

Chemical and isotopic composition of Lower Vindhyan organic rich sediments: Role of chemical alteration and grain size distribution

TARUN K. DALAI

Department of Earth Sciences, Indian Institute of Science Education and Research-Kolkata, Mohanpur, West Bengal 741252, INDIA (dalai@iiserkol.ac.in)

Several grey and black shales samples from the Lower Vindhyan section in the Central India have been collected. The samples have been chosen to represent various degrees of chemical alteration; those collected from the surface are extensively weathered whereas those collected from deeper in the mine cuts are relatively fresh. These samples have been analyzed for major ion composition, C_{org} and $\delta^{13}C$ of bulk organic matter.

The major ion compositions indicate influence of both chemical alteration and grain size distributions driven by mineralogical sorting. Abundances of bulk organic content (C_{org}) show significant positive correlation with Na/Al and an inverse correlation with K/Na. In contrast, C_{org} exhibits a weak positive correlation with Si/Al. Together, these observations indicate that organic carbon content in these samples are controlled by various degrees of chemical alteration and that the influence of grain size distributions and mineralogical sorting may be rather weak. It is unclear to what extent the original relationship between the grain size and C_{org} has been lost by chemical alteration.

Carbon isotopic composition ($\delta^{13}C$) of bulk organic matter shows a significant positive correlation with ($1/C_{org}$). A first order interpretation of this trend is that relatively fresh organic matter is characterized by more negative $\delta^{13}C$ values whereas less negative $\delta^{13}C$ values represent organic matter that are altered by exchanging carbon with the weathering solution. Our results are in contrast to those observed by Van Os *et al.* [1]. Abundances of specific organic compounds, a suite of trace elements and grain size distributions would be measured to better understand the role of chemical alteration, grain size distributions and specific organic compounds in influencing the abundances of metals, organic carbon and carbon isotope composition of organic matter of these organic rich sediments.

[1] Van Os *et al.* (1996) *Aquatic Geochemistry* **1**, 303-312.

XPS heating with mass spectrometry: Tackling chalk, coccolith and calcite surfaces

K.N. DALBY*, N. BOVET AND S.L.S. STIPP

Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark (*kdalby@nano.ku.dk)

Chalk hosts significant quantities of the North Sea oil and biogenic calcite ($CaCO_3$) is a major component of the chalk. The biogenic calcite is in the form of coccoliths, precipitated by some species of single-celled marine algae. To understand the complex recrystallisation behavior of natural chalk, abiogenic calcite is often used as a model system. Abiogenic calcite is also used as a proxy for chalk during surface reactivity studies¹.

In this study to examine similarities and differences between the biogenic and abiogenic calcite surfaces, we used X-ray photoelectron spectroscopy (XPS), coupled with an *in situ* residual gas analyzer (RGA), to examine natural chalk, cultured coccoliths and natural abiogenic calcite (Iceland Spar). We characterised, compared and contrasted the surface of the natural and model systems before, during and after heating to 500 °C. The samples were heated to mimic reservoir conditions and to investigate the kinetics of the decarbonation reaction.

High resolution carbon 1s (C 1s) XPS spectra of the samples show differences in the surface composition. All samples display C-C bonds at 285.0 and CO_3 bonds at 290.1 eV. In addition, the chalk and coccoliths show evidence of C-OH (287.0 eV) and COOH (289.0 eV) compounds coating the surfaces. The ratio of all four C contributions is variable between the various samples of chalk and coccoliths. These coatings could prevent recrystallisation and dissolution of ancient coccoliths in chalk.

During heating to 500 °C, both H_2O and CO_2 are released by all samples. The abiogenic calcite contains water-rich inclusions and these 'explode' during heating, producing spikes in the mass spectrometer data. No evidence of inclusions exist in the chalk or coccolith samples, which release H_2O and CO_2 at a more constant rate. During the heating experiments, the C-OH and COOH coatings are removed from the surfaces of the coccoliths and chalk, and the surface composition becomes more similar to the abiogenic calcite. Ongoing work will examine sample reactivity, including dissolution rates of chalk and coccolith surfaces before and after heating.

[1] Bovet *et al.* (2011) *This Issue*.