

Characterization of hydrous species in hydrous and nominally anhydrous minerals by ^1H solid state NMR spectroscopy

L. LINGNER, M. FECHTELKORD AND R. DOHMEN

Institut für Geologie, Mineralogie, und Geophysik,
Ruhr-Universität Bochum, 44780 Bochum, Germany,
(Michael.Fechtelkord@ruhr-uni-bochum.de)

Nominally H_2O -free minerals (NAMs) like olivine and pyroxenes are considered to be significant reservoirs for H_2O in the upper mantle (e.g., Bai and Kohlstedt), which would drastically influence a number of physical properties of the mantle and processes related to these. The presence of H in small amounts may dominate the point defect chemistry of these minerals. Thus, depending on the exact incorporation mechanism and structural environment, physical properties like electrical conductivity and strain rates change compared to the completely dry mineral. The coordination of H in NAMs has been inferred so far either indirectly from the measurement of transport properties (e.g., Kohlstedt and Mackwell, 1998) or by interpretation of IR spectra.

Here we present ^1H -solid state NMR spectroscopy as an alternative way to study the structural arrangement of H in nominally anhydrous minerals. A number of gem quality single crystals of NAMs like diopside and olivine as well as hydrous minerals like hydrogrossular and analcime were selected and prepared for both IR and ^1H -NMR spectroscopy. The NMR spectra of hydrous minerals, where the coordination of H is well known, are used as a reference for comparison with the NAMs (Yesinowski *et al.* 1988). The pure ^1H NMR signals in NAMs were derived by suppressing the probehead proton and background signal with a special DEPTH pulse sequence (Corey and Ritchie 1988). It was possible to identify clear ^1H -signals using this technique, despite the significant Fe-content and the small amounts of H (< 1000 ppm) of the samples.

Preliminary results show that protons in diopsides are located in the structure as isolated (no neighboring H present) hydroxyl groups of a single coordination type. The chemical shift of the very narrow single ^1H -signal is at approximately 1.8 ppm, which excludes the formation of silanol groups, but implies an association with Al^{3+} on a Si site, as was suggested by e.g., Stalder (2004).

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The Deep Biosphere: Quantitative and taxonomic constraints through microbial lipids

JULIUS S. LIPP AND KAI-UWE HINRICHS

Organic Geochemistry Group, Dept. of Geosciences,
University of Bremen, 28359 Bremen, Germany
(jlipp@uni-bremen.de, khinrichs@uni-bremen.de)

The deep biosphere contains up to one third of the total carbon in live cells of our planet (Parkes *et al.*, 2000; Whitman *et al.*, 1998). Recent studies have provided information on metabolic activities and quantities of deeply buried prokaryotic cells, while fundamental questions remain regarding the taxonomic composition (e.g. Biddle *et al.*, 2006; Inagaki *et al.*, 2006). For example, various techniques appear to disagree already at the domain level on who actually dominates this vast ecosystem.

We analyzed intact polar lipids (IPLs), a marker for live prokaryotic cells in a set of sediment samples from a depth range of 0.01 to 367 mbsf from sites at Peru margin, Cascadia Margin, Demerara Rise, and Equatorial Pacific (RV Sonne SO147, ODP Legs 201, 204, 207, and IODP Expeditions 301 and 311). The observed IPL concentrations range from 4 to 16,000 ng mL⁻¹ sediment and display a similar concentration-depth relationship as observed in a global compilation of direct counts of active cells (cf. Parkes *et al.*, 2000). Surface sediments are clearly dominated by bacterial IPLs with possible admixtures of eukaryotic lipids. Concentrations of bacterial lipids decline rapidly within the first 10 cmbsf to levels significantly lower than those of their archaeal counterparts. The analysis of ODP/IODP samples from deeply-buried horizons shows evidence for bacterial lipids in about 20% of samples analyzed to date. On the basis of these observations in combination with results of degradation experiments of archaeal and bacterial IPLs under typical anaerobic sedimentary conditions (Pamela Rossel *et al.*, unpubl. data), we interpret the predominance of archaeal IPLs as evidence for a far more important role than suggested by other techniques.

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