Re-Os depositional age for extremely thermally mature Upper Carboniferous organic-rich shales, Western Ireland: Challenges and insights

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^{187}Re-^{187}Os dating of organic-rich rocks using Cr^{VI}-H_2SO_4 digestion is a relatively new method for dating sedimentation, however, the method can yield accurate and precise ages [1]. The Re-Os systematics in black shales has been shown to be undisturbed by hydrocarbon maturation and chlorite-grade metamorphism [1, 2]. To test applicability of the Re-Os geochronometer on black shales that have experienced elevated palaeotemperatures (320-350°C [3]) samples from a well-preserved single bed (~30 cm) of organic-rich (TOC = ~ 3.9%, [3]) shale (*Bilinguites bilinguis* marine band, R_{2b1}) from the thermally overmature (T_{max} = 350°C [3]) Upper Carboniferous Clare Basin of Western Ireland were analysed. The samples have high and variable Re and Os contents, 32 – 228 and 0.3 – 1.3 ppb, respectively. The $^{187}Re/^{188}Os$ ratios are high, ranging from 900 – 2300 and correlate positively with highly radiogenic $^{187}Os/^{188}Os$ compositions (5.6 – 12.6). All Re-Os data (n = 10) yield a preliminary Re-Os isochron Model 3 age of 308 ± 14 Ma (MSWD = 38, 2σ), with an initial $^{187}Os/^{188}Os$ of 0.86 ± 0.39. Despite a significant range in the Re-Os isotopic data, the determined date is less precise (4.5 %, 2σ) than several recently published Re-Os organic-rich sediment dates (often <1%, 2σ, [cf. 1, 2]) determined using the same analytical protocols. However, the Re-Os date for Bashkirian *B. bilinguis* bed is indistinguishable (within uncertainty) from the interpolated age of the Global Stratigraphic Scale [4]. The imprecision of the Re-Os date is a reflection of the variable initial $^{187}Os/^{188}Os$ compositions of the sampled horizon (0.72 to 1.07 calculated at 308 Ma). This variation may record changes in the Os water column chemistry during deposition or minor transport/diffusion of Re and Os caused by extreme thermal maturation [5].

[1] Selby & Creaser (2005) *Geology* **33**, 545-548. [2] Kendall *et al.* (2004) *EPSL* **222**, 729-740. [3] Goodhue & Clayton (1999) *Marine & Petrol. Geol.* **16**, 667-675. [4] Menning *et al.* (2006) *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **240**, 318-372. [5] Yang *et al.* (2009) *EPSL* doi:10.1016/j.epsl.2009.01.019.

Triple isotopic signature of oxygen in the equatorial Pacific

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The triple isotopic signature of oxygen is a tracer used to investigate gross production in the world's oceans. Mass independent fractionation in the stratosphere results in dissolved oxygen in seawater stemming from atmospheric oxygen having a different triple oxygen isotopic signature than dissolved oxygen resulting from photosynthesis. This signature is quantified through $^{17}\Delta$ where $^{17}\Delta = [\ln(\delta^{17}O/1000 + 1) - 0.516 \cdot \ln(\delta^{18}O/1000 + 1)] \times 10^6$. In the mixed layer, $^{17}\Delta$ is a tracer of gross production. Below the mixed layer, $^{17}\Delta$ is reflective of the interplay of various processes, including local biological production, vertical mixing, and lateral transport.

We have measured $^{17}\Delta$ in profiles in the upper 200 m of the water column at eight stations in the equatorial Pacific along 125°W and at two stations along 140°W. In these profiles, we find intriguing maxima of $^{17}\Delta$ below the euphotic zone. The $^{17}\Delta$ of surface waters ranges from 45 to 75 per meg at the various stations whereas the $^{17}\Delta$ of the deep maxima range from 105 to 125 per meg and typically occurs at 100 to 140 m depth. Interestingly, on the equator there is no maximum in $^{17}\Delta$ below the euphotic zone. We explore possible mechanisms for creating these maxima, including the possibility of local production below the 1% light level.

Additionally, surface measurements of $^{17}\Delta$ and of another gas tracer, O_2/Ar, measured along 125°W and 140°W in the Equatorial Pacific in September and October, 2007, are used to constrain gross production and net community production in this climatically important area. In particular, an underway mass spectrometer was used to measure O_2/Ar, providing a dataset of continuous measurements of net community production along these two longitudes. These two tracers – $^{17}\Delta$ and O_2/Ar – yield insights on biological uptake, a process that is important both in its own right and in terms of its affect on other trace elements and isotopes.