# Retracing diagenetic pathways in diffusion controlled marine sediments: hydrogeochemical modelling with PHREEQC

E.T. ARNING[1]*, Y. FU[2], W. VAN BERK[2] AND H.-M. SCHULZ[1]

[1]Helmholtz Centre Potsdam GFZ, D-14473 Potsdam, Germany (*correspondence: earning@gfz-potsdam.de) (schulzhm@gfz-potsdam.de)

[2]TU Clausthal, Departement of Hydrogeology, D-38678 Clausthal-Zellerfeld, Germany (fyjsw0302@hotmail.com, wolfgang.van.berk@tu-clausthal.de)

Marine sediments undergo a wide range of early diagenetic processes. Controlling factors for these processes like sulphate reduction, iron reduction or methanogenesis are for example the primary mineralogy of sediments and the amount and kind of organic matter.

Major conversion products of early diagenetic processes are carbon dioxide and methane. So far, hydrogeochemical models to simulate carbon mass balance and species distribution as results of coupled equilibrium and irreversible reactions are lacking. Therefore, we are developing a hydrogeochemical model, which will enable us to retrace and predict hydrochemical composition of pore waters, conversion of mineral phases, and composition of coexisting gas phases.

In our approach, diagenetic signals in sediments will be retraced by modelling the redox-conversion of metabolizable organic carbon. Diagenetic signals to be retraced are aqueous solutions, mineral and gas phases. The theoretical background is based on chemical thermodynamics and the applied hydrogeochemical modelling tool is PHREEQC [1].

Successful modelling results were obtained for the open, diffusion controlled system of Hydrate Ridge sediments, ODP Leg 204 Site 1246 [2]. Modelled pore water concentration profiles reach measured pore water concentrations in the zone of sulphate reduction as well as in the methanogenic zone. Furthermore, modelled contents of secondary diagenetic phases like methane and greigite ($Fe_3S_4$) in specific sediment depths were consistent with measured values. With PHREEQC it was also possible to calculate the gas compposition in different sediment depths. Beside methane (>93 mol%) up to 1 mol% CO2(g) and 6 mol% N2(g) are present in sediments of the methanogenic zone.

[1] Parkhurst & Appelo (1999) *USGS, Water resources investigation report* **99-4250**, 312 p. [2] Tréhu *et al*. (2003) *Proc. ODP, Init. Repts*. **204**.

# Sources and properties of carbon in Earth's oldest rocks

G. ARRHENIUS[1]*, C. DARAIO[2], A. MISRA[2], M.L. RUDEE[3], H.S. PEREZ[4], A. LEPLAND[5] AND M. VAN ZUILEN[6]

[1]SIO, La Jolla CA 92093-0218 (*correspondence: arrhenius@ucsd.edu)

[2] CalTech 105-50, Pasadena CA 91125 (daraio@caltech.edu, abha@caltech.edu)

[3] Electrical & Computer Engineering, UCSD, La Jolla CA 92093-0407 (rudee@ecepops.ucsd.edu

[4]SIO, La Jolla CA 92093-0218 (hperez@ucsd.edu)

[5]Norges Geol. Undersogelse, N7491 Trondheim (Aivo.Lepland@ngu.no)

[6]Centre for Geobiology, Univ of Bergen, N-5020 Bergen (Mark.Zuilen@geo.uib.no)

Elemental carbon in the oldest known sedimentary rocks on Earth - organogenic, terrestrial inorganic and potentially meteoritic, are investigated with the ultimate purpose of establishing the earliest traces of life on Earth. Evidence for the origin and mode of formation is sought in the carbon ultrastructure . Meteoritic carbon is distinguished from terrestrial organogenic (= biogenic) carbon by the accompanying concentrations of platinum metal elements The oldest known supracrustal rocks on Earth in Greenland (ISB) contain several genetic types of carbon. One appears in iron carbonates with carbon as graphite precipitated by disproportionation of the siderite. Another type of carbon occurs in the banded iron formation, commonly accepted as a sedimentary deposit. A third source of ISB carbon, potentially biogenic, is a carbonaceous shale discovered by Rosing and with spatial extent recently explored by coring. The 3.4 to 3.2 Ga deposits in the Barberton Greenstone Belt (BGB), S.Africa offer exceptional opportunities for the study of carbon in an early Archean sedimentary environment and contain objects that deserve analysis as possible organic structures . Both Barberton sediments and shungites are extensively permeated by mobile bitumen, obscuring primary sedimentary carbon features.