Different sources of bacterial methane revealed by radiocarbon dating – Example from glacially deformed sediments, Denmark

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Methane is widespread in the Quaternary deposits, up to 200 m thick, of northern Denmark. Seabed sediments of the coastal seas are also rich in gas. Moreover, seeps and authigenic methane-derived carbonates are observed along the coast. Stable isotope data show that all of the methane is bacterial in origin, although radiocarbon datings of methane from different areas show a large variation, Fig. 1.
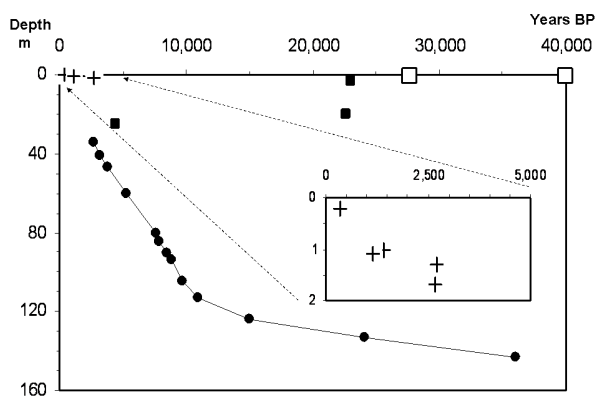

Figure 1. Methane radiocarbon ages. Circles = Skagen-3 well; solid squares = shallow wells; open squares = submarine seeps; crosses = seabed sediments.

In areas characterized by continuous deposition, the age of methane increases with the depth and age of the sediment: Skagen-3 well and piston cores [1]. However, methane from seeps [2] and some shallow wells is much older than would have been expected from its depth of occurrence. The shallow high-age methane is most likely derived from organic-rich interglacial marine deposits which were deformed and brought to shallower depths during the last ice-age, as is nicely illustrated in nearby coastal cliff exposures.

References

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Nickel immobilization by coprecipitation with calcite

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Nickel contamination from industrial and mining activities can pose a serious risk to groundwater. Because Ni is toxic to plants and animals, data describing its behaviour and fate are required for valid assessment of risk and designing effective remediation strategies. Because the interaction of calcite with Ni controls its distribution in calcareous environments, better understanding of the mechanisms responsible for nickel uptake would improve modelling capabilities.

This work investigated calcite's affinity for Ni and extent of partitioning into calcite precipitated from electrolyte solutions under strictly controlled conditions. Experimental conditions and all solution variables were held constant for each run and varied systematically in separate experiments.

Ni was moderately partitioned from solution into calcite. For dilute solid solutions ($X_{Ni} < 0.001$), λ_{Ni} was estimated to be ~1 at pCO_2 1 and $10^{-3.5}$ atm and was weakly dependent on calcite precipitation rate in the range of 3-230 nmoles m^{-2} s^{-1}. Changing pCO_2 does not imply any change in Ni incorporation mechanism, in spite of the significant impact of pCO_2 on calcite surface speciation. Ni molar fraction in the solid is directly proportional to Ni concentration in the solution. The fit of the data to such a model is good evidence that Ni is incorporated as a true solid solution, not simply by physical trapping.

Extrapolation of our experimental results to lower recrystallization rates (~10^{-2} nmol m^{-2} s^{-1}) gives λ_{Ni} ~1.5. It may be that this value is never exceeded in any natural or laboratory calcite (re)crystallization process so λ_{Ni} may always lie within the limits of $1 - 1.5$. Ni follows the behaviour of other elements with $\lambda > 1$ (Cd, Mn, Co) for which equilibrium λ values are never achieved.

The effect of coprecipitation on nickel retardation in natural systems depends on λ_{Ni} and on the thickness of a surface layer of solid solution equilibrated with the aqueous phase within a given period of interest. Coprecipitation will be important if large enough amounts of secondary calcite precipitate and if precipitation / recrystallization rates are high compared with transport rates in the solution. Considering a flow rate of ~10 m/year and Ni concentration 1μM, Ni flux would be 0.3 nmol m^{-2} s^{-1}, which is compatible with calcite recrystallization rates. With λ_{Ni} obtained in this work, the mass distribution coefficient of Ni^{2+} to calcite was calculated to be $K_d = 4$ at pH~8 and $K_d = 0.5$ at pH~6.5 for one (re)crystallized monolayer of calcite. This results in corresponding retardation factors R = 37 and 6. This means that solid solution partitioning to calcite can lead to a significant reduction in Ni mobility over a wide pH range.