Characterization of microbial activity by petroleum compositional changes using ultra-high resolution mass spectrometry techniques (FT-ICR-MS)

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Introduction & Methods

Most of the world petroleum reserves are biodegraded with the largest oil reserves being found on the flanks of foreland basins in Canada and Venezuela. Coal as another essential energy source is also known to being partially biodegraded yielding to biogenic gas.

In this study, the compositional changes of fossil fuels during biodegradation in lab experiments and in natural reservoir profiles under aerobic and anaerobic conditions will be shown as well as indicators of microbiological activity.

The fossil fuel compositions were analyzed using an ultra-high resolution Fourier Transform-Ion Cyclotron Resonance-Mass Spectrometry (Bruker12T FT-ICR-MS) and GC-MS techniques. For FT-ICR-MS the ionization methods used include Electrospray (ESI) in positive and negative ion mode as well as Atmospheric Pressure Photoionization (APPI) in positive ion mode.

Results & Discussion

One example of compositional changes during biodegradation of bitumen and assessment of microbial activity is shown in Fig. 1.

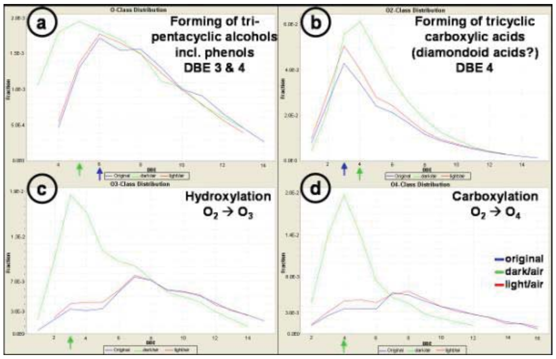

Figure 1: Changes in oxygen compound systematics of aerobic biodegradation lab experiments of oil sands bitumen: a. alcohols, b. carboxylic acids, c. hydroxy-carboxylic acids, d. dicarboxylic acids. All oxygen compound classes (O1-4) are becoming strongly enriched in the absence of light whereas under light no or only minor changes are observed.

Thermodynamic properties of carbonate liquids: required for models of carbonate stability in the mantle

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Not only is mantle carbonate an important reservoir in the global carbon cycle, it also plays a key role in mantle melting processes. Mantle carbonate, of which $MgCO_3$ and $CaCO_3$ are the most important components, has been shown to have a major effect on both the depth of melting and the resultant magma composition (e.g., Dasgupta et al., 2006). In order to fully explore under what T-P conditions mantle carbonate can be subducted into the lower mantle, as well as to examine all possible temperature, pressure, and composition conditions where mantle carbonate influences melting, the number of phase equilibrium experiments needed is prohibitive. Therefore, thermodynamic models of mantle melting that incorporate carbonate are of considerable interest. In order to achieve this, thermodynamic data on $CaCO_3$ and $MgCO_3$ liquids are needed, including their heat capacity, enthalpy, volume, and compressibility. By mixing the alkaline earth carbonates with the alkali carbonates, liquidus temperatures are lowered to those below decomposition (< 1300K), permitting measurement of various thermodynamic properties to be made. This method also tests whether the molar volume, compressibility, and heat capacity of carbonate liquids mix ideally with respect to composition, allowing the partial molar liquid properties for $CaCO_3$ and $MgCO_3$ to be derived. Previous work in the system Li_2CO_3-Na_2CO_3-K_2CO_3-$CaCO_3$ by Liu and Lange (2003) has shown that the volume and thermal expansion mix ideally. In this study, we show that the compressibility and heat capacity of Li_2CO3-Na_2CO_3-K_2CO_3-$CaCO_3$ liquids also mix ideally with respect to composition at one bar. Compressibility measurements were made on eleven liquids (four containing ≤ 50 mol% $CaCO_3$) using frequency-sweep acoustic interferometery at one bar between 800 and 1300 K. When the ideal mixing model for compressibility is applied,

$$\beta_T(X) = \sum X_i \frac{\overline{V}_{i.T}}{\overline{V}_T}\left(\overline{\beta}_{i.T_{1100K}} + \frac{\partial \overline{B}_i}{\partial T}(T - 1100\,K)\right)$$

fitted partial molar compressibilities are acquired (Table 1).

Carbonate Component	$\beta_{T,1100K} \pm 1\sigma$ (10^{-2} GPa^{-1})	$\partial\beta_T/\partial T \pm 1\sigma$ (10^{-2} GPa^{-1})
$CaCO_3$	5.36 ± 0.13	0.0061 ± 0.0010
Li_2CO_3	8.09 ± 0.06	0.0044 ± 0.0008
Na_2CO_3	10.62 ± 0.07	0.0103 ± 0.0006
K_2CO_3	14.09 ± 0.06	0.0135 ± 0.0004

Table 1. Partial molar compressibilities for the carbonates.

A Perkin-Elmer Diamond differential scanning calorimeter is being used to measure liquid heat capacities. We have applied our results to a thermodynamic analysis of the fusion curve of $CaCO_3$ in order to constrain its one-bar enthalpy and entropy of fusion in addition to the pressure dependence of the compressibility (bulk modulus) of $CaCO_3$ liquid (K_0'), using a 3rd-order Birch-Murnaghan equation of state. Currently, our best estimate for the K_0' of $CaCO_3$ liquid is 4.5 ± 0.5. Though DSC measurements are ongoing, our preliminary estimate for the enthalpy of fusion for $CaCO_3$ at one bar is 67.5 ± 0.5 kJ/mol for a one-bar metastable melting temperature of 1295°C.