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Rhenium–Osmium Isotope Measurements in Marine Shale Reference Material SBC-1: Implications for Method Validation and Quality Control

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In this study, the USGS black shale reference material SBC-1 was investigated as a matrix-matched reference material for both intra-laboratory calibration and inter-laboratory comparison of high-precision Re-Os dating for organic-rich sedimentary rocks. This reference material was analysed for Re-Os isotopic composition by three digestion protocols – inverse *aqua regia*, CrO_3-H_2SO_4 and H_2O_2-HNO_3. The results for SBC-1 obtained by inverse *aqua regia* digestion yielded similar Re mass fractions but slightly (~ 5%) higher Os mass fractions and lower $^{187}Os/^{188}Os$ values than the CrO_3-H_2SO_4 and H_2O_2-HNO_3 digestions. The data set of inverse *aqua regia* digestion exhibited strong correlations in plots of $^{187}Os/^{188}Os$ vs. $1/^{192}Os$ and $^{187}Os/^{188}Os$ vs. $^{187}Re/^{188}Os$, which may signify the incorporation of detrital Re and Os into organic matter in the Re-Os system. Similar correlations were also observed for the CrO_3-H_2SO_4 digestion data set, but not for that of H_2O_2-HNO_3. The data indicate that there is an amount of non-hydrogenous Os in SBC-1 and that CrO_3-H_2SO_4 and H_2O_2-HNO_3 digestions would minimise liberation of the non-hydrogenous Os component. We propose that SBC-1 may be a more suitable reference material to monitor the influence of detrital Re and Os on Re-Os isochron age data, especially for samples with less organic matter and more siliceous detritus.

Keywords: organic-rich sedimentary rock, Re-Os dating, digestion methods, detrital component, binary mixing.

Rhenium and osmium are organophilic and arguably redox-sensitive, allowing the uptake of Re and Os into organic matter during the deposition of sedimentary rocks (Colodner *et al.* 1993, Levasseur *et al.* 1998, Poirier 2006, Yamashita *et al.* 2007). The Re-Os isotope system can therefore be used to date the depositional age of organic-rich sedimentary rocks (e.g., Ravizza and Turekian 1989, Cohen and Coe 1999, Creaser *et al.* 2002, Hannah *et al.* 2004, Creaser and Selby 2005, Selby and Creaser 2005, Xu *et al.* 2009, Rooney *et al.* 2010, Zhu *et al.* 2013). High-precision Re-Os geochronology of organic-rich sedimentary rocks faces critical challenges, primarily because they contain both detrital (exogenous or non-hydrogenous) and organic (endogenous or hydrogenous) components typically characterised by relatively high Re and low Os mass fractions. The rationale is to liberate Re and Os from

hydrogenous components while limiting the dissolution of non-hydrogenous components in the digestion scheme.

Previous application of the ^{187}Re–^{187}Os system to the dating of organic-rich sedimentary rocks has achieved imprecise Re-Os results because of deficiencies in chemical preparation and mass spectrometry protocols (Ravizza and Turekian 1989). Cohen and Coe (1999) and Creaser *et al.* (2002) used improved analytical and mass spectrometry protocols [including Carius tube digestion with the inverse *aqua regia* isotope-dilution technique and isotope ratio determinations by negative-thermal ionisation mass spectrometry (N-TIMS)] and were able to determine Re-Os depositional ages with 3–8% uncertainty. Subsequently, some studies achieved much better uncertainties (≤ 1%, e.g., Georgiev *et al.* 2011, Georgiev *et al.* 2017). However,

some studies suggest that the inverse *aqua regia* digestion method liberates detrital (non-hydrogenous) Os, which may cause scatter in the data and imprecise Re-Os isochron ages (Selby and Creaser 2003, Kendall *et al.* 2004, 2009, Yin *et al.* 2017). Appropriate digestion methods should completely liberate Re and Os in organic matter while avoiding the liberation of Re and Os from siliceous detritus (Selby and Creaser 2003, Yin *et al.* 2017). Previous studies have proposed CrO_3-H_2SO_4 and H_2O_2-HNO_3 digestions as alternatives for the measurement of Re-Os in organic-rich sedimentary rocks (Selby and Creaser 2003, Yin *et al.* 2017), as they yielded better Re-Os regression analyses and more precise isochron ages than those obtained by the inverse *aqua regia* digestion method.

In addition, different matrix–detritus proportion is also a key factor in the liberated contents of Re and Os. Thus, matrix-matched reference materials (RMs) of similar lithology to the material being analysed are important for quality control, validation of analytical methods and inter-laboratory comparison. Currently, some Re-Os isotopic data are reported from organic-rich shale reference materials, such as SGR-1b, SDO-1 and SCO-1 (Meisel and Moser 2004, Cumming *et al.* 2014, Du Vivier *et al.* 2014, Percival *et al.* 2016, Yin *et al.* 2017). However, few works focused on the influence of detrital Re-Os on the Re-Os isotope system of organic-rich shales. Yin *et al.* (2018) reported Re-Os data for SGR-1b using three different digestion methods (involving inverse *aqua regia*, CrO_3-H_2SO_4 and H_2O_2-HNO_3) but the results obtained by these methods did not show significant differences. SGR-1b is representative of petroleum- and carbonate-rich shales from the Mahogany zone of the Green River Formation (USA), which possess extremely high contents of organic matter. The RM contains very high Re and Os mass fractions, and the contributions of Re and Os from non-hydrogenous components on the Re-Os system cannot be distinguished. However, for shales with low contents of organic matter and low Re and Os mass fractions, contributions from non-hydrogenous components cannot be ignored. In this study, in order to evaluate the contributions of Re and Os from non-hydrogenous components to the Re-Os system, we present the Re-Os composition for the organic-rich sedimentary rock RM SBC-1 using three different digestion methods: (a) inverse *aqua regia*, (b) CrO_3-H_2SO_4 and (c) H_2O_2-HNO_3. SBC-1 is a marine shale from the Lower Conemaugh Group, upper Pennsylvanian Glenshaw Formation (USA). Compared with SGR-1b, SBC-1 contains much lower organic carbon (C_{org}), Re and Os mass fractions, and higher Al_2O_3 and SiO_2 (Table 1). The mineralogy of SBC-1 is dominated by muscovite, quartz, kaolinite and chlorite. Therefore, SBC-1 may be a more suitable reference material to monitor the influence of Re-Os

isotopic compositions by detrital material, especially for samples with less organic matter and more siliceous detritus.

Experimental method

Materials and reagents

SBC-1 was purchased from the US Geological Survey (USGS). Mass fractions of major element oxides in SBC-1 are listed in Table 1 along with those of SGR-1b. A powdered sample of RM SBC-1 was shaken vigorously in a glass bottle before weighing to achieve a random distribution of particles.

The acids used in this study (HNO_3, HBr and HCl) were purified using DST-1000 sub-boiling stills (Savillex Corporation, Eden Prairie, MN, USA). HNO_3 was heated on a hot plate at 350 °C and purged with clean air for ~ 2 h to reduce its Os blank before distillation by sub-boiling (Li *et al.* 2014). De-ionised water (18.2 MΩ cm; from a Millipore purification system), hydrogen peroxide (30%, guaranteed reagent) and CCl_4 (HPLC grade) were used to prepare the solutions. The CrO_3-H_2SO_4 solution was prepared using the method of Selby and Creaser (2003) by dissolving 2 g of CrO_3 (Puratronic®; Alfa Aesar, Johnson Matthey Co., Ltd., Heysham, UK) in 10 ml of 2 mol l^{-1} H_2SO_4 (ACS grade; Thermo Fisher Scientific Inc., Waltham, MA, USA). Because this solution contains abundant Re and Os, it was purified prior to use. Clean air was bubbled through the solution at ~ 100 °C to remove volatile OsO_4. The volumetric ratio of H_2O_2 to HNO_3 in H_2O_2-HNO_3 is 5:1, which is optimal in achieving complete spike–sample equilibrium and minimising the incorporation of detrital Re and Os by selectively dissolving hydrogenous Re and Os in organic matter/metals (Yin *et al.* 2017).

Table 1.
Reference data (USGS) of major element mass fractions (in % *m/m*) for reference materials SGR-1b and SBC-1

Analyte	SBC-1	SGR-1b
C_{tot}	2.08	28.0
C_{org}	1.23	24.8
SiO_2	47.6	28.2
Al_2O_3	21.0	6.52
CaO	2.95	8.38
MgO	2.60	4.44
K_2O	3.45	1.66
Na_2O	< 0.15	2.99
Fe_2O_{3T}	9.71	3.03

The borosilicate Carius tubes used here, similar to those of Shirey and Walker (1995), were 3 mm thick, each with a volume of ~ 210 ml to withstand the high pressures generated during H_2O_2-HNO_3 digestion. Fluoropolymer (PFA; Savillex, LLC, Eden Prairie, MN, USA) vials were cleaned with 50% *v/v aqua regia* and Milli-Q water, filled with concentrated HBr and heated overnight at 100 °C to ensure minimum Os blank interference during separation and micro-distillation (Li *et al.* 2014). Finally, all the vials were rinsed with Milli-Q water and air-dried.

Chemical separation and purification of Re and Os

Approximately 0.2–0.5 g powder test portions were weighed and placed in Carius tubes. The powders were dissolved and equilibrated with known amounts of ^{185}Re and ^{190}Os in ~ 10 ml inverse *aqua regia*, CrO_3-H_2SO_4 and H_2O_2-HNO_3. Osmium was extracted by solvent extraction into CCl_4 and back-extracted into concentrated HBr (Cohen and Waters 1996, Pearson and Woodland 2000), with subsequent purification by micro-distillation (Roy-Barman 1993). The Re fraction was separated and purified using anion column chromatography. Detailed procedures of the inverse *aqua regia*, CrO_3-H_2SO_4, and H_2O_2-HNO_3 dissolution methods are described by Li *et al.* (2014, 2015a, b), Selby and Creaser (2003) and Yin *et al.* (2017), respectively.

Mass spectrometry

Measurements of Re and Os were undertaken at the state Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China. The technique used to determine Os by mass spectrometry is described by Li *et al.* (2014, 2015a, b). Osmium was loaded onto Pt filaments and measured as OsO_3^- by negative-thermal ionisation mass spectrometry (N-TIMS) using the electron multiplier mode on a Thermo Fisher Scientific Inc (Creaser *et al.* 1991, Völkening *et al.* 1991). Repeated analyses of the Os standard solution (Merck Chemical AA standard solution) yielded a mean ^{187}Os/^{188}Os value of 0.12036 ± 0.00025 (2s, n = 18) for the period of the analysis, which is in good agreement with the value measured on the same mass spectrometer in Faraday cup mode (0.12022 ± 0.00020; 2s, n = 14; Li *et al.* 2010). Rhenium was determined by inductively coupled plasma-mass spectrometry (with a Thermo Fisher Scientific Inc). A conventional low-volume quartz impact bead spray chamber with a Peltier cooled (3 °C) and 0.4 ml min^{-1} borosilicate nebuliser (MicroMist GE Corporation, Port Melbourne, Vic., Australia) was used for the measurements. Ion lens settings, nebuliser gas flow rate and torch position were optimised daily using a 10 ng ml^{-1} tuning In-Ce standard solution to obtain high instrument sensitivity and low levels of oxide production. A peristaltic pump was not used, as free aspiration of the nebuliser provided better signal stability. The details of measurements by ICP-MS are described by Li *et al.* (2014).

Results and discussion

Procedural blanks

Total procedural blanks obtained using the CrO_3-H_2SO_4 (10 ml) digestion method range from 39.6 to 68.9 pg (mean: 52 ± 14 pg; 1s, n = 4) for Re and 0.5 to 0.8 pg (mean: 0.7 ± 0.1 pg, 1s, n = 4) for Os. The blank ^{187}Os/^{188}Os isotopic composition was 0.213 ± 0.028 (1s, n = 4). For the inverse *aqua regia* digestion method, the total procedural blanks obtained for Re and Os range from 3 to 6 pg (mean: 4.3 ± 1.8 pg, n = 8) and 0.2 to 0.6 pg (mean: 0.4 ± 0.2 pg, n = 4), respectively, with mean blank ^{187}Os/^{188}Os isotopic compositions of 0.336 ± 0.032 (1s, n = 4). Total procedural blanks obtained using H_2O_2-HNO_3 digestion are similar to those using the inverse *aqua regia* digestion. The data from each analytical batch were corrected for the procedural blank. Rhenium blank contributions in this study were < 0.15% for the inverse *aqua regia* and H_2O_2-HNO_3 digestion methods and < 1.7% for the CrO_3-H_2SO_4 digestion method. Osmium blank contributions from all three digestion methods were < 3%. The Re and Os blank contributions for individual samples are given in Table 2.

Re–Os mass fractions and isotopic composition of SBC-1

Rhenium–osmium isotope results for SBC-1 using H_2O_2-HNO_3, CrO_3-H_2SO_4 and inverse *aqua regia* digestion techniques are presented in Table 2 and shown in Figure 1. Rhenium contents obtained by the digestion methods were similar within analytical uncertainty (inverse *aqua regia*, 11.2 ± 0.1 ng g^{-1}, n = 8, 1s; CrO_3-H_2SO_4, 11.0 ± 0.1 ng g^{-1}; and H_2O_2-HNO_3, 11.0 ± 0.1 ng g^{-1}, n = 10, 1s), while Os content and Os isotope data exhibit some differences. The inverse *aqua regia* digestion yielded slightly (~ 6%) higher Os mass fractions (101 ± 4 pg g^{-1}, n = 8, 1s) and a lower ^{187}Os/^{188}Os value (4.89 ± 0.42, n = 8, 1s), than those obtained by CrO_3-H_2SO_4 digestion (97 ± 3 pg g^{-1} for Os, 5.19 ± 0.20 for ^{187}Os/^{188}Os, n = 10, 1s) and H_2O_2-HNO_3 digestion (96 ± 1 pg g^{-1} for Os, 5.29 ± 0.08 for ^{187}Os/^{188}Os, n = 10, 1s). The mean Re and Os mass fractions and ^{187}Os/^{188}Os ratio for

Table 2.
Re-Os results for SBC-1 obtained using inverse *aqua regia*, CrO_3-H_2SO_4 and H_2O_2-HNO_3 digestions

Digestion method	Mass (g)	Re (ng g⁻¹)	2SE	Os (pg g⁻¹)	2SE	POBC (%)		¹⁹²Os (pg g⁻¹)	¹⁸⁷Os/¹⁸⁸Os	2SE	¹⁸⁷Re/¹⁸⁸Os	2SE
						Re	Os					
Inverse *aqua regia*	0.4250	11.5	1.1	103.4	0.1	0.09	0.91	26.9	4.479	0.008	842	79
	0.4894	11.2	0.5	108.2	0.1	0.08	0.76	28.9	4.158	0.008	763	33
	0.4867	11.2	0.1	97.4	0.1	0.08	0.84	23.6	5.307	0.012	930	7
	0.4940	11.1	0.3	99.0	0.2	0.08	0.82	24.4	5.127	0.014	894	24
	0.5865	11.2	0.5	98.7	0.2	0.07	0.69	24.2	5.167	0.010	907	39
	0.5824	11.2	0.3	100.2	0.2	0.07	0.69	24.8	5.070	0.012	883	25
	0.7950	11.1	0.3	98.4	0.1	0.05	0.51	24.1	5.216	0.007	907	22
	0.7857	11.2	0.2	106.7	0.1	0.05	0.48	27.4	4.603	0.005	800	17
Mean value		11.2	0.1	101.5	4.1	0.07	0.71	25.5	4.89	0.42	866	58
CrO_4-H_2SO_4	0.5163	10.9	0.2	95.5	0.2	0.92	1.42	23.2	5.317	0.014	925	21
	0.5300	10.9	0.2	99.2	0.1	0.90	1.33	24.5	5.103	0.010	875	15
	0.3807	11.0	0.3	104.0	0.4	1.24	1.77	26.6	4.664	0.022	812	19
	0.3861	10.9	0.3	96.5	0.2	1.24	1.88	23.4	5.302	0.019	913	22
	0.4411	11.0	0.1	96.4	0.2	1.07	1.65	23.4	5.295	0.019	917	10
	0.3524	10.9	0.4	98.1	0.2	1.35	2.02	24.1	5.170	0.013	891	34
	0.3558	11.4	0.3	100.6	0.6	1.28	1.96	24.7	5.167	0.037	903	22
	0.2882	11.1	0.2	96.8	0.1	1.63	2.51	23.7	5.219	0.012	915	13
	0.3043	11.0	0.1	97.2	0.1	1.55	2.37	23.7	5.265	0.009	908	10
	0.3252	11.0	0.1	94.2	0.1	0.12	2.29	22.7	5.376	0.007	951	12
Mean value		11.0	0.1	97.9	2.8	1.13	1.92	24.0	5.19	0.20	901	37
H_2O_2-HNO_3	0.3276	11.0	0.4	96.8	0.2	0.12	1.26	23.7	5.190	0.019	908	31
	0.3311	10.9	0.2	98.3	0.3	0.12	1.23	24.0	5.233	0.022	892	16
	0.4009	11.0	0.3	95.2	0.1	0.10	1.05	23.0	5.348	0.010	932	25
	0.4060	11.0	0.2	96.7	0.3	0.10	1.02	23.7	5.156	0.021	906	15
	0.4313	10.9	0.1	95.7	0.2	0.09	0.97	23.3	5.294	0.023	922	6
	0.4376	10.9	0.2	97.4	0.2	0.09	0.94	23.6	5.350	0.021	906	13
	0.4766	11.0	0.2	97.2	0.2	0.08	0.86	23.7	5.277	0.013	910	19
	0.2659	11.1	0.1	95.1	0.1	0.15	1.58	23.1	5.274	0.006	936	6
	0.2531	11.2	0.1	96.4	0.4	0.15	1.64	23.3	5.371	0.020	942	12
	0.2518	11.1	0.1	95.3	0.1	0.15	1.67	22.9	5.408	0.007	947	6
Mean value		11.0	0.1	96.4	1.1	0.11	1.22	23.4	5.29	0.08	920	18
Mean value for all data		11.1	0.2	98.4	3.4	0.46	1.32	24.2	5.14	0.30	898	44

SE, standard error = $s/\sqrt{n}$. POBC, percentage of blank contributions for each sample.

SBC-1 obtained by all three digestion methods are 11.1 ± 0.2 ng g⁻¹, 98 ± 3 pg g⁻¹ and 5.14 ± 0.30 (*n* = 28, 1*s*), respectively. The Re-Os data for SGR-1b reported by Yin *et al.* (2017) are also shown in Figure 1 for comparison. For SGR-1b, the mean Re-Os mass fraction and ¹⁸⁷Os/¹⁸⁸Os ratio using inverse *aqua regia* are consistent with those using H_2O_2-HNO_3 and CrO_3-H_2SO_4, within uncertainties. All measurements for SGR-1b gave an average Re mass fraction of 34.6 ± 0.2 ng g⁻¹, an Os mass fraction of 440 ± 1 pg g⁻¹ and an ¹⁸⁷Os/¹⁸⁸Os ratio of 1.790 ± 0.002 (*n* = 17, 1*s*), suggesting SGR-1b is a highly homogeneous organic-rich reference material in terms of Re-Os mass fraction and isotopic composition. Compared with SGR-1b, SBC-1 contains lower Re and Os mass fractions and has a higher ¹⁸⁷Os/¹⁸⁸Os ratio.

The procedural blank may provide an explanation for the small differences between individual samples. However, in plots of percentage of Os blank contribution vs. ¹⁸⁷Os/¹⁸⁸Os, no significantly negative correlations were observed for SBC-1 (Figure 2), suggesting variation of the Os isotope is not controlled by blank contributions. In plots of ¹⁸⁷Os/¹⁸⁸Os ratio versus inverse common Os mass fraction and ¹⁸⁷Re/¹⁸⁸Os (Figure 3), all the data for SBC-1 show strong positive correlations. Similar correlations have also been reported for mafic rocks (Meisel *et al.* 2001, Ishikawa *et al.* 2014, Li *et al.* 2014, 2015a, b). Li *et al.* (2015a, b) proposed that these relationships signify binary mixing between endmembers with different isotopic compositions. For SBC-1, it is possible that Os isotopic inhomogeneity was attained between organic matter (hydrogenous Os
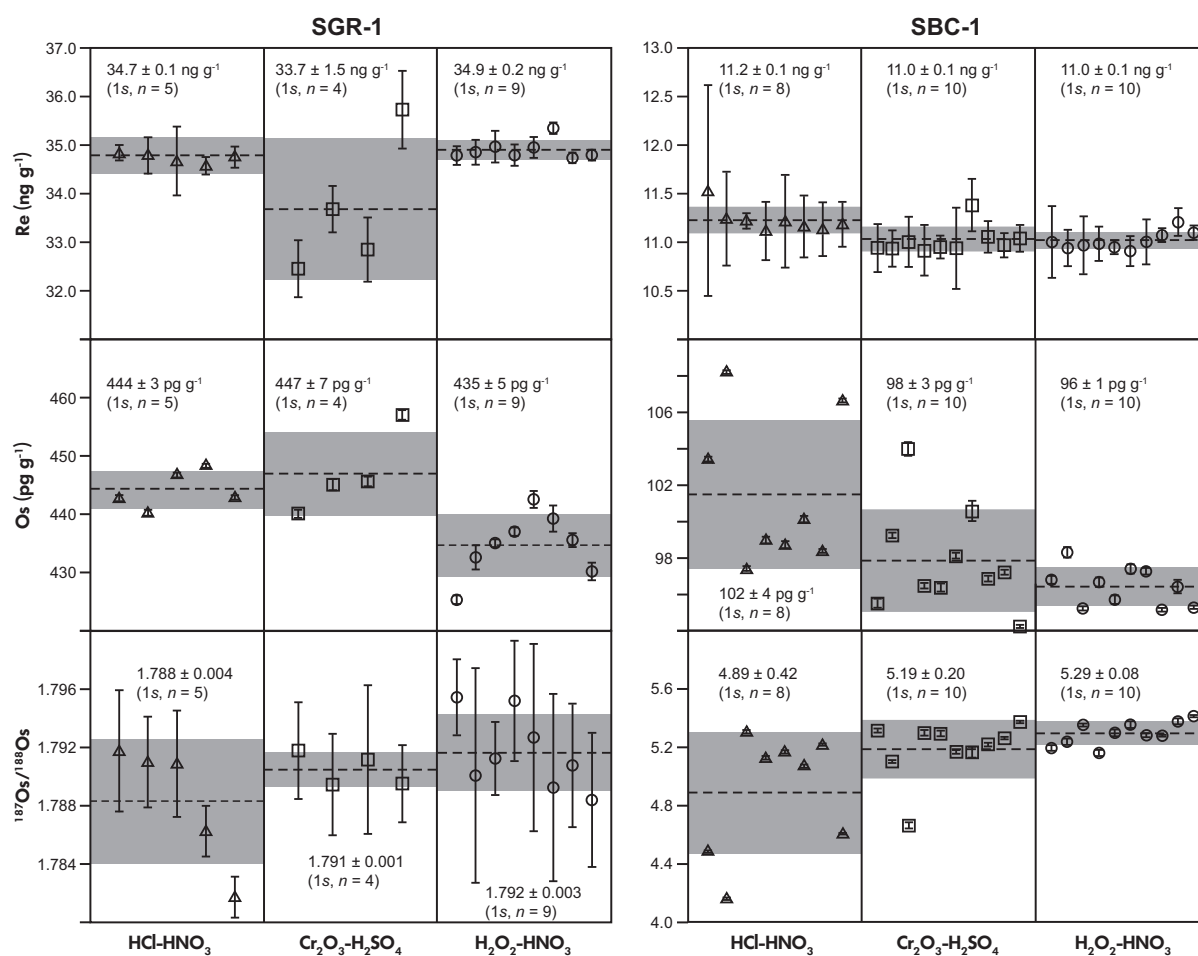
Figure 1. Re and Os mass fractions, and $^{187}Os/^{188}Os$ ratios for SGR-1b (left) and SBC-1 (right) determined using inverse *aqua regia* (triangles), CrO_3-H_2SO_4 (squares), and H_2O_2-HNO_3 (circles). Bars represent 2 standard error (2SE) for data obtained in this study. Dotted lines represent mean values. The shaded areas represents 1 standard deviation (1s) of the mean value. Data for SBC-1 were determined in this study; data for SGR-1b are from Yin *et al.* (2017).

component) and detritus (non-hydrogenous Os component; Creaser *et al.* 2002, Selby and Creaser 2003, Kendall *et al.* 2004). Rhenium and Os in organic matter are derived from seawater, which is characterised by a high $^{187}Re/^{188}Os$ ratio (3200–5300 for present-day seawater, Kendall *et al.* 2009). Since Re is more readily incorporated into organic matter under highly reducing conditions than Os (Yamashita *et al.* 2007), organic matter tends to possess high $^{187}Re/^{188}Os$ ratios. Hence, ancient organic-rich sedimentary rocks are generally characterised by high $^{187}Re/^{188}Os$ and corresponding high radiogenic $^{187}Os/^{188}Os$ values. The Re-Os isotopic composition of detritus is unclear and may be dependent on the isotopic composition of the source rock. For SBC-1, the detrital component is characterised by much lower $^{187}Re/^{188}Os$ and non-radiogenic $^{187}Os/^{188}Os$ values than that of present-day hydrogenous components. Thus,

the incorporation of a very small amount of detrital Re and Os could significantly affect the total $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios (Figure 3). In contrast to SBC-1, SGR-1b does not show strong correlations in plots of $^{187}Os/^{188}Os$ ratio versus inverse common Os mass fraction and $^{187}Re/^{188}Os$ (Figure 3), suggesting negligible contribution from detrital Re and Os.

Under a constant detrital Os flux, the Re and Os contribution from detrital components is more pronounced for organic-rich sedimentary rocks with small amounts of hydrogenous Re and Os. SGR-1b is a petroleum- and carbonate-rich shale that contains 24.8% *m/m* C_{org}, 28.2% *m/m* SiO_2, 6.5% *m/m* Al_2O_3 and 8.38% *m/m* CaO (Table 1), whereas the marine shale reference material SBC-1 contains much lower C_{org} (1.2% *m/m*) and much higher
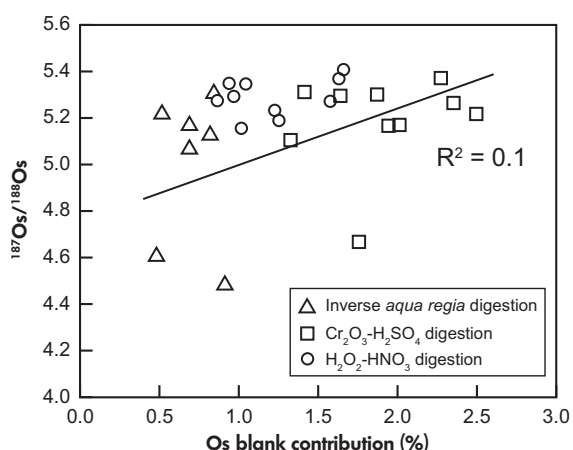
Figure 2. $^{187}Os/^{188}Os$ versus the percentage of Os blank contribution for all measurements of SBC-1. The data for SBC-1 show no obvious correlations between $^{187}Os/^{188}Os$ and the percentage of Os blank contribution.

SiO_2 (47.6% *m/m*) and Al_2O_3 (21.0% *m/m*). The major element data and mineral assemblages of SBC-1 show the

potential for larger contributions provided that acids digest some of the detritus.

Powder heterogeneity may be a possible cause for some discrepancies of Re-Os isotopic compositions in individual analyses. There are three outliers for the inverse *aqua regia* digestion and one outlier for the Cr_2O_3 digestion have significantly higher Os mass fractions and lower $^{187}Os/^{188}Os$ isotope ratios in SBC-1 (Figure 3). Eliminating these outliers, the mean values for inverse *aqua regia* and Cr_2O_3 digestion are more consistent with the data of H_2O_2-HNO_3 digestion, which are 98 ± 1 ng g^{-1} (for Os), 5.18 ± 0.09 (for $^{187}Os/^{188}Os$) and 97 ± 2 ng g^{-1} (for Os), 5.25 ± 0.06 (for $^{187}Os/^{188}Os$), respectively. These outliers seem to be partly caused by the inhomogeneous distribution of organic matter (hydrogenous Os component) and detritus (non-hydrogenous Os component) in SBC-1.

Comparison of digestion methods

Inverse *aqua regia* digestion can leach both hydrogenous and non-hydrogenous Re and Os, whereas CrO_3-H_2SO_4 and H_2O_2-HNO_3 selectively digest the organic
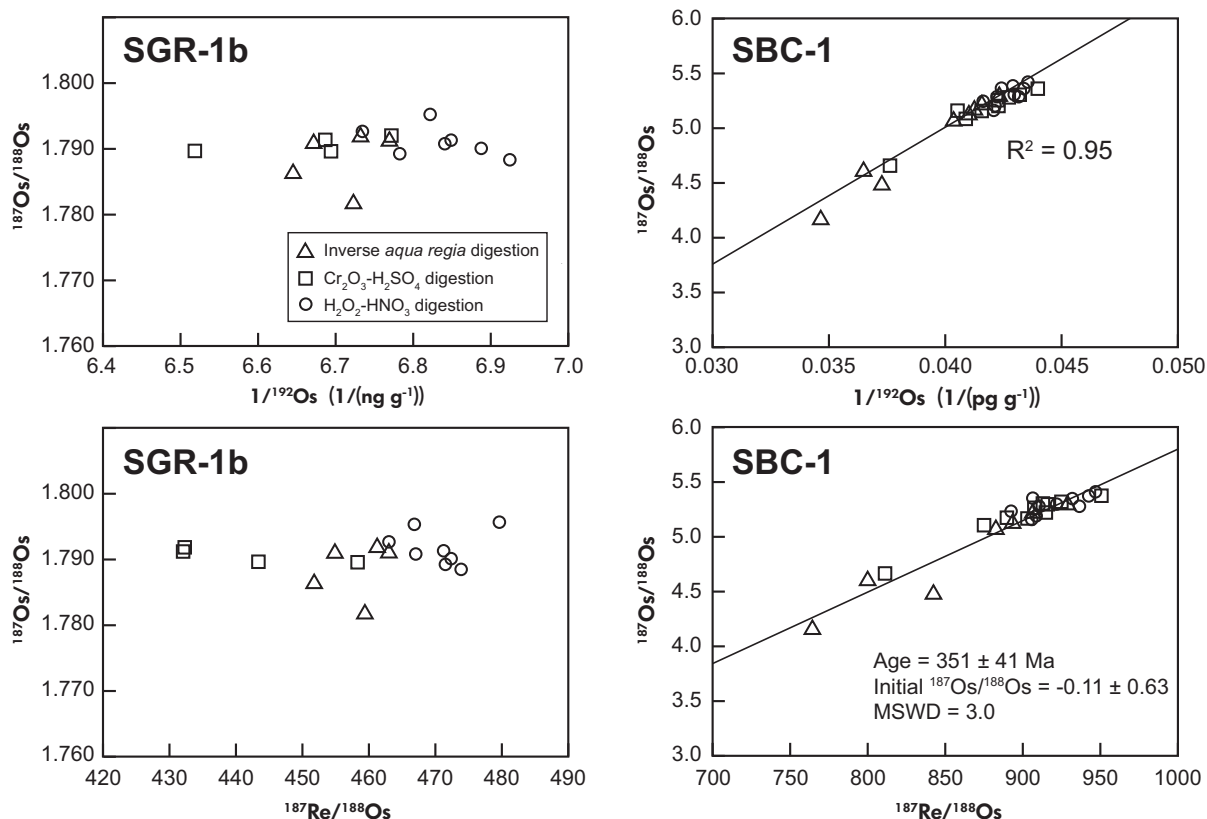
Figure 3. $^{187}Os/^{188}Os$ versus $1/^{192}Os$ and $^{187}Os/^{188}Os$ versus $^{187}Re/^{188}Os$ diagrams for all measurements of SGR-1b (left) and SBC-1 (right). The data for SGR-1b show no obvious correlations, whereas the SBC-1 data show strong positive correlations and define an apparent isochron. Data for SGR-1b are from Yin *et al.* (2017).
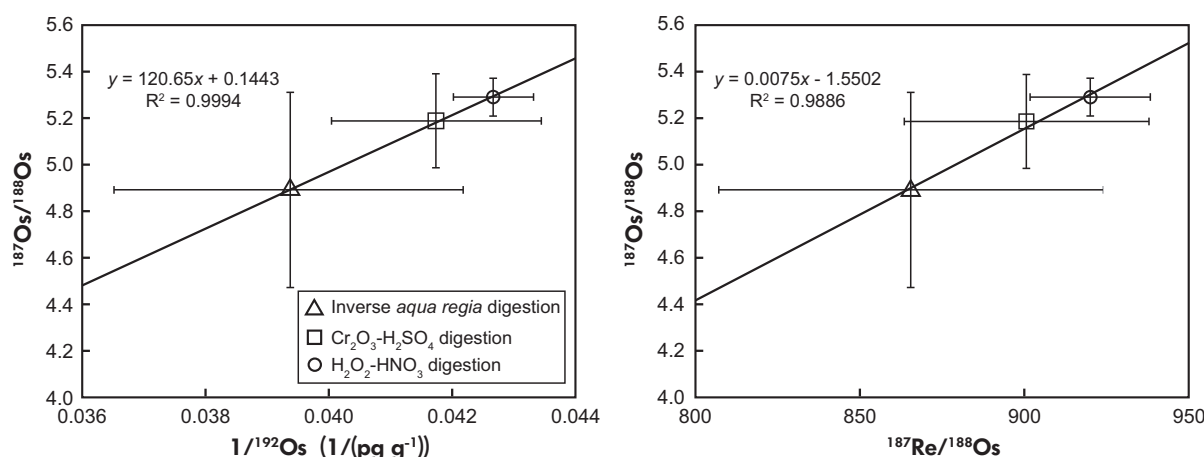
Figure 4. Mean ^{187}Os/^{188}Os versus $1/^{192}$Os and mean ^{187}Os/^{188}Os versus ^{187}Re/^{188}Os diagrams for SBC-1 determined by inverse *aqua regia*, CrO$_3$-H$_2$SO$_4$, and H$_2$O$_2$-HNO$_3$ digestions. Bars represent 1 standard deviation (1s) of mean values.

component and limit the liberation of detrital Re and Os (Selby and Creaser 2003, Kendall *et al.* 2004, 2009, Yin *et al.* 2017). Although the CrO$_3$-H$_2$SO$_4$ and H$_2$O$_2$-HNO$_3$ digestions achieved better Re-Os regression analyses and more precise isochron ages than inverse *aqua regia* digestion, there is no direct evidence showing that they leach less detrital Re and Os. Given that Re and Os are strongly enriched in organic matter, Re-Os mass fraction and isotope data determined by these alternative digestion methods are usually consistent with those of inverse *aqua regia* digestion within uncertainty. However, SBC-1 may contain high detrital Re and Os contents. To further evaluate the ability of the various digestions to selectively digest organic matter, we compared Re-Os data for SBC-1 obtained using inverse *aqua regia* with data obtained using the CrO$_3$-H$_2$SO$_4$ and H$_2$O$_2$-HNO$_3$ digestion methods.

Although all values from all digestions overlap within the reproducibility of the method, the mean Re-Os values obtained using the three digestion methods define a tight linear array on ^{187}Os/^{188}Os versus $1/^{192}$Os and ^{187}Os/^{188}Os versus ^{187}Re/^{188}Os diagrams, suggesting that these methods extract different proportions of the detrital Os component (Figure 4). The H$_2$O$_2$-HNO$_3$ digestion yielded the lowest mean Os mass fraction and the highest mean ^{187}Os/^{188}Os value. This implies that the H$_2$O$_2$-HNO$_3$ digestion method is preferable in selectively extracting the radiogenic Os component, which is representative of organic matter in SBC-1. A higher Os mass fraction and non-radiogenic ^{187}Os/^{188}Os values were predominant in inverse *aqua regia* data, indicating that the inverse aqua extracts multiple components (or minerals) including those that were not digested by H$_2$O$_2$-HNO$_3$.

As discussed in the above section, apparent isochron lines and a strong correlation between ^{187}Os/^{188}Os and $1/^{192}$Os in replicate analyses of individual organic-rich sedimentary rocks may signify the incorporation of detrital Os in different proportions. The inverse *aqua regia* and CrO$_3$-H$_2$SO$_4$ digestions yield strong correlations between ^{187}Os/^{188}Os and $1/^{192}$Os, and well-defined apparent isochron lines (Figure 5). The data set of H$_2$O$_2$-HNO$_3$ digestion also shows certain correlations, although they are not as significant as the former two (Figure 5c1, c2). In contrast to the data set of inverse *aqua regia*, the H$_2$O$_2$-HNO$_3$ data tend to be tightly clustered, further suggesting that H$_2$O$_2$-HNO$_3$ digestion minimises the incorporation of non-hydrogenous (detrital) Re and Os. Similar correlations and apparent isochron lines were also obtained with CrO$_3$-H$_2$SO$_4$ digestion (Figure 5b1, b2), indicating that some detrital Os is also liberated when using this digestion method.

Effect of the detrital component on Re-Os systematics in organic matter

A comparison of Re-Os data for SBC-1 obtained using the three digestion methods indicates significant amounts of Os in detrital components and confirms that CrO$_3$-H$_2$SO$_4$ and H$_2$O$_2$-HNO$_3$ digestions liberate less detrital Os than inverse *aqua regia*. The mean ^{187}Re/^{188}Os and ^{187}Os/^{188}Os values by CrO$_3$-H$_2$SO$_4$ digestion (901 ± 37 and 5.19 ± 0.20, respectively) and H$_2$O$_2$-HNO$_3$ digestion (920 ± 18 and 5.29 ± 0.08, respectively) are higher than those by inverse *aqua regia* digestion (866 ± 58 and 4.89 ± 0.42, respectively). The intermediate precisions of ^{187}Re/^{188}Os and ^{187}Os/^{188}Os values obtained using the
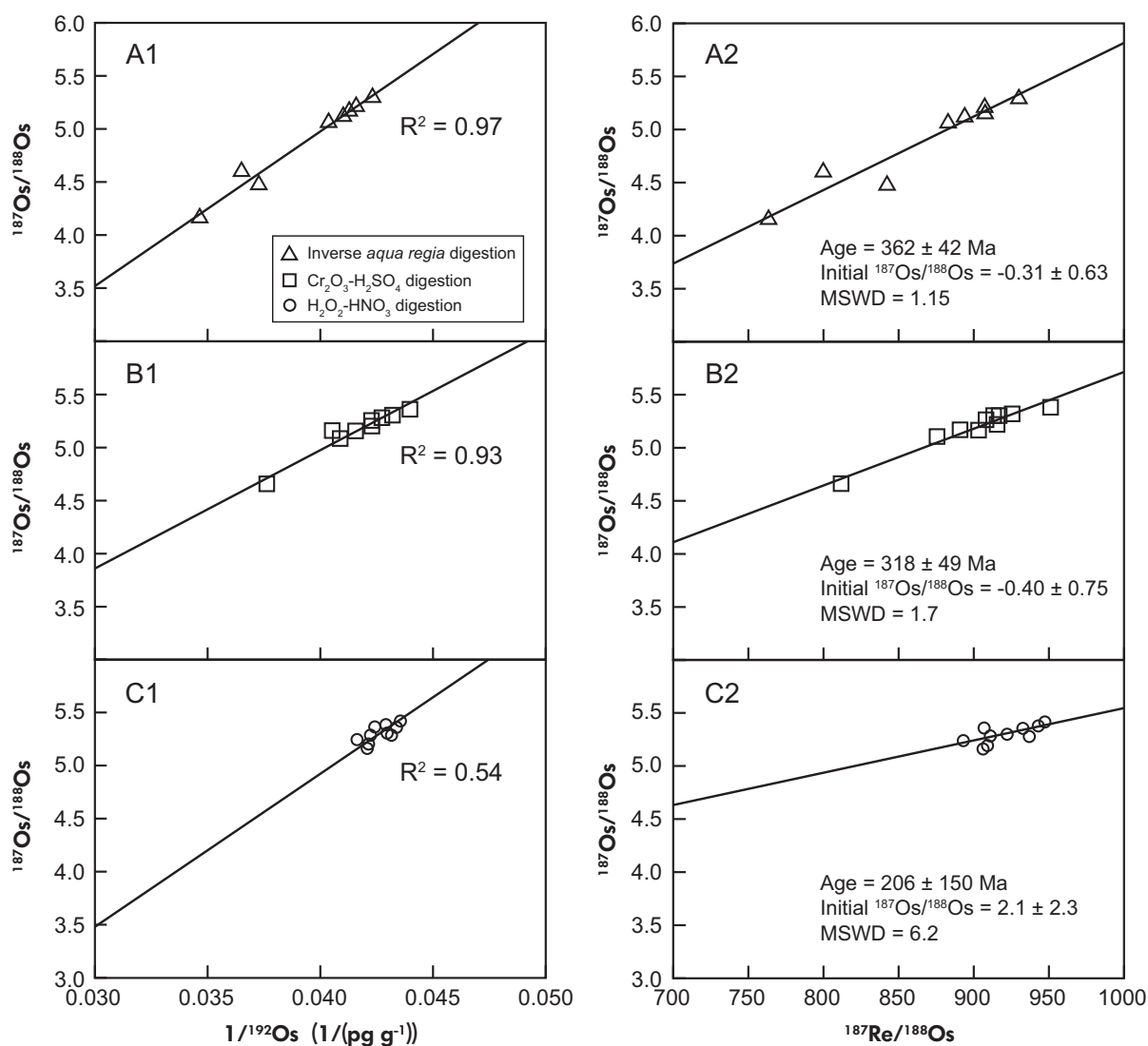
**Figure 5.** $^{187}Os/^{188}Os$ versus $1/^{192}Os$ and $^{187}Os/^{188}Os$ versus $^{187}Re/^{188}Os$ diagrams for SBC-1 determined by inverse *aqua regia* (A1 and A2), CrO_3-H_2SO_4 (B1 and B2), and H_2O_2-HNO_3 (C1 and C2) digestions.

CrO_3-H_2SO_4 and H_2O_2-HNO_3 digestion methods are better than those of inverse *aqua regia* digestion. These results indicate that the incorporation of detrital Os significantly alters $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ ratios, resulting in data that deviate from the Re-Os isotopic composition in organic matter components. This may explain, in part, the scatter (beyond analytical uncertainty) in the Re-Os isochron for inverse *aqua regia* digestion (e.g., Ravizza and Turekian 1989, Ravizza *et al.* 1991, Cohen and Coe 1999, Creaser *et al.* 2002).

Improved digestion methods usually achieve Re-Os isochron ages slightly younger than those determined by inverse *aqua regia* (e.g., Selby and Creaser 2003, Kendall *et al.* 2004, 2009, Yin *et al.* 2017), suggesting that the incorporation of detrital Os also affects the accuracy of

Re-Os isochron ages. In this study, duplicate analyses of SBC-1 using inverse *aqua regia* defined an apparent Re-Os isotope regression line, with a Re-Os age of 362 ± 42 Ma (n = 8, MSWD = 1.15; Figure 5a2). This age is inconsistent with the actual depositional age of the late Pennsylvanian Glenshaw Formation (305–302 Ma). The apparent isochrons of replicate analyses for individual samples may not accurately record the radiogenic ingrowth of ^{187}Re–^{187}Os; instead, they may reflect binary mixing of detrital and organic components (Li *et al.* 2015b). A similar apparent Re-Os isotope regression line (I_M) would form at the time of deposition, and considering the different initial isotopic compositions of detrital and organic matter, the age defined by this initial mixing line (t_0) would be older than the zero age. Consequently, this initial mixing line would combine with the actual Re-Os isochrons recording ingrowth of
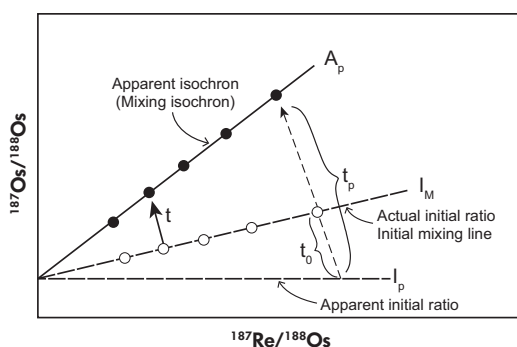
Figure 6. Diagram showing the formation of an apparent mixing isochron (A_p) due to binary mixing (modified from Li *et al*. 2015b), where t_0 is the age defined by the initial mixing line, t is the actual depositional age, and t_p is the apparent mixing age defined by the mixing isochron.

^{187}Re–^{187}Os and yield ages (t_p) older than the depositional age (t, Figure 6). Duplicate analyses of SBC-1 using CrO_3-H_2SO_4 and H_2O_2-HNO_3 define a linear relationship in $^{187}Re/^{188}Os$–$^{187}Os/^{188}Os$ coordinates (Figure 5b2, c2). These two digestion methods yield a shallower slope for the initial mixing line, and therefore, the apparent isochron ages (t_p) are closer to the actual age (t_0).

Conclusions

Rhenium and Os mass fractions in the USGS black shale reference material SBC-1 were measured using inverse *aqua regia*, CrO_3-H_2SO_4 and H_2O_2-HNO_3 digestion. The inverse *aqua regia* digestion yielded slightly higher Os mass fractions and lower $^{187}Os/^{188}Os$ ratios than those obtained using CrO_3-H_2SO_4 digestion or H_2O_2-HNO_3 digestion. All three digestions yielded tight positive correlations between $^{187}Os/^{188}Os$ and $1/^{192}Os$, $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$, suggesting that SBC-1 contains significant amounts of detrital Re and Os. The results demonstrate that H_2O_2-HNO_3 digestion is able to selectively digest organic matter and minimise the liberation of Re and Os from detritus in comparison with the inverse *aqua regia* and CrO_3-H_2SO_4 protocols. The data obtained using H_2O_2-HNO_3 digestion may represent the Re-Os isotopic composition of hydrogenous components in SBC-1. Based on the present results, combined with our previous study of USGS black shale RM SGR-1b (Yin *et al*. 2017), we conclude that SGR-1b and SBC-1 are suitable matrix-matched RMs for validation and quality control in the analysis of Re-Os in organic-rich sedimentary rocks with high and low abundances of Re and Os, respectively.

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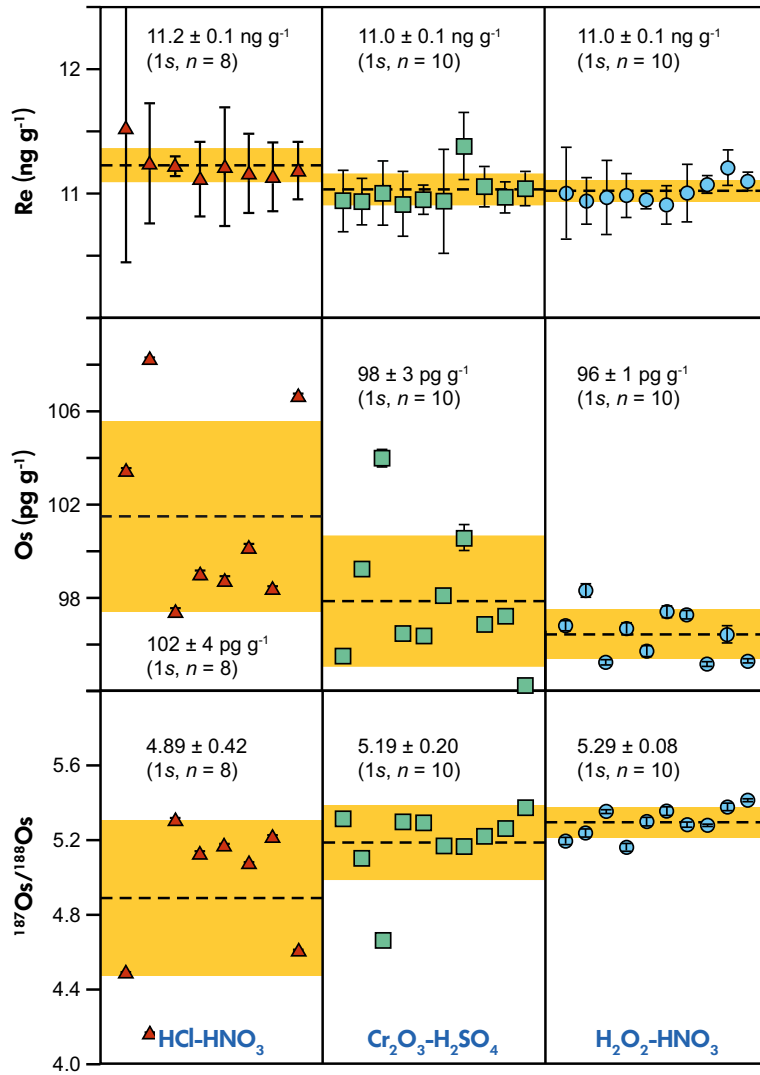
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