

RHENIUM-OSMIUM GEOCHRONOLOGY

Organic-rich black shale was sampled at station 18SUB-W054 (Fig 1 of manuscript, coordinates 70° 11' 7.89" N, 84° 37' 56.61" W). Samples were collected over a 1.1 m interval with 2.8 m of horizontal spread. Collected samples were sedimentologically indistinguishable. To expose the freshest surfaces possible, samples were trimmed using a rock saw and then hand-polished using a diamond-encrusted polishing pad to remove cutting marks and eliminate any potential for metal contamination from the saw blade. Once cut and polished, the samples were crushed to a fine (~100 µm) powder in a SPEX 8500 Shatterbox using a zirconium ceramic grinding container and puck in order to homogenize any Re and Os heterogeneity present in the samples (e.g., Kendall et al., 2009). Re and Os isotopic abundances and compositions were determined at the GEOTOP laboratory at Université du Québec à Montréal following Meisel et al. (2003).

The $\text{Cr}^{\text{VI}}\text{O}_3\text{-H}_2\text{SO}_4$ digestion method was employed for Re-Os analysis of these samples as this method has been shown to preferentially liberate hydrogenous Re and Os without incorporating any detrital Os budget and thus yields more accurate and precise dates (Selby and Creaser, 2003). Sample powders each weighing ca. 0.8 g together with a mixed tracer (spike) solution enriched in ^{190}Os and ^{185}Re were dissolved in 8 ml of a $\text{Cr}^{\text{VI}}\text{O}_3\text{-H}_2\text{SO}_4$ solution (0.25 g $\text{Cr}^{\text{VI}}\text{O}_3$ per ml of 4N H_2SO_4) in a sealed carius tube for 48 hours at 220°C (Shirey and Walker, 1995; Selby and Creaser, 2003).

Rhenium and Os isotope analyses of the organic-rich sedimentary units followed methods developed over the past three decades and are briefly outlined below (Morgan and Walker, 1989; Shirey and Walker, 1995; Birck et al., 1997; Selby and Creaser, 2003; Cumming et al., 2013). Osmium was isolated using solvent extraction (CHCl_3) and further purified using micro-distillation (Cohen et al., 1996; Birck et al., 1997). The Re of the resultant Os-extracted solution was isolated and purified using $\text{NaOH-(CH}_3)_2\text{CO}$ solvent extraction and anion column chromatography methods. All Re and Os isotopic measurements were determined by negative thermal ionization mass spectrometry (NTIMS) (Creaser et al., 1991; Völkening et al., 1991) at the Yale University Geochemistry and Geochronology Center. The purified Re and Os fractions were loaded onto Ni and Pt filaments, respectively with the isotopic measurements performed using a Thermo Scientific Triton-Plus multi-collector thermal ionization mass spectrometer via static Faraday collection for Re and ion-counting using a secondary electron multiplier in peak-hopping mode for Os. For the $\text{Cr}^{\text{VI}}\text{O}_3\text{-H}_2\text{SO}_4$ solution total procedural blanks during this study were 36.3 ± 1.4 pg and 0.3 ± 0.04 pg (1 S.D., $n = 7$) for Re and Os, respectively, with an average $^{187}\text{Os}/^{188}\text{Os}$ value of 0.22 ± 0.15 ($n = 7$). Uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ were determined by propagation of all uncertainties in Re and Os mass spectrometer measurements,

blank abundances and isotopic compositions, spike calibrations and reproducibility of standard Re and Os isotopic values. The Re–Os isotopic data including the 2σ calculated uncertainties for $^{187}\text{Re}/^{188}\text{Os}$ and $^{187}\text{Os}/^{188}\text{Os}$ and the associated error correlation function (ρ) were used to calculate a Re–Os isochron date using Isoplot V. 4.15 and the λ ^{187}Re constant of $1.666 \times 10^{-11}\text{a}^{-1}$ (Ludwig, 2009). Final age uncertainty includes the uncertainty in the decay constant, which permits a direct comparison with other chronometers (e.g., U–Pb zircon dates; Smoliar et al., 1996). As a monitor of mass spectrometry reproducibility, two in-house Re and Os standard solutions were analyzed. The Re standard is a solution made from 0.137 g of zone-refined Re metal (99.999%, H-Cross company) in a 4N HNO_3 solution and yields an average $^{185}\text{Re}/^{187}\text{Re}$ ratio of 0.59881 ± 0.0006 (2 S.D., $n = 8$) for the analytical interval of this study. The Os isotope standard, DROsS, yields an average $^{187}\text{Os}/^{188}\text{Os}$ ratio of 0.16104 ± 0.00015 (2 S.D., $n = 8$), both of which agree with previous studies (Nowell et al., 2008; Rooney et al., 2010).

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