

OSMIUM ISOTOPIC EVIDENCE AGAINST AN IMPACT AT THE FRASNIAN-FAMENNIAN BOUNDARY

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ABSTRACT. Two sections across the Frasnian-Famennian boundary were analyzed for Re and Os concentrations and $^{187}\text{Os}/^{188}\text{Os}$ ratios to evaluate evidence for a meteoritic input coincident with this boundary and its associated mass extinction. These sections are from a siltstone and shale sequence at Irish Gulf in New York, US and a calcareous shale and ferromanganese oxide sequence at La Serre in France. The Irish Gulf section, with an initial $^{187}\text{Os}/^{188}\text{Os}$ of about 0.49, does not show the characteristic meteoritic Os imprint with an $^{187}\text{Os}/^{188}\text{Os}$ of about 0.13. The integrity of the section with regard to Re and Os retention is indicated by the construction of an isochron with an age of 388 ± 41 Ma, consistent with independently determined ages for the Frasnian-Famennian boundary. Although the La Serre section, with Os concentrations as high as 33 ppb and Re concentrations ranging from 1.4 to 7.4 ppb, might be expected to show excellent evidence for a meteoritic contribution, the highly radiogenic isotopic composition ($^{187}\text{Os}/^{188}\text{Os}$ 2.42-3.61) instead suggests recent massive Re loss or addition of radiogenic Os. These possibilities prevent the reconstruction of an initial $^{187}\text{Os}/^{188}\text{Os}$ value for the boundary for this site. Assuming reasonable Re concentrations prior to loss, the Os isotopic composition is inconsistent with a large meteoritic component. This inconsistency emphasizes that platinum group element (PGE) concentrations are not reliable indicators of extraterrestrial addition.

INTRODUCTION

McLaren (1970) proposed a meteorite impact as the cause of the late Devonian (Frasnian-Famennian boundary) mass extinction. The proposition that a meteorite impact can be an important agent for mass extinctions has been extended to the Cretaceous-Tertiary (K-T) boundary with some signal success (Alvarez and others, 1980). Using anomalous iridium enrichments as an indication of the presence of meteoritic material, this marker was successfully used to recognize the K-T boundary event throughout the world. The same approach has been applied to establish evidence for a meteorite impact(s) at the Frasnian-Famennian boundary. Minor iridium anomalies have been found in Frasnian-Famennian (F-F) sections in New York (Over and others, 1997), the Canning Basin of Western Australia (Playford and others, 1984), Steinbruch Schmidt of Germany (McGhee and others, 1986) and Luoxiu of south China (Wang and others, 1991). However, the Luoxiu section was the only one with an increase in Ir coincident with the boundary, with 350 ppt on a carbonate-free basis against a background of 40 ppt (Wang and others, 1991). The Ir anomalies at the K-T boundary, however, are much greater—as much as 630 ppb (Sawlowicz, 1993).

Iridium can be concentrated by geochemical, sedimentologic or biological processes (Turekian, 1982). In the Canning Basin, Ir is found proportional to the density of *Frutexitis* microfossils (Orth, 1989; Nicoll and Playford, 1993); at Steinbruch Schmidt, the Ir anomalies are not at the boundary horizon but associated with clay partings in the limestone sequence (McGhee and others, 1986). Also, sections in Alberta, Canada (Geldsetzer and others, 1987) and the Northwest Territories, Canada

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(Goodfellow and others, 1988, 1989) showed no evidence of excess Ir. H. Geldsetzer found a large positive Ir anomaly in the La Serre section (as reported at a 1991 Calgary meeting on Event Markers in Earth History by Kerr, 1992), but Girard and others (1997) resampled the section and were unable to reproduce his results, suggesting that the earlier reported high value may have been due to diagenetic concentration, including the possibility of recent remobilization. In addition, Girard and others (1997) report that further paleontological investigation suggested the F-F boundary was lower in the section than Geldsetzer's samples.

Microtektites commonly occur in many K-T sections, but are not associated with any of the F-F boundary sections. Claeys and others (1992) found glassy spherules in Senzeille, Belgium, but they appeared to be 7 m above the F-F boundary, although the stratigraphic control was poor. Another section near Hony, Belgium (Claeys and Casier, 1994; Claeys and others, 1994) found similar microtektites in a 1.5 m interval bracketed by *Pa. linguiformis* and *Pa. triangularis*, and 2 to 3 cm above the F-F boundary based on lithostratigraphic correlation with conodont-constrained German sections. Wang and others (1993) found spherules approximately 1.5 Ma after the F-F boundary in south China.

Claeys and Casier (1994) suggest the Siljan Ring structure in Sweden as a potential impact crater producing the spherules based on geochemical similarities between the host rock and the spherules, but at 52 km in diameter, it is considerably smaller than the Chixulub crater associated with the K-T boundary. It may be responsible for the Belgian microspherules, but it could not be responsible for their global distribution. McGhee (1996) reviewed six possible impact structures from the late Devonian in support of his hypothesis of multiple small impacts. Four are poorly dated, and only the Siljan structure in Sweden is a large enough impact and in the right time range to cause global effects (McGhee, 1996). None of the deep sea floor from the period remains, though, so any evidence for an impact in the deep ocean has been lost.

Turekian (1982) proposed that the size of the radiogenic ^{187}Os component is an index of extraterrestrial versus crustal Os (and, by association, Ir). The Re/Os of meteorites is about a factor of 400 less than that for the Earth's crust, and this difference results in a much lower $^{187}\text{Os}/^{188}\text{Os}$ for meteorites than for the crust. It is then possible to distinguish Ir-rich sediment layers derived from crustal weathering and those from meteorite impacts associated with extinctions. Luck and Turekian (1983) established that the K-T boundary indeed had a meteoritic $^{187}\text{Os}/^{188}\text{Os}$ signature, and confirmed that the Os (and Ir) were of meteorite impact origin. Although Turgeon and others (2007) also found no evidence for a meteorite impact at the F-F boundary, their focus was on providing an accurate Re-Os age for the boundary and their four samples lie 8.4 m, 2.9 m, 0.80 m below the boundary and 6.4 m above it; this sampling strategy would not be expected to capture a small impact that might have pushed a system on the cusp of climate change over the tipping point.

SAMPLE SITE AND METHODOLOGY

Two F-F boundary layers were examined in this study, one from western New York and the other from La Serre, France. We collected samples from the former and received samples from the latter by W. D. Goodfellow (Mineral Resources Division, Geological Survey of Canada). Samples from the interbedded shales and siltstone of the upper Hanover Shale Member of the Java Formation were collected at high resolution from the Irish Gulf locality in Erie County, New York (fig. 1, table 1) with eleven samples from 30 cm below to 12 cm above the boundary, including two samples at the boundary. The geology for this sequence is discussed in Over (2002) and Over and others (1997).

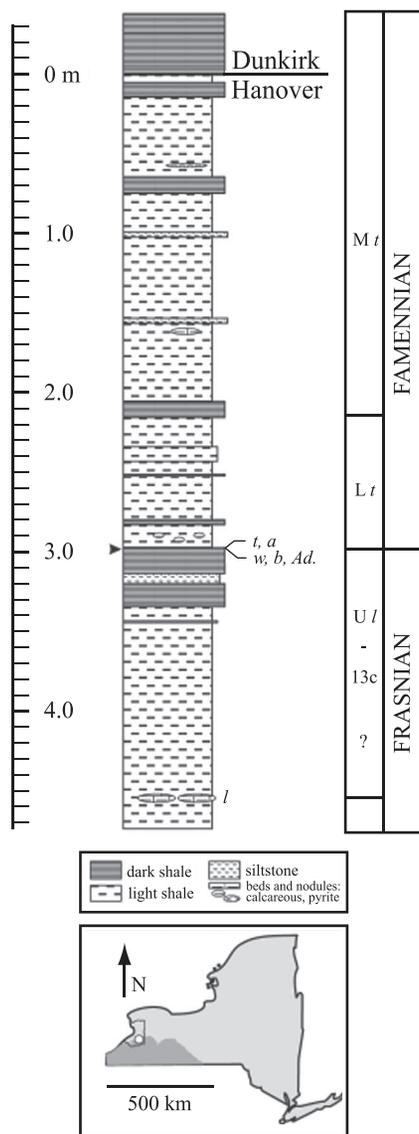


Fig. 1. Location, stratigraphic section, and conodont zonation of the Frasnian-Famennian boundary interval at Irish Gulf section, Erie County, New York, USA. Colden Quad, UTM 17T068484(E)472724(N). Abbreviations: *a* = *Icriodus alternata*; *Ad.* = *Ancyrodella*; *b* = *Palmatolepis bogartensis*; *l* = *P. linguiformis*; *t* = *P. triangularis*; *w* = *P. winchelli*; U and L refer to Upper and Lower; 13c = Montagne Noire Zone 13c.

Samples were powdered and prepared for isotope analysis according to standard procedures (Williams, ms, 2002). Osmium isotopic compositions and concentrations were measured on either NIMA-B (TIMS) or an Element 2 (HR-ICP-MS), both at Woods Hole Oceanographic Institution. Osmium concentrations were determined by isotope dilution coincident with the $^{187}\text{Os}/^{188}\text{Os}$ measurements. The errors on concen-

TABLE 1
Re and Os data measured in Irish Gulf and La Serre profiles through the Frasnian-Famennian boundary

Sample	cm from boundary	[Os] ppt	[Re] ppb	2SE	$\left(\frac{^{187}\text{Re}}{^{188}\text{Os}}\right)_{\text{today}}$	$\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{today}}$	SE (%)	$\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{initial}}$
Irish Gulf								
IG12B	+12	433	25.71	0.50	380	2.811	0.36	0.42
IG10A	+2	39	0.31	0.71	44	1.481	0.68	1.21
IG09K	+1	433	11.67	0.58	148	1.343	0.74	0.41
IG09J	0	312	11.78		219	1.869	0.52	0.49
FF2	0	409	12.89	0.58	179	1.657	0.60	0.53
IG09I	-1	345	10.35	0.58	169	1.615	0.62	0.55
IG09E	-6	264	6.48	0.58	135	1.361	0.73	0.51
IG08C	-12	131	2.28	1.00	94	1.177	0.85	0.59
IG07F	-20	251	7.36	0.71	165	1.571	0.64	0.53
IG07C	-23	201				2.146	0.47	
rep.		220				2.433	0.41	
avg.		205	9.09	0.71	262	2.289	0.44	0.64
IG05	-30	265	16.68	0.58	425	3.379	0.30	0.71
La Serre								
LS18	+15	33,457	1.65	0.50	0.31	2.425		2.42
LS16	+2.5	3,641	1.4	0.58	2.42	2.643		2.64
LS15	-2	8,151	7.53	0.58	6.37	3.614		3.58

Initial $^{187}\text{Os}/^{188}\text{Os}$ ratios are calculated for the F-F profiles given the ^{187}Re decay constant ($1.666 \times 10^{-11} \text{ yr}^{-1}$) from Smoliar and others (1996), an age of 376.5 Ma (Tucker and others, 1998) and solving each sample for the equation:

$$\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{present}} = \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{initial}} + \left(\frac{^{187}\text{Re}}{^{188}\text{Os}}\right) \times (e^{\lambda t} - 1)$$

This indicates the relative consistency of the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio throughout the depositional sequence. None of the individual samples indicates a significant meteoritic component.

trations and isotope ratios are calculated from the internal errors on the measurement (table 1).

Rhenium concentrations were determined on separate fractions of the same powders by isotope dilution on an Element 2 HR-ICP-MS at Yale University, with values being averaged from two to twelve replicates for each measurement, with most samples run in triplicate. Details of the procedures, data for rhenium concentrations and method validation experiments are discussed in detail in the Appendix.

RESULTS AND DISCUSSION

The modern and initial $^{187}\text{Os}/^{188}\text{Os}$ values and Re and Os concentrations are listed in table 1.

Evidence for a Meteorite Impact at the F-F Boundary

Using the Re and Os concentrations, Os isotopic compositions and a decay constant of $1.666 \times 10^{-11} \text{ yr}^{-1}$ (Smoliar and others, 1996) we calculated the initial

$^{187}\text{Os}/^{188}\text{Os}$ values at the time of the F-F boundary (376.5 Ma from Tucker and others, 1998) for the Irish Gulf section (table 1). It is evident that despite elevated osmium concentrations, the initial $^{187}\text{Os}/^{188}\text{Os}$ profile with depth at Irish Gulf shows no evidence for an instantaneous addition of significant extraterrestrial matter at the boundary.

The situation at the La Serre section is more complicated than the Irish Gulf section. The La Serre samples show Os concentrations as high as 33 ppb and Re concentrations of less than 10 ppb. The extraordinary osmium concentrations are more than 165 times the most concentrated organic-rich sediment reported by Ravizza and Turekian (1992), far more than expected for typical sedimentary enrichment mechanisms such as a condensed depositional sequence or enhanced global weathering of shales. In addition, the enrichment over average black shale concentrations is far greater than the twenty-fold enrichment over background levels observed in the Canning Ridge Australian sequence associated with apparent organic scavenging (Nicoll and Playford, 1993). If the measured $^{187}\text{Re}/^{188}\text{Os}$ is used to calculate the initial $^{187}\text{Os}/^{188}\text{Os}$ ratio (2.4–3.6, table 1), there is virtually no change from the modern measured $^{187}\text{Os}/^{188}\text{Os}$ value. For the highest Os concentration samples, it would have required 13.4 ppm of Re for an initial $^{187}\text{Os}/^{188}\text{Os}$ value of 0.13, or 11.3 ppm of Re for an initial $^{187}\text{Os}/^{188}\text{Os}$ value of 0.49—a factor of more than 100 higher than typical black shales. A combination of recent Re loss and/or a massive importation of highly radiogenic Os would result in the observed values, but either modification prohibits calculation of meaningful initial $^{187}\text{Os}/^{188}\text{Os}$ values.

If the original Re/Os were at the upper end of values observed in the Irish Gulf section, or other late Devonian black shales, then a high unknown initial Re/Os with recent loss of Re would mask a small meteoritic contribution of Os with a $^{187}\text{Os}/^{188}\text{Os}$ of about 0.13. For this reason, no definite statement about the *complete* absence of a meteoritic Os signature at La Serre can be made.

The cautionary note provided by these observations is that a high Os concentration, with a concordant high Ir concentration and low Re concentration, as expected for meteorites, is not in itself diagnostic of a meteorite signature. The definitive evidence for a meteoritic impact requires an Os isotope signature.

An Isochron at the F-F Boundary at Irish Gulf and the Integrity of the Re/Os System

An isochron from the Re-Os data for the Irish Gulf section constructed with a Model 3 solution in Isoplot (Ludwig, 2003), over a 42 cm depth profile at Irish Gulf produces an age of 388 ± 41 (2σ) Ma (fig. 2). This age is within error of the value from Re-Os dating reported by Turgeon and others (2007) of the boundary, 373 Ma with an uncertainty of less than 1.4 percent. It is also consistent with the age of 376.1 ± 3.6 Ma of Kaufmann (2006) based on zircon U/Pb dates. The larger error in our results is probably not due to analytical error but indicates either slight diagenetic mobility of Re and/or Os, or inhomogeneity in the Os concentrations. One methodological difference in our techniques is that our Re concentrations were measured on separate sample aliquots; tables in the supplemental material illustrate our evaluation of the reproducibility of the Re concentrations. One data point, IG10A, is excluded because of probable loss of Re, indicated by an anomalously high calculated initial $^{187}\text{Os}/^{188}\text{Os}$ value of 1.21. The calculated $^{187}\text{Os}/^{188}\text{Os}$ initial value for individual depths ranges from 0.41 to 0.71 while the initial $^{187}\text{Os}/^{188}\text{Os}$ value calculated from the isochron is 0.49 ± 0.16 . The La Serre section has significant Re and/or Os mobility and therefore does not yield information on initial $^{187}\text{Os}/^{188}\text{Os}$ values. The initial $^{187}\text{Os}/^{188}\text{Os}$ value from the isochron at Irish Gulf is consistent with three other published values for Devonian shales (table 2). Both the Ravizza and Turekian (1989) value of 0.75 ± 0.40 and the Selby

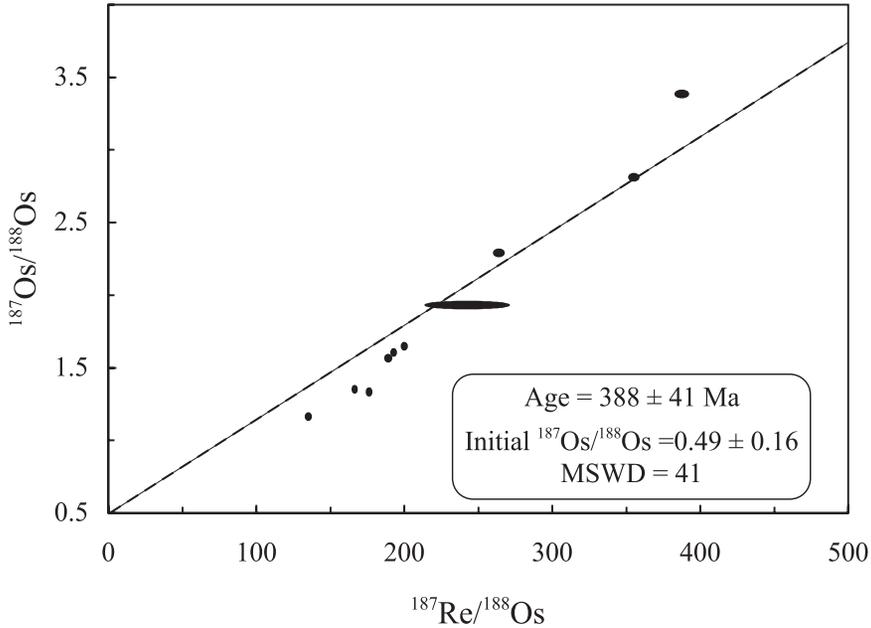


Fig. 2. Isochron for Irish Gulf samples, where the slope of the line predicts the age of the rock while the intercept represents the initial $^{187}\text{Os}/^{188}\text{Os}$ value. The age estimate, initial $^{187}\text{Os}/^{188}\text{Os}$ value and errors were calculated using an Isoplot Model 3 solution.

and Creaser (2005) value of 0.42 ± 0.01 are for the Devonian-Mississippian boundary, ~ 16 Ma later than the F-F boundary. The Turgeon and others (2007) values of 0.45 ± 0.02 and 0.47 ± 0.04 were also determined on sequences of shale immediately above and below the Frasnian-Famennian boundary. Although the errors are significant, the Devonian initial $^{187}\text{Os}/^{188}\text{Os}$ value (~ 0.4 to 0.5) is considerably lower than the modern value of ~ 1.07 , but approaches the lowest values for the early Cenozoic and late Mesozoic (Veizer, 1989). These results imply that the end of the Devonian was not dominated by black shale weathering as the supply of highly radiogenic Os comes mainly from the weathering of old black shales. The relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ in seawater of the late Devonian compared to the early Cenozoic, implies strong weathering of granitic material in the late Devonian that was not rich in radiogenic Os (Chen and others, 2005).

TABLE 2
Estimates of the initial $^{187}\text{Os}/^{188}\text{Os}$ marine value during the late Devonian

Reference	Initial $^{187}\text{Os}/^{188}\text{Os}$ (2 s.d.)
Ravizza and Turekian (1989)	0.75 ± 0.40
Selby and Creaser (2005)	0.42 ± 0.01
Turgeon and others (2007)	$0.45 \pm 0.02, 0.47 \pm 0.04$
This work	0.49 ± 0.16

Our initial value is calculated from the intercept of the isochron from the Irish Gulf samples.

CONCLUSIONS

The Irish Gulf section through the Frasnian-Famennian boundary shows no indication of a meteoritic Os and therefore an Ir imprint, even for several samples at the F-F boundary. The integrity of the Re-Os system is confirmed by the fact that an isochron constructed from our data yield an age comparable to other ages for the Frasnian-Famennian boundary.

The La Serre section indicates clear recent loss of Re from and importation of radiogenic Os to the system. Because of these post-depositional modifications, we are not able to establish the absence of a meteoritic Os signature that is masked by radiogenic ingrowth from an uncertain amount of original Re. The La Serre section reinforces the fact that high Os and Ir and low Re concentrations do not necessarily indicate a meteorite impact. The Os isotopic composition provides the unique indicator for such an event.

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APPENDIX

Rhenium Method Reproducibility and Sample Homogeneity

The standard procedure for measuring Re concentrations was to weigh in triplicate 0.1 g of finely ground material and ash at 400°C overnight in a porcelain crucible. After cooling, the sample was transferred into a Teflon vial, rinsing the crucible with water several times to ensure quantitative transfer. ^{185}Re spike sufficient to produce a measured $^{185}\text{Re}/^{187}\text{Re}$ of between 2 and 4.5 was weighed in triplicate and added to the sample. 5 mL of 16 M nitric acid was added and the sample was heated at 200°C overnight on a hot plate. Then 5 mLs of an HF-HCl-HNO₃ solution in a volumetric ratio of 1:1:4 was added, it was heated overnight and dried down. If all precipitate was eliminated, the sample was then dried under filtered air. If any precipitate remained, the digestion process was repeated until the solution was clear. The solution was dried down and brought back up in 10 mLs of 0.5 M distilled nitric acid.

The samples were then run through ion-exchange columns using 1 mL of AG1X-8 200-400 mesh resin. The resin was first cleaned with 4 N nitric acid in increments of 10 mL, 5 mL and 5 mL. It was then conditioned with 0.5 N nitric acid in three steps of 1 mL, 1 mL and 5 mL. The 10 mL sample was loaded, and the matrix eluted in three steps of 5 mL 0.5 N distilled nitric acid. The Re was eluted with 4 N nitric acid in four steps of 3 mL, 3 mL, 3 mL and 1 mL. The elution was dried down and brought up in 0.5 N distilled nitric acid for ICP-MS analysis.

The samples were run in low resolution mode on an Element 2 (ThermoFinnegan) and mass 188 was monitored to correct for the contribution of ^{187}Os on ^{187}Re . Acid and procedural blanks were negligible. The ^{185}Re spike was calibrated with a series of four spiked standards with varying measured $^{185}\text{Re}/^{187}\text{Re}$ ratios to have a concentration of $1.701 \pm 0.84\%$ (2σ) ng Re/g and a $^{185}\text{Re}/^{187}\text{Re}$ ratio of $16.721 \pm 0.4\%$ (2σ). Correction for mass bias was made using sample-standard bracketing.

To verify the homogeneity of the sample powder, samples ranging from 0.09 to 1.07 g were run, but there was no correlation between sample weight and either Re concentration or variation from the average Re value. The two samples that were furthest away from the average Re concentration had the highest ($^{185}\text{Re}/^{187}\text{Re}$)_{measured} value, indicating that ideal spike-sample ratio was a controlling factor on the uncertainty of the concentration determination. The average Re concentration was 11.86 ± 0.57

ppb (2σ , $n=10$) for samples with $(^{185}\text{Re}/^{187}\text{Re})_{\text{measured}}$ values between 2 and 3.8, while the Re concentration was 12.12 ± 2.51 ppb (2σ , $n=12$) for samples with $(^{185}\text{Re}/^{187}\text{Re})_{\text{measured}}$ values between 2 and 4.6. Two samples, IG09J-5 and IG09J-6, were spiked prior to the ashing procedure, and one sample, IG09J-7, was not ashed, all with no apparent effect on the resulting Re concentration. The largest sample, at 1.07 g, did not completely dissolve after three rounds of HF-HCl-HNO₃ digestion, and so the supernatant and residue were separated. The residue was subject to further digestion, then both samples were put through separate columns. Both samples gave the same calculated Re concentration, indicating that the spike and sample Re had reached isotopic equilibration prior to being separated. The five method replicate samples IG09J-9 through IG09J-13 had an average Re concentration of 11.97 ± 0.32 ppb ($2s.d.$, $n=5$)

The standard deviation of the Re concentrations was determined from the ensemble of samples based on standard statistical methods. The observations for IG09J were excluded from this error calculation since they represented a variety of procedures and so are not appropriate for the assessment of the error of a common procedure used in all the other measurements. The absolute standard error for the ensemble is 0.50. The standard error of the mean for each sample composed of one or more observations was determined based on this value of the standard error of the ensemble (Davies, 1954). The error on the Os concentration was determined from the error of the replicate analyses, and should be a maximum error that includes true elemental heterogeneity from a "nugget" effect and not simply the analytical error. The error on the $^{187}\text{Re}/^{188}\text{Os}$ ratio was the square root of the sum of the squares of the percent errors on the Re concentrations, Os concentrations, Os isotopic compositions and Re isotopic compositions. The error on the Re isotopic composition included the uncertainty on the IUPAC value of the natural isotope abundances of Re, the error on the Re spike calibration and the average error of the measured $^{185}\text{Re}/^{187}\text{Re}$ ratio.

TABLE A-1

Replicate Re concentration determinations for sample IG09J, at the F-F boundary

Sample	Comments	sample weight (g)	Re (ppb)	$\frac{^{185}\text{Re}}{^{187}\text{Re}}_{\text{measured}}$	error on mean ratio (%)
IG09J-2		0.16	15.94	4.12	1.11
IG09J-3		0.35	10.97	4.56	0.88
IG09J-4 residue	incomplete dissolution	1.07	11.61	2.08	1.32
IG09J-4 supernatant	incomplete dissolution	1.07	11.42	2.14	0.55
IG09J-5	spiked prior to ashing	0.21	12.34	3.35	0.47
IG09J-6	spiked prior to ashing	0.46	11.61	3.79	0.39
IG09J-7	no ashing	0.20	11.74	1.98	0.59
IG09J-9		0.09	12.11	3.32	0.09
IG09J-10		0.10	12.15	3.05	0.05
IG09J-11		0.16	11.89	2.40	0.11
IG09J-12		0.10	11.94	3.34	0.05
IG09J-13		0.10	11.77	3.03	0.10

The error on the mean ratio is the internal error of the mass spectrometric measurement.

TABLE A-2
Re concentrations measured in Irish Gulf and La Serre profiles through the Frasnian-Famennian boundary

Sample	cm from boundary	Re (ppb)	Average Re (ppb)	2 s.e.
Irish Gulf				
IG12B-1	+12	24.15	25.71	0.50
rep.		24.69		
rep.		26.61		
rep.		26.38		
IG10A-1	+2	0.29	0.31	0.71
rep.		0.32		
IG09K	+1	11.49	11.67	0.58
rep.		11.83		
rep.		11.68		
FF2	0	13.16	12.89	0.58
rep.		12.96		
rep.		12.54		
IG09I	-1	10.47	10.35	0.58
rep.		10.19		
rep.		10.38		
IG09E	-6	6.44	6.48	0.58
rep.		6.21		
rep.		6.78		
IG08C	-12	2.28	2.28	1.00
IG07F	-20	7.03	7.36	0.71
rep.		7.69		
IG07C	-23	9.09	9.09	1.00
IG05	-30	16.62	16.68	0.58
rep.		16.69		
rep.		16.72		
La Serre				
LS18-1	+15	1.83	1.65	0.50
rep.		1.64		
		1.54		
		1.62		
LS16-1	+2.5	1.35	1.40	0.58
rep.		1.45		
rep.		1.41		
LS15	-2	7.96	7.53	0.58
rep.		7.49		
rep.		7.15		

REFERENCES

- Alvarez, L. W., Alvarez, W., Asaro, F., and Michel, H. V., 1980, Extraterrestrial cause for the Cretaceous-Tertiary extinction: *Science*, v. 208, p. 1095–1108, doi:10.1126/science.208.4448.1095.
- Chen, D., Qing, H., and Li, R., 2005, The Late Devonian Frasnian-Famennian (F/F) biotic crisis: Insights from $\delta^{13}\text{C}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{org}}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic systematics: *Earth and Planetary Science Letters*, v. 235, p. 151–166, doi:10.1016/j.epsl.2005.03.018.

- Claeys, P., and Casier, J. G., 1994, Microtektite-like impact glass associated with the Frasnian-Famennian boundary mass extinction: *Earth and Planetary Science Letters*, v. 122, p. 303–315, doi:10.1016/0012-821X(94)90004-3.
- Claeys, P., Casier, J. G., and Margolis, S. V., 1992, Microtektites and Mass Extinctions: Evidence for a Late Devonian Asteroid Impact: *Science*, v. 257, p. 1102–1104, doi:10.1126/science.257.5073.1102.
- Claeys, P., Kyte, F. T., and Casier, J. G., 1994, Frasnian-Famennian boundary: mass extinctions, anoxic oceans, microtektite layers, but not much iridium?, *in* New developments regarding the K/T event and other catastrophes in history: Houston, Texas, University of Houston-Clear Lake and the Lunar and Planetary Institute, LPI Contribution No. 825, p. 22–24.
- Davies, O. L., 1954, Appendix 3C: Computation of variance: *Grouped Data, Statistical Methods in Research and Production*: London and Edinburgh, Oliver and Boyd, p. 292.
- Geldsetzer, H. H. J., Goodfellow, W. D., McLaren, D. J., and Orchard, M. J., 1987, Sulfur-isotope anomaly associated with the Frasnian-Famennian extinction, Medicine Lake, Alberta, Canada: *Geology*, v. 15, p. 393–396, doi:10.1130/0091-7613(1987)15<393:SAAWTF>2.0.CO;2.
- Girard, C., Robin, E., Rocchia, R., Froget, L., and Feist, R., 1997, Search for impact remains at the Frasnian-Famennian boundary in the stratotype area, southern France: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 132, p. 391–397, doi:10.1016/S0031-0182(97)00049-7.
- Goodfellow, W. D., Geldsetzer, H. H. J., McLaren, D. J., Orchard, M. J., and Klapper, G., 1988, The Frasnian-Famennian extinction: Current results and possible causes, *in* McMillan, N. J., Embry, A. F., and Glass, D. J., editor, *Devonian of the World, International Symposium on the Devonian System*, Calgary, Canada: Canadian Society of Petroleum Geologists, Memoir 14, p. 9–21.
- 1989, Geochemical and isotopic anomalies associated with the Frasnian-Famennian extinction: *Historical Biology*, v. 2, p. 51–72, doi: 10.1080/08912968909386490.
- Kaufmann, B., 2006, Calibrating the Devonian Time Scale: A synthesis of U-Pb ID-TIMS ages and conodont stratigraphy: *Earth-Science Reviews*, v. 76, p. 175–190, doi:10.1016/j.earscirev.2006.01.001.
- Kerr, R. A., 1992, Another impact extinction?: *Science*, v. 256, p. 1280, doi:10.1126/science.256.5061.1280.
- Luck, J. M., and Turekian, K. K., 1983, Osmium-187/Osmium-186 in Manganese Nodules and the Cretaceous-Tertiary Boundary: *Science*, v. 222, p. 613–615, doi:10.1126/science.222.4624.613.
- Ludwig, K., 2003, *Isoplot 3.00, A Geochronological Toolkit for Microsoft Excel*: Berkeley, California, Berkeley Geochronology Center, Special Publication No. 4.
- McGhee, G. R., Jr., 1996, *The Late Devonian Mass Extinction: The Frasnian-Famennian crisis*: New York, Columbia University Press, 378 p.
- McGhee, G. R., Jr., Orth, C. J., Quintana, L. R., Gilmore, J. S., and Olsen, E. J., 1986, Late Devonian “Kellwasser Event” mass-extinction horizon in Germany: No geochemical evidence for a large-body impact: *Geology*, v. 14, p. 776–779, doi:10.1130/0091-7613(1986)14<776:LDKEMH>2.0.CO;2.
- McLaren, D. J., 1970, Time, life, and boundaries: *Journal of Paleontology*, v. 44, p. 801–815.
- Nicoll, R. S., and Playford, P. E., 1993, Upper Devonian iridium anomalies, conodont zonation and the Frasnian-Famennian boundary in the Canning Basin, Western Australia: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 104, p. 105–113, doi:10.1016/0031-0182(93)90123-Z.
- Orth, C. J., 1989, Geochemistry of the bio-event horizons, *in* Donovan, S. K., editor, *Mass extinctions: processes and evidence*: New York, Columbia University Press, p. 37–72.
- Over, D. J., 2002, The Frasnian/Famennian boundary in central and eastern United States: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 181, p. 153–169, doi:10.1016/S0031-0182(01)00477-1.
- Over, D. J., Conaway, C. A., Katz, D. J., Goodfellow, W. D., and Gregoire, D. C., 1997, Platinum group element enrichments and possible chondritic Ru:Ir across the Frasnian-Famennian boundary, western New York State: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 132, p. 399–410, doi:10.1016/S0031-0182(97)00064-3.
- Playford, P. E., McLaren, D. J., Orth, C. J., Gilmore, J. S., and Goodfellow, W. D., 1984, Iridium anomaly in the Upper Devonian of the Canning Basin, Western Australia: *Science*, v. 226, p. 437–439, doi:10.1126/science.226.4673.437.
- Ravizza, G., and Turekian, K. K., 1989, Application of the ^{187}Re - ^{187}Os system to black shale geochronometry: *Geochimica et Cosmochimica Acta*, v. 53, p. 3257–3262, doi:10.1016/0016-7037(89)90105-1.
- 1992, The osmium isotopic composition of organic-rich marine sediments: *Earth and Planetary Science Letters*, v. 110, p. 1–6, doi:10.1016/0012-821X(92)90034-S.
- Sawlowicz, Z., 1993, Iridium and other platinum-group elements as geochemical markers in sedimentary environments: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 104, p. 253–270, doi:10.1016/0031-0182(93)90136-7.
- Selby, D., and Creaser, R. A., 2005, Direct radiometric dating of the Devonian-Mississippian time-scale boundary using the Re-Os black shale geochronometer: *Geology*, v. 33, p. 545–548, doi:10.1130/G21324.1.
- Smoliar, M. I., Walker, R. J., and Morgan, J. W., 1996, Re-Os ages of group IIA, IIIA, IVA, and IVB iron meteorites: *Science*, v. 271, p. 1099–1102, doi:10.1126/science.271.5252.1099.
- Tucker, R. D., Bradley, D. C., Ver Straeten, C. A., Harris, A. G., Ebert, J. R., and McCutcheon, S. R., 1998, New U-Pb zircon ages and the duration and division of Devonian time: *Earth and Planetary Science Letters*, v. 158, p. 175–186, doi:10.1016/S0012-821X(98)00050-8.
- Turekian, K. K., 1982, Potential of $^{187}\text{Os}/^{186}\text{Os}$ as a cosmic versus terrestrial indicator in high iridium layers of sedimentary strata, *in* Silver, L. T., and Schultz, P. H., editors, *Geological implications of impacts of large asteroids and comets on the Earth*: Geological Society of America, Special Paper, v. 190, p. 243–249.

- Turgeon, S. C., Creaser, R. A., and Algeo, T. J., 2007, Re-Os depositional ages and seawater Os estimates for the Frasnian-Famennian boundary: Implications for weathering rates, land plant evolution, and extinction mechanisms: *Earth and Planetary Science Letters*, v. 261, p. 649–661, doi:10.1016/j.epsl.2007.07.031.
- Veizer, J., 1989, Strontium isotopes in seawater through time: *Annual Reviews of Earth and Planetary Sciences*, v. 17, p. 141–167, doi:10.1146/annurev.ea.17.050189.001041.
- Wang, K., Orth, C. J., Attrep, M., Jr., Chatterton, B. D. E., Hou, H., and Geldsetzer, H. H. J., 1991, Geochemical evidence for a catastrophic biotic event at the Frasnian-Famennian boundary in south China: *Geology*, v. 19, p. 776–779, doi: 10.1130/0091-7613(1991)019<0776:GEFACB>2.3.CO;2.
- Wang, K., Attrep, M., Jr., and Orth, C. J., 1993, Global iridium anomaly, mass extinction, and redox change at the Devonian-Carboniferous boundary: *Geology*, v. 21, p. 1071–1074, doi: 10.1130/0091-7613(1993)021<1071:GIAMEA>2.3.CO;2.
- Williams, G. A., ms, 2002, The transport of osmium from the continents to the oceans: New Haven, Connecticut, Yale University, Ph. D. thesis, 154 p.