

Re-Os depositional ages and seawater Os estimates for the Frasnian-Famennian Boundary

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Four TOC-rich shales spanning the Frasnian-Famennian (F-F) Boundary were recovered in a drillcore (West Valley NX#1) from Cattaraugus in western New York (USA) and radiometrically dated using Re-Os [1]. Two of the black shales (WVC785 from ~2.1 m below-, and WVC754 from ~5.6 m above the F-F Boundary, respectively) yield statistically overlapping ages of ca. 373 Ma with uncertainties of <1.4%, and provide a new absolute age constraint on the F-F Boundary. Based on cyclostratigraphic analysis, the covered interval likely represents only ~200-300 kyrs.

This date is ~3.5 Ma younger than the proposed F-F Boundary age of 376.5 Ma obtained by interpolation of U-Pb dates from volcanic zircon [2], and within uncertainty of the ICS accepted date of 374.5 ± 2.6 Ma [3] obtained by “statistical fit of a composite biostratigraphic zonation to selected radiometric ages”. A third date (from sample WVC802, ~7.5 m beneath the F-F Boundary) yields an imprecise age of ca. 358 Ma, owing to a limited Re/Os range.

The initial $^{187}\text{Os}/^{188}\text{Os}$, reflecting contemporaneous seawater Os values, are low for all samples (0.41 to 0.48), and similar to the value of 0.42 reported for the Exshaw Fm (Canada) at the Devonian-Mississippian Boundary (361 Ma) [4]. This may suggest fairly constant and low global continental weathering rates during the Late Devonian, although in view of the short residence time of Os in seawater ($\sim 1-4 \times 10^4$ yr), further measurements are needed to assess potential short-term variation in seawater Os ratios.

Despite high (~2-3%) TOC contents, the shale bed (WVC777) at the F-F Boundary has ~3-9× lower Re contents, along with low and restricted ranges in $^{187}\text{Os}/^{188}\text{Os}$ and $^{187}\text{Re}/^{188}\text{Os}$, but only marginally lower Os contents. As Re is efficiently removed from seawater under even slightly reducing conditions, the Frasnian-Famennian ocean appears to have been depleted with respect to Re, possibly indicating an exhaustion of the Re seawater reservoir owing to high burial rates of redox-sensitive elements under dysoxic/anoxic conditions leading up to the F-F Boundary [5].

[1] Kendall B.S. et al. (2004) *EPSL* **222**, 729-740.

[2] Tucker R.D. et al. (1998) *EPSL* **134**, 175-186.

[3] Williams E.A., Friend P.F. and Williams B.P.J. (2000) *Geol. Soc. London Spec. Publ.* **180**, 1-21.

[4] Selby D. and Creaser R.A. (2005) *Geology* **33**, 545-548.

[5] Algeo T.J. (2004) *Geology* **32**, 1057-1060.