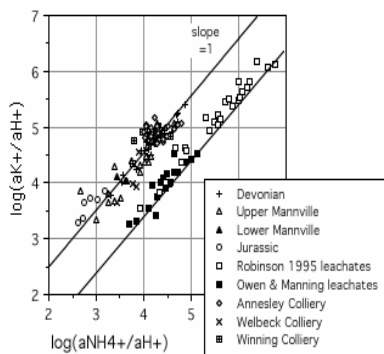
Systematic variation between NH_4^+ and K^+ in deep waters

References
[1] Manning, D.A.C. and Hutcheon, I. E. (2004) *Applied Geochemistry*, in press.

4.4.P01

CaO nucleation preceding carbonate growth in dying microbial particles (subsurface environment)

J. HLADIL[1] AND A. GEMPERLE[2]

[1] Inst. of Geology, Acad. Sci. CR, Prague (hladil@gli.cas.cz)
[2] Inst. of Physics, dtto (gemper@fzu.cz)

The limestones beneath the surface on San Salvador Island, Bahamas (depth 2.5 m, sedim. age ~125 ka) contain small peloids and cements, which were diagenetically (marine /land vadose zone) rebuilt into a nanometric mesh of fossilized microbial objects (ovoids and rods 50–200 nm). A small number of particles were alive or dormant. The SEM/TEM characteristics indicate both small bacteria and extracellular secretions.

Replacement by carbonate was studied using the TEM. 1) Organic matter only: No mineral phases were detected, but several objects contain shapes comparable with ribosomes and micro-filaments. 2) Necrotic matter with CaO nuclei: Small opaque dots consist of single or aggregated crystals of tetragonal or triangular outlines (3–15 nm); individual crystals to densely spaced formations were observed (max. 5×10^4 /μm^3). The electron diffraction features provided evidence of face-centered cubic structures of B1 type (NaCl-like), with the strongest 2nd and 3rd reflections at 0.240 and 0.170 nm, by mean lattice parameter of 0.4813 nm. The difference of +0.0011 (pure CaO ~0.4802 nm) is explained by the presence of Sr (X-ray maps). Rare oxides of close lattice parameters (Mn-, Y-, etc.) were eliminated by element chemistry. 3) Amorphous carbonate is gradually erasing the CaO spots. 4) Soft and skeletal crystal frameworks: The interiors of nanoscale organic particles tend to be filled with carbonate crystal (1, max. 5 domains). It starts from delicate skeletal frameworks with thin 1nm elements. Unstable proto-lattices can slowly reassemble, if decomposed by energy of transmission electron beam. 5) Carbonate crystals: Spontaneous fills by aragonite prevail; vaterite is not defined (although rare ovoid shapes are suspect). Subsequently, calcite replacing aragonite along sharp boundaries was observed. Calcite lamellae are orientated oblique to fuzzy growth bands and aragonite twinning, if developed. Inclusions were gradually obliterated and part of them also centrifugally expelled to surface. More than 95% of crystals do not exceed the rounded surface of the host particle.

Origination of CaO in wet and "cold" conditions is very unusual. It can be facilitated by stronger Ca^{2+} transport into particles, and with dying, by transition from chemautotrophic depletion in CO_2+H_2O to early necrotic coagulation (in experiments, also coagulation in glutaraldehyde solutions can slightly catalyze the growth of CaO seeds). However, the proper reasons of crystallization and blocking against the hydration are practically unknown. {Project: GAAV A3013209}.