



Understanding gas shales using inorganic, ternary geochemical systematics.

Sudeshna Basu (1), Adrian Jones (1), and Alexander Verchovsky (2)

(1) Department of Earth Sciences, University College London, London WC1E 6BT (sudeshna.basu@ucl.ac.uk), (2) Planetary and Space Sciences Research Institute, Open University, Milton Keynes MK7 6AA(sasha.verchovsky@open.ac.uk)

We have developed a new approach of simultaneous analyses of carbon, nitrogen and noble gases, for isotopic and elemental compositions in bulk shales from different depths (11785 to 11909 feet) of a core from the Haynesville Bossier formation to decouple the different trapped components. This is preceded by major, minor and trace elemental analyses to understand their paleo productivity, tectonic and redox conditions of deposition as well as constraining their alteration and weathering.

5 to 10 mg of samples have been combusted from 200-1200°C in incremental steps of 100°C. Based on $\delta^{13}\text{C}$, we identify both marine+lacustrine ($\delta^{13}\text{C} \sim -25 \text{‰}$ C/N ~ 5) and minor continental organic matter ($\delta^{13}\text{C} \sim -27 \text{‰}$ C/N ~ 60) in the samples, in agreement with observations from elemental compositions. Extremely depleted $\delta^{13}\text{C}$ of $\leq -34 \text{‰}$ in some temperature steps, can be attributed to methanogenesis. Two carbonate populations, primary ($\delta^{13}\text{C} \sim 0$ to 2‰) and diagenetic ($\delta^{13}\text{C} \sim -13$ to -11‰) can also be identified. We have been able to identify the multiple C components present in the samples, including very minor ones, without resorting to acid treatment. The bulk N $\delta^{15}\text{N}$ values vary from -1.2 to $+6.4 \text{‰}$ but show a wide range from -15 to 15‰ within individual steps. By suitable modelling, we constrain the primary $\delta^{15}\text{N}$ to be 5 to 8‰ identifiable in very high temperature steps of heating. This is possible if there is penetration of hot fluids that eliminates organic N along a reaction front leaving it fractionated, but leaves behind an unreacted core of residual nitrogen unaffected by isotopic fractionation (Boudou et al., 2008). Our study indicates that using bulk N values as primary signatures to constrain the redox conditions of deposition or thermal maturity of shales as is the practice, should be done with caution. Simultaneously obtained noble gases were used to constrain gas retention in the samples. Deviations of measured $4\text{He}/40\text{Ar}^*$ (where 40Ar^* represents radiogenic 40Ar after correcting for contribution from atmospheric Ar) from expected values has been used to monitor gas loss by degassing.

Boudou, J., Schimmelmann, A., Ader, M., Mastalerz, M., Sebiló, M., Gengembre, L., 2008. Organic nitrogen chemistry during low grade metamorphism. *Geochimica Cosmochimica Acta* 72, 1199-1221.