

## Re-Os isotopes and redox-sensitive elements of the Himalayan black shales: Implications to marine anoxia near the Pc-C boundary

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Present study attempts to determine the timing and its implications related to changes in the redox state of seawater at around the Pc-C boundary using Re-Os isotopes and redox-sensitive elements of black shales sampled from an underground phosphrite mine (Maldeota, Dehradun) just overlying the Pc-C boundary in the Lower Tal formation of the Lesser Himalaya, India. The measured  $^{187}\text{Re}/^{188}\text{Os}$  ratios of these shales vary widely (51 to 137), but linearly with that of  $^{187}\text{Os}/^{188}\text{Os}$  (1.363 to 2.116). Following the bivariate approach that used by Singh *et al.* [1], the  $^{187}\text{Re}/^{188}\text{Os}$ - $^{187}\text{Os}/^{188}\text{Os}$  systematics of these shales provided a depositional age of  $541 \pm 8$  ( $2\sigma$ ) Ma with an initial  $^{187}\text{Os}/^{188}\text{Os}$  value of  $0.90 \pm 0.02$  ( $2\sigma$ ). The Re-Os age of black shales obtained in this study is quite consistent with the reported radiometric ages for Pc-C boundary at other locations of the world.

Geochemical compositions of black shales deposited near the Pc-C boundary is observed to be different than that of the overlying sequences of black shales. The average Al-normalized values of organic carbon ( $C_{\text{org}}/\text{Al}$ ) and redox-sensitive elements (Re/Al, Os/Al, V/Al, Cr/Al, Cu/Al) of these shales are found to be significantly higher compared to that of black shales [1] overlying ~3 m above [2], but separated by a phosphrite sequence from these shales. This enrichment of  $C_{\text{org}}$  and trace elemental ratios in the black shales deposited at 541 Ma indicates a highly euxinic seawater near the Pc-C boundary. The inferences from this study of reducing seawater chemistry at the Pc-C boundary can find application in understanding the causative factors of the Cambrian explosion of life. For example, the highly euxinic state of seawater could have imposed a mass extinction [3], which subsequently led to large diversification in biology resulting into Cambrian explosion of life.

[1] Singh, Trivedi & Krishnaswami (1999) *Geochim. Cosmochim. Acta* **63**, 2381–2392. [2] Sharma, Rao, Azmi, Gopalan & Pantulu (1992) *Curr. Sci.* **62**, 528–530. [3] Kimura & Watanabe, *Geology* **29**, 995–998.

## Non-isothermal dehydroxylation kinetics of common sheet-like phases and their informational value

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Studying the decomposition kinetics by thermal analyses (e.g. Thermogravimetry, Differential Thermal Analysis, Differential Scanning Calorimetry) of rock forming minerals have a long tradition in Earth Sciences. Often observed rate laws have been used for mechanistic interpretation of the reactions. Classical approaches (Avrami, Time to a Given Fraction TGF) focus on model fitting techniques to extract single values of the apparent activation energy  $E_a$  and the 'rate determining step' is derived from the value of the exponent in the Avrami equation. From the physico-chemical point of view such interpretations are for most reactions commonly wrong and have often been criticised especially in the chemistry literature [1-3].

Isoconversional treatment of model-free non-isothermal datasets give, in contrast to the classical methods,  $E_a$  as a function of  $\alpha$ . Variation of  $E_a$  with  $\alpha$  are a clear sign that the reaction rate is determined by more than one parallel or sequential step and that classical treatment is not feasible. In such a case, mechanistic interpretation of the kinetic experiments is only possible in combination with information gained from simulations (Density-functional-theory (DFT) models [4, 5]) or *in situ* diffraction and spectroscopic methods.

Here, the dehydroxylation kinetics of two natural occurring phases, lizardite and brucite, are taken as examples for contrasting behaviour of the rate determining reaction step. Lizardite dehydroxylation illustrates a highly dynamic and predominantly increasing evolution of  $E_a$  with  $\alpha$  [6] indicating that several different steps become rate determining, whereas brucite dehydration evolves with a nearly constant  $E_a$  indicating that only one step is rate determining over the entire reaction progress. The possible rate determining steps will be discussed.

[1] Galwey (2004) *Thermochim. Acta.* **413**, 139–183. [2] Vyazovkin & Wight (1997) *Annu. Rev. Phys. Chem.* **48**, 125–149. [3] Vyazovkin (2000) *New. J. Chem.* **24**, 913–917. [4] Molina-Montes *et al.* (2008) *J. Phys. Chem. B* **112**, 7051–7060. [5] Churakov *et al.* (2004) *J. Phys. Chem. B* **108**, 11567–11574. [6] Trittschack & Grobety (submitted) *Eur. J. Mineral.*