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Precise and accurate Re–Os isotope dating of organic-rich sedimentary rocks by thermal ionization mass spectrometry with an improved H_2O_2-HNO_3 digestion procedure

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ABSTRACT

This contribution presents a new method for Re–Os isotope dating organic-rich sedimentary (ORS) rocks by thermal ionization mass spectrometry using an H_2O_2–HNO_3 solution as the digestion medium, rather than CrO_3–H_2SO_4 or inverse *aqua regia*. The main underlying principle of this method is that H_2O_2–HNO_3 digestion would preferentially liberate hydrogenous Re and Os, and minimize the dissolution of non-hydrogenous detrital Re and Os, thereby providing more accurate and precise ages. A series of tests were performed, and the experimental data demonstrate the fundamental controls on spike–sample equilibrium and that the amount of detrital Re and Os incorporated into the system are subjected to the volumetric ratio of H_2O_2 to HNO_3. The optimum method is a H_2O_2:HNO_3 ratio of 5 to complete spike–sample equilibration, and to minimize the amount of detrital Re and Os in the system. A comparison of our new method with inverse *aqua regia* and CrO_3–H_2SO_4 showed that the three techniques yield indistinguishable Re–Os results, suggesting complete spike–sample equilibrium was achieved by all of the digestion techniques. Moreover, the data show that our new technique leaches out the least amount of detrital Re and Os isotopes relative to conventional methods Thus, we propose the H_2O_2–HNO_3 method may increase the precision and accuracy of Re–Os depositional ages of organic-rich sedimentary systems.

1. Introduction

Over the past 25 years, improvements in chemical separation procedures and mass spectrometry have enabled the application of Re–Os isotopic systematics to the precise dating of organic-rich sedimentary rocks (ORS) [1–14]. Both Re and Os are preferentially concentrated in anoxic organic-rich sediments via redox reactions near the sediment–water interface. As such, they are hydrogenous in nature, acting as a closed radiometric system following deposition. Thus, the Re–Os isotope system can be used to date ORS, assuming negligible amounts of non-hydrogenous Re and Os in detrital silicates and as inclusions in silicates, and non-hydrogenous sulfides and oxides [1–3,15].

The conventional method of Re–Os dating of ORS involves the dissolution of powdered whole-rock samples in an inverse *aqua regia* digestion medium in a Carius tube at 240 °C for 48 h [1,3]. Using this method, any non-hydrogenous Re and Os present in the sample is leached and mixed with hydrogenous Re and Os during digestion, thereby affecting the precision and accuracy of the data. This effect has been demonstrated in several studies and may explain, in part, the degree of scatter in Re–Os isochrons extending beyond any ascribed analytical uncertainty [1,3,15]. To increase the precision and accuracy of Re–Os ages of ORS, Selby and Creaser [4] used a CrO_3–H_2SO_4 solution, rather than inverse *aqua regia*, as the digestion medium to selectively dissolve the organic component by limiting the detrital Os in the rock. However, the CrO_3–H_2SO_4 dissolution technique has several limitations: 1) it may dissolve some non-hydrogenous components of the rock [16]; 2) it often contains significant amounts of Re, which cannot be sufficiently removed, causing unusually high blank levels [4] and [8]; 3) the solution is highly toxic; and 4) the existence of high concentration of Cr^{6+} can interfere with the separation of Re from the CrO_3–H_2SO_4 solution during anion exchange chromatography, and additional procedures to reduce Cr^{6+} to Cr^{3+} (e.g., using SO_2 gas) [16], can be complicated.

To overcome these limitations, we developed an improved digestion method as a potential replacement for conventional

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methods of analyzing Re–Os isotopes in ORS. Hydrogen peroxide (H_2O_2) in a nitric acid medium (herein referred to H_2O_2–HNO_3) is typically used to oxidize organic matter in soil and sediments [17], and this approach may be safer and cleaner than CrO_3–H_2SO_4. In this study, we compared the H_2O_2–HNO_3, inverse *aqua regia*, and CrO_3–H_2SO_4 digestion methods to evaluate the efficiency of their selective dissolution of hydrogenous Re and Os in the geochemical reference standards SGR-1b (black shale, USGS) and BIR-1a (basalt, USGS). The data demonstrate that the H_2O_2–HNO_3 approach minimizes the incorporation of detrital Re and Os by selectively dissolving hydrogenous Re and Os in organic matter/metals, compared with inverse *aqua regia* and CrO_3–H_2SO_4. In addition, we evaluated the influence of detrital Re and Os on Re–Os isochron age data and the initial Os isotopic composition.

2. Experimental section

2.1. Samples and reagents

Powdered aliquots of organic-rich sedimentary rocks (black shale) from the Dabaoshan Deposit (23°34′N, 113°42′E) in Guangdong Province, South China, were analyzed together with the geological reference materials SGR-1b (USGS) and BIR-1a (USGS).

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. Deionized 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 [4] by dissolving 2 g of CrO_3 (Puratronic®, Alfa Aesar) in 10 mL of 2 mol l^{-1} H_2SO_4 (ACS grade, Thermo Fisher Scientific). Because this solution contains abundant Re and Os, it must be purified prior to use. The Os blank can be reduced by bubbling clean air through the solution at ~100 °C to remove volatile OsO_4. The CrO_3–H_2SO_4 solution had a very high Re blank, mean = 0.075 ± 0.032 ng mL^{-1} (n = 8; one standard deviation, 1SD), and attempts to purify it by solvent extraction using tetra propyl ammonium iodide (TPAI) [4] in chloroform were unsuccessful. Similar observations were made by Kendall et al. [8], who suggested Re does not partition into TPAI in the presence of Cr^{6+}.

The borosilicate Carius tubes used, similar to those of Shirey and Walker [18], were 3 mm thick, with a volume of ~210 mL, in order to withstand the high pressures generated in the H_2O_2–HNO_3 digestion process. Fluoropolymer (PFA; Savillex) 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 [19]. Finally, all the vials were rinsed with Milli-Q water and air-dried.

2.2. Chemical separation and purification of rhenium and osmium

Due to the distinct non-hydrogenous and hydrogenous Os isotopic compositions of ORS [4,6,15], the complete digestion of Os defines a Re–Os mixing isochron [20]. Thus, the selective dissolution of hydrogenous Os and Re, and minimizing the effect of non-hydrogenous Os in ORS are crucial in Re–Os geochronology.

Approximately 0.1–0.5 g of sample powder was weighed and placed in each Carius tube. The powders were dissolved and equilibrated with known amounts of ^{185}Re and ^{190}Os in 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-extraction into concentrated HBr [21,22], with subsequent purification by micro-distillation. The Re fraction was separated and purified using anion column chromatography. Detailed procedures of the inverse *aqua regia* and CrO_3–H_2SO_4 dissolution methods are described by Li et al. [19,23] and Selby and Creaser [4], respectively.

For H_2O_2–HNO_3 dissolution, 1.5 mL of concentrated HNO_3 and 7.5 mL of H_2O_2 (30%) were added to the Carius tube while it was chilled in a bath containing a freezing mixture of liquid N_2 and ethanol. The Carius tube was heated in an oven at 120 °C for 4 h, and then 220 °C for 24 h. After decomposition, Os was separated using solvent extraction by CCl_4, followed by back-extraction into concentrated HBr. The Os was further purified by micro-distillation. Re was separated and purified by anion chromatography techniques [23].

2.3. Mass spectrometry

The technique of analyzing Os by mass spectrometry is described by Li et al. [19,23]. Os was loaded onto Pt filaments and measured as OsO_3^- by negative-thermal ionization mass spectrometry (N-TIMS) using the electron multiplier mode on a Thermo-Finnigan Triton [24,25] at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China. Repeated analyses of the Os standard solution (Merck Chemical AA standard solution) yielded a mean $^{187}Os/^{188}Os$ value of 0.12026 ± 25 (2 SD, n = 18) for the period of analysis. These values are in good agreement with the value measured on the same mass spectrometer in Faraday cup mode (0.12022 ± 2; 2 SD, n = 14) [26].

Rhenium was analyzed by inductively coupled plasma–mass spectrometry (Thermo Elemental X2 Series) at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry. A conventional low-volume quartz impact bead spray chamber with a Peltier cooled (3 °C) and 0.4 mL min^{-1} borosilicate nebulizer (MicroMist GE) were used for the measurements. Ion lens settings, nebulizer gas flow rate, and torch position were optimized daily using a 10 ng mL^{-1} tuning In–Ce standard solution to obtain high instrument sensitivity and low oxide production levels. A peristaltic pump was not used, as free aspiration of the nebulizer provided better signal stability. The details of measurements by ICP–MS are described by Li et al. [19].

2.4. Procedural blanks

Total procedural blanks obtained using the CrO_3–H_2SO_4 (10 mL) digestion method range from 0.58 to 0.95 ng (mean of 0.75 ± 0.32 ng; 1 SD, n = 8) for Re and 0.33 ± 0.29 pg (1 SD, n = 8) for Os. The blank $^{187}Os/^{188}Os$ isotopic compositions range from 0.18 to 0.25, averaging 0.206 ± 25 (1 SD, n = 8). Using the *aqua regia* digestion method, the total procedural blanks for Re and Os range from 3 to 6 pg (mean of 4.3 ± 1.8 pg; n = 8) and 0.2–0.6 pg (mean of 0.36 ± 0.22 pg; n = 8), respectively, with blank $^{187}Os/^{188}Os$ isotopic compositions ranging from 0.27 to 0.48 (mean of 0.336 ± 32; n = 8). The total procedural blank values obtained using H_2O_2–HNO_3 digestion are the same as those using the *aqua regia* method. The data from each analytical batch were corrected for the procedural blank. The concentrations of Re and Os blanks of SGR-1b, BIR-1a, and ORS were negligible for the *aqua regia* and H_2O_2–HNO_3 methods; however, CrO_3–H_2SO_4 digestion produced a high Re blank value, causing high uncertainty.

2.5. Tests and calibration of the H_2O_2–HNO_3 digestion method

Inverse *aqua regia* and CrO_3–H_2SO_4 are commonly used to digest and oxidize Os to its highest oxidation state [4,16,18,27,28]. All common Os separation techniques, including distillation and solvent extraction procedures, such as the CCl_4 technique [22], are based on the preferential liberation/extraction of Os in its high-

Table 1
Re–Os isotope composition of reference material SGR-1b obtained by digestion under varying volumetric ratios of H_2O_2 and HNO_3, inverse *aqua regia*, and CrO_3–H_2SO_4.

No	Digestion medium	Mass (g)	Re (ng/g)	2SE	Os (ng/g)	2SE	$^{187}Os/^{188}Os$	2SE	$^{187}Re/^{188}Os$	2SE
1	CrO_3-H_2SO_4 (8 mL)	0.1913	32.45	0.59	0.440	0.001	1.7918	0.0033	432	8
2		0.2027	33.68	0.48	0.445	0.001	1.7895	0.0035	443	6
3		0.1005	32.84	0.66	0.446	0.001	1.7912	0.0051	432	9
4		0.4010	35.74	0.80	0.457	0.001	1.7895	0.0026	458	10
5	Inverse aqua regia (2 mL	0.2169	34.83	0.16	0.443	0.001	1.7918	0.0042	461	2
6	HCl + 6 mL HNO_3)	0.4177	34.78	0.37	0.440	0.001	1.7910	0.0031	463	5
7		0.2243	34.66	0.71	0.447	0.001	1.7909	0.0036	455	9
8		0.2469	34.56	0.18	0.448	0.000	1.7863	0.0017	452	2
9		0.2462	34.74	0.22	0.443	0.001	1.7817	0.0014	459	3
10	H_2O_2 (8 mL)	0.2331	34.89	1.72	0.462	0.002	1.7574	0.0039	441	22
11		0.2418	34.90	0.24	0.474	0.003	1.5580	0.0090	421	4
12		0.217	34.77	0.35	0.447	0.003	1.7118	0.0129	453	5
13		0.2136	34.74	0.42	0.474	0.008	1.6479	0.0278	423	9
14		0.2278	34.99	0.34	0.440	0.006	1.7231	0.0174	462	8
15		0.2563	34.91	0.39	0.471	0.006	1.7542	0.0179	433	7
16	H_2O_2:HNO_3 = 7:1 (7 mL	0.2392	34.97	0.37	0.465	0.001	1.8005	0.0032	441	5
17	H_2O_2 + 1 mL HNO_3)	0.2637	35.05	0.35	0.457	0.001	1.7892	0.0036	449	5
18		0.2265	34.56	0.18	0.450	0.001	1.7222	0.0045	447	3
19		0.2451	34.46	0.49	0.495	0.001	1.5691	0.0034	398	6
20		0.1929	34.76	0.14	0.495	0.003	1.5568	0.0064	401	3
21	H_2O_2:HNO_3 = 6:1 (6 mL	0.2208	35.13	0.12	0.438	0.001	1.7752	0.0057	469	2
22	H_2O_2 + 1 mL HNO_3)	0.2306	34.81	0.08	0.433	0.002	1.7867	0.0090	469	3
23		0.1937	34.78	0.06	0.432	0.002	1.7889	0.0069	471	2
24	H_2O_2:HNO_3 = 5:1 (7.5 mL H_2O_2+	0.2157	34.79	0.19	0.425	0.001	1.7955	0.0026	480	3
25	1.5 mL HNO_3)	0.2089	34.86	0.26	0.433	0.002	1.7901	0.0074	472	4
26		0.2103	34.97	0.33	0.435	0.001	1.7913	0.0025	471	4
27		0.1922	34.80	0.22	0.437	0.001	1.7952	0.0041	467	3
28		0.1933	34.96	0.21	0.443	0.001	1.7927	0.0064	463	3
29		0.1949	35.35	0.12	0.439	0.002	1.7893	0.0064	472	2
30		0.2164	34.74	0.11	0.436	0.001	1.7908	0.0042	467	2
31		0.2084	34.80	0.11	0.430	0.002	1.7884	0.0046	474	2
32	H_2O_2:HNO_3 = 4:1 (6 mL	0.2265	34.96	0.26	0.437	0.002	1.7891	0.0081	469	4
33	H_2O_2 + 1.5 mL HNO_3)	0.2042	34.98	0.48	0.445	0.004	1.8008	0.0073	466	8
34		0.2096	35.00	0.16	0.442	0.002	1.7894	0.0063	464	3
35		0.2316	34.77	0.06	0.436	0.001	1.7857	0.0041	466	2
36	H_2O_2:HNO_3 = 3:1 (6 mL	0.2057	34.83	0.07	0.438	0.001	1.7907	0.0027	466	1
37	H_2O_2 + 2 mL HNO_3)	0.1970	34.83	0.12	0.436	0.002	1.7862	0.0054	467	2
38		0.1921	34.56	0.11	0.427	0.001	1.7876	0.0030	475	2
39	H_2O_2:HNO_3 = 1:1 (4 mL	0.2270	34.67	0.18	0.430	0.001	1.7918	0.0017	473	3
40	H_2O_2 + 4 mL HNO_3)	0.1855	34.69	0.08	0.436	0.001	1.7918	0.0022	466	2
41		0.2141	34.64	0.20	0.427	0.001	1.7878	0.0052	476	3
Mean for CrO_3-H_2SO_4 (n = 4,1SD)			33.68	1.47	0.447	0.007	1.7905	0.0012	441	12
Mean for inverse aqua regia (n = 5,1SD)			34.72	0.10	0.444	0.003	1.7883	0.0043	458	5
Mean for H_2O_2 (n = 6,1SD)			34.87	0.09	0.461	0.015	1.6921	0.0767	439	16
Mean for H_2O_2:HNO_3 = 7:1 (n = 5,1SD)			34.76	0.25	0.472	0.021	1.6876	0.1177	427	25
Mean for H_2O_2:HNO_3 = 6:1 (n = 3,1SD)			34.91	0.19	0.435	0.003	1.7836	0.0073	470	1
Mean for H_2O_2:HNO_3 = 5:1 (n = 9,1SD)			34.91	0.20	0.435	0.005	1.7917	0.0026	471	5
Mean for H_2O_2:HNO_3 = 4:1 (n = 4,1SD)			34.93	0.11	0.440	0.005	1.7912	0.0066	466	2
Mean for H_2O_2:HNO_3 = 3:1 (n = 3,1SD)			34.74	0.16	0.433	0.006	1.7881	0.0023	469	5
Mean for H_2O_2:HNO_3 = 1:1 (n = 3,1SD)			34.67	0.02	0.431	0.005	1.7905	0.0023	471	5
Mean for inverse aqua regia and CrO_3–$H2SO_4$ (n = 8,1SD)			34.25	1.05	0.445	0.005	1.7893	0.0033	451	12
Mean for H_2O_2 and H_2O_2:HNO_3 (n = 32,1SD)			34.84	0.18	0.446	0.019	1.7555	0.0712	457	21
Mean for H_2O_2 and H_2O_2:HNO_3 = 7:1 (n = 11,1SD)			34.82	0.18	0.466	0.018	1.6900	0.0921	434	21
Mean for H_2O_2:HNO_3 range from 6:1 to 1:1 (n = 21,1SD)			34.85	0.18	0.435	0.005	1.7897	0.0048	470	4

Uncertainties on each digestion in this study all are estimated by error propagation of uncertainties in N-TIMS (Os and $^{187}Os/^{188}Os$) and ICP-QMS (for Re) measurements (2SE).

est oxidation state (OsO_4). The existence of numerous Os–organic complexes and different Os oxidation states in ORS pose a potential obstacle for the determination of Os concentration and isotopic composition by isotope dilution, as they prevent equilibration between the sample and the added spike. Thus, the accurate determination of Os concentrations and isotopic compositions requires complete spike–sample equilibration by the oxidation of all Os species to OsO_4 through digestion.

Our technique was inspired by the method of Paul et al. [29] for Os analysis in surface and subsurface water samples, in which hydrogen peroxide is used to oxidize Os from both the sample and spike to the highest oxidation state (OsO_4). In our study, a series of tests using varying volumetric ratios of H_2O_2 and HNO_3 were performed to optimize Os oxidation and achieve complete spike–sample equilibrium. To eliminate the influences of other factors, the CCl_4 extraction, micro-distillation, and N-TIMS analyses were performed under the same conditions for all tests. The calibration was carried out on SGR-1b several times with a decreasing volumetric ratio of H_2O_2:HNO_3, from pure H_2O_2, and from ratios of 7:1 to 1:1, at 220 °C for 24 h, to compare the oxidation efficiency of the oxidant mixed in varying proportions of the two solutions.

The effect of the proportion of HNO_3 in the H_2O_2–HNO_3 on the amount of detrital Re–Os incorporated into the system was tested using BIR-1a, as it has a relatively homogenous Re–Os concentration and isotopic composition [20,30]. Every test was performed under the same conditions.

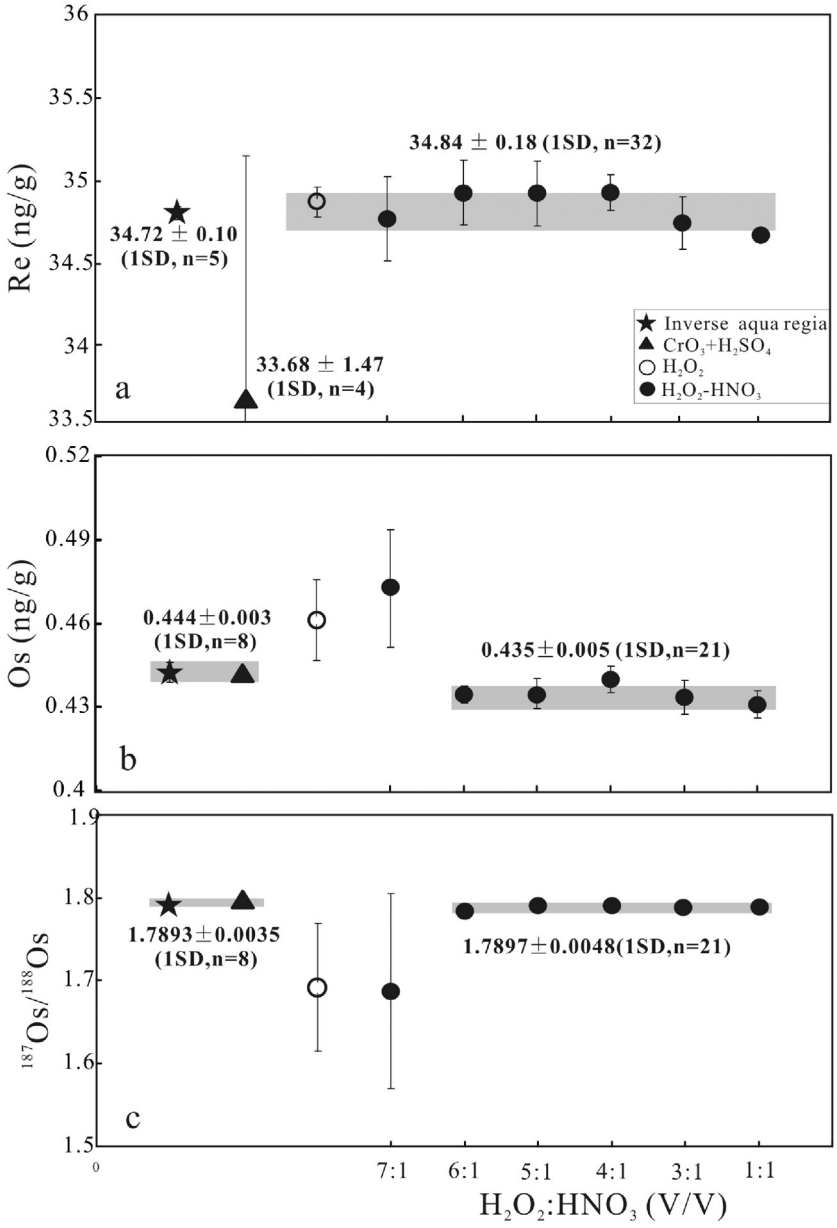

Fig. 1. (a) Average Re concentrations, (b) Os concentrations, and (c) $^{187}Os/^{188}Os$ values of SGR-1b, digested with inverse *aqua regia*, CrO_3–H_2SO_4, H_2O_2, and varying volumetric ratios of H_2O_2 and HNO_3. Error bars are 1 standard deviation (1 SD; Table 1), and are only shown when greater than the symbol size. The shaded band in (a) represents the mean Re concentration of all digestion methods, and shaded bands in (b) and (c) represent the mean Os concentrations and $^{187}Os/^{188}Os$ values obtained by conventional methods and H_2O_2–HNO_3 digestion (volumetric ratio ranging from 6:1 to 1:1), respectively.

3. Results and discussion

3.1. Effect of Os oxidation at differing volumetric ratios of H_2O_2 and HNO_3

The results of Re–Os isotope analyses of SGR-1b at different volumetric ratios of H_2O_2–HNO_3 are listed in Table 1. The Re–Os isotopic composition of the standard was first determined by conventional digestion methods, the results of which are listed in Table 1. The mean values for Re and Os by inverse *aqua regia* digestion are 34.72 ± 0.10 ng g^{-1} and 0.444 ± 0.003 ng g^{-1}, respectively, with $^{187}Os/^{188}Os = 1.7883 \pm 0.0043$ (1 SD, n = 5). The average Re concentration determined by CrO_3–H_2SO_4 digestion is comparable, but with a larger uncertainty (33.68 ± 1.47 ng g^{-1}, 1SD, n = 4), likely due to the high total procedural Re blank of this method. The Os data obtained by inverse *aqua regia* are in good agreement with the data obtained by CrO_3–H_2SO_4 digestion ($Os = 0.447 \pm 0.007$ ng g^{-1} and $^{187}Os/^{188}Os = 1.7905 \pm 0.0012$, 1SD, n = 4), indicating the Os concentration and isotope composition of SGR-1b are relatively homogenous and that the contribution of detrital Os in the reference material is minor. Thus, this sample is appropriate for validating the H_2O_2 and H_2O_2–HNO_3 digestion methods.

Table 1 lists the recoveries of Re using both H_2O_2 and H_2O_2–HNO_3 at different volumetric ratios, to examine the efficiency of Re extraction. Fig. 1a shows the Re concentrations of SGR-1b as a function of the different digestion methods and conditions. Both H_2O_2 and H_2O_2–HNO_3 digestions yielded almost constant Re concentrations, of which the mean (34.84 ± 0.18 ng g^{-1}; 1 SD, n = 32) is indistinguishable from that obtained by inverse *aqua regia* digestion (34.72 ± 0.10 ng g^{-1}; 1 SD,

Table 2
Re–Os isotope composition of reference material BIR-1a obtained by digestion under varying volumetric ratios of H_2O_2 and HNO_3, inverse *aqua regia*, and CrO_3–H_2SO_4.

No	Digestion medium	Mass (g)	Re (ng/g)	2SE	Os (ng/g)	2SE	$^{187}Os/^{188}Os$	2SE	$^{187}Re/^{188}Os$	2SE
1	H_2O_2:HNO_3 = 1:2 (4 mL H_2O_2 + 8 mL HNO_3)	0.6103	0.635	0.007	0.1433	0.0007	0.1339	0.0013	21.35	0.26
2	H_2O_2:HNO_3 = 1:1 (4 mL H_2O_2 + 4 mL HNO_3)	0.6179	0.575	0.006	0.1146	0.0005	0.1342	0.0024	24.17	0.29
3	H_2O_2:HNO_3 = 2:1 (8 mL H_2O_2 + 4 mL HNO_3)	0.6237	0.457	0.005	0.1055	0.0004	0.1344	0.0018	20.86	0.23
4	H_2O_2:HNO_3 = 4:1 (8 mL H_2O_2 + 2 mL HNO_3)	0.9754	0.400	0.004	0.0868	0.0002	0.1346	0.0007	22.24	0.21
5	H_2O_2:HNO_3 = 5:1 (10 mL H_2O_2 + 2 mL HNO_3)	0.8247	0.366	0.004	0.0767	0.0002	0.1344	0.0016	23.01	0.28
6	Inverse aqua regia (2.5 mL HCl + 7.5 mL HNO_3)	0.7411	0.692	0.010	0.3649	0.0011	0.1334	0.0003	9.13	0.14
7	CrO_3–H_2SO_4 (10 mL)	0.5865			0.1120	0.0002	0.1334	0.0007		

Uncertainties on each digestion in this study all are estimated by error propagation of uncertainties in N-TIMS (Os and $^{187}Os/^{188}Os$) and ICP-QMS (for Re) measurements (2SE).

n = 5). This suggests that both pure H_2O_2 and an H_2O_2–HNO_3 solution can completely extract Re from organic-rich materials, such as the black shale (SGR-1b).

In contrast, there are obvious discrepancies in both the Os concentration and $^{187}Os/^{188}Os$ value of SGR-1b obtained by different digestion methods (Fig. 1b–c). The H_2O_2 and H_2O_2–HNO_3 (7:1) methods yielded significantly higher Os concentrations (0.466 ± 0.018 ng g^{-1}; 1 SD, n = 11) and lower $^{187}Os/^{188}Os$ values (1.690 ± 0.092; 1 SD, n = 11) than those obtained by inverse *aqua regia* analysis (Table 1). Given that the H_2O_2 and H_2O_2–HNO_3 solutions are milder than *aqua regia*, we deduced that the higher Os concentrations and lower Os isotopic ratios, coupled with poor reproducibility, were caused by disequilibrium between the spike and sample. This suggests the solutions were not able to fully oxidize Os from both the spike and sample to OsO_4, meaning they are not appropriate digesting media for Re–Os chemistry. However, when volumetric ratios of H_2O_2–HNO_3 were ≤6:1, reproducibility was high (mean Os concentration of 0.435 ± 0.005 ng g^{-1}; mean $^{187}Os/^{188}Os$ of 1.7897 ± 0.0048; 1 SD, n = 21). These data are consistent with those obtained from CrO_3–H_2SO_4 and inverse *aqua regia* digestions (Fig. 1b–c), indicating volumetric ratios of ≤6:1 H_2O_2:HNO_3 are optimum to achieve spike–sample equilibrium.

3.2. Effect of detrital Re and Os at different volumetric ratios of H_2O_2 and HNO_3

Although H_2O_2–HNO_3 solutions at ratios of ≤6:1 can fully digest and oxidize Os from both the sample and spike, the different proportions of HNO_3 in the mixture may dissolve detrital material, releasing non-hydrogenous Re and Os, and causing scatter in the isochron regressions. Thus, the solution should be mixed at an optimum volumetric ratio of H_2O_2:HNO_3 to minimize the input of non-hydrogenous Os. To this end, experiments were conducted on BIR-1a, containing only non-hydrogenous Re and Os; the results are listed in Table 2 and plotted in Fig. 2. The resu lts show that Re and Os concentrations in BIR-1a increase with an increasing proportion of HNO_3 in the digestion solution (Fig. 2a–b). Moreover, the concentrations of Re and Os using this digestion method are lower than those obtained by the inverse *aqua regia* method,

and at a volumetric ratio of 5, H_2O_2–HNO_3 digestion yields lower Os than the CrO_3–H_2SO_4 method (Table 2). We did not observe any systematic variability in $^{187}Os/^{188}Os$ values with varying proportions of H_2O_2 and HNO_3, and the ratios are within error of those obtained by conventional methods (Table 2; Fig. 2c). This suggests that the Re and Os concentration, as well as the Os isotopic composition of BIR-1a, are homogeneous, and that the proportion of HNO_3 in the H_2O_2–HNO_3 solution has a significant effect on the leaching of Re and Os from certain silicate materials. In addition, the smaller the proportion of HNO_3 in the solution, the lower the amounts of detrital Re and Os incorporated into the system. Our experiments also show that like CrO_3–H_2SO_4, H_2O_2–HNO_3 can leach significant amounts of non-hydrogenous Re and Os from rock samples.

3.3. Optimized methodology

Hydrogen peroxide in a nitric acid medium was chosen as the digestion medium in this study because: 1) it is less toxic than conventionally used solutions; 2) it provides significantly lower Re blanks than CrO_3; and 3) the solution minimizes the incorporation of non-hydrogenous Re and Os into the system. Our experiments show that a volumetric ratio of H_2O_2:HNO_3 = 5 facilitates the most precise and reproducible results for ORS, and minimizes the incorporation of detrital Re and Os, completely leaching and oxidizing Re and Os from both the spike and the sample. Under these conditions, SGR-1b yielded Re = 34.84 ± 0.18 ng g^{-1}, Os = 0.435 ± 0.006 ng g^{-1} (1 SD; n = 18), and $^{187}Os/^{188}Os = 1.7908 \pm 0.0037$ (1 SD; n = 18).

3.4. Effect of detrital Os on the Re–Os isotopic system

Our new digestion method was developed to improve Re–Os geochronology for organic-rich sedimentary rocks, and was compared with conventional methods; i.e., inverse *aqua regia* and CrO_3–H_2SO_4 digestion. This included evaluating the contributions of detrital Re and Os to the system under variable conditions (Table 3). Although the Re and Os concentrations of the samples obtained by inverse *aqua regia* and H_2O_2–HNO_3 digestion methods are similar (Table 3), the $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$ values of the five ORS samples obtained by H_2O_2–HNO_3 are higher than those obtained by inverse *aqua regia* digestion. Although the Os concentrations obtained by CrO_3–H_2SO_4, inverse *aqua regia*, and H_2O_2–HNO_3 are similar to each other, the Re concentrations obtained by the three methods vary. The regression of the data acquired by inverse *aqua regia* (calculated using Isoplot software [31]) yields an age of 223 ± 18 Ma (2σ, n = 5, MSWD = 63), with initial $^{187}Os/^{188}Os = 0.59 \pm 0.14$ (Fig. 3a). The Re–Os isochron of data obtained using CrO_3–H_2SO_4 digestion yields an imprecise age of 170 ± 52 Ma (2σ, n = 5, MSWD = 30), with initial $^{187}Os/^{188}Os = 0.91 \pm 0.40$ (Fig. 3b), due to large uncertainties in the Re data caused by the correction of high total procedural Re blanks. In contrast, the isochron of the data acquired by H_2O_2–HNO_3 digestion yields a more precise age of 211 ± 11 Ma (2σ, n = 5, MSWD = 11) and a higher initial $^{187}Os/^{188}Os$ value of 0.67 ± 0.09 (Fig. 3a).

Detrital material is a source of non-hydrogenous Re and Os in ORS that may cause scatter on Re–Os isochrons [4,6]. The scatter effect is more pronounced for a sample containing relatively small amounts of hydrogenous Re and Os under a constant influx of total Re and Os, such as the Dabaoshan black shales (Re = ~2 ng g^{-1}, [32]; Os = ~0.03–0.05 ng g^{-1} [33]). Thus, it is important to assess the effects of detrital Re and Os on the results of Re–Os geochronology. The $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$ values of the Dabaoshan black shales obtained by inverse *aqua regia* are lower than those determined using H_2O_2–HNO_3 digestion (Table 3), suggesting that the former digestion liberated more stable detrital Os, with low Re/Os values. This causes greater scatter, an older Re–Os isochron age (223 ± 18 Ma, 2σ; MSWD = 63), and a lower $^{187}Os/^{188}Os_i$ value

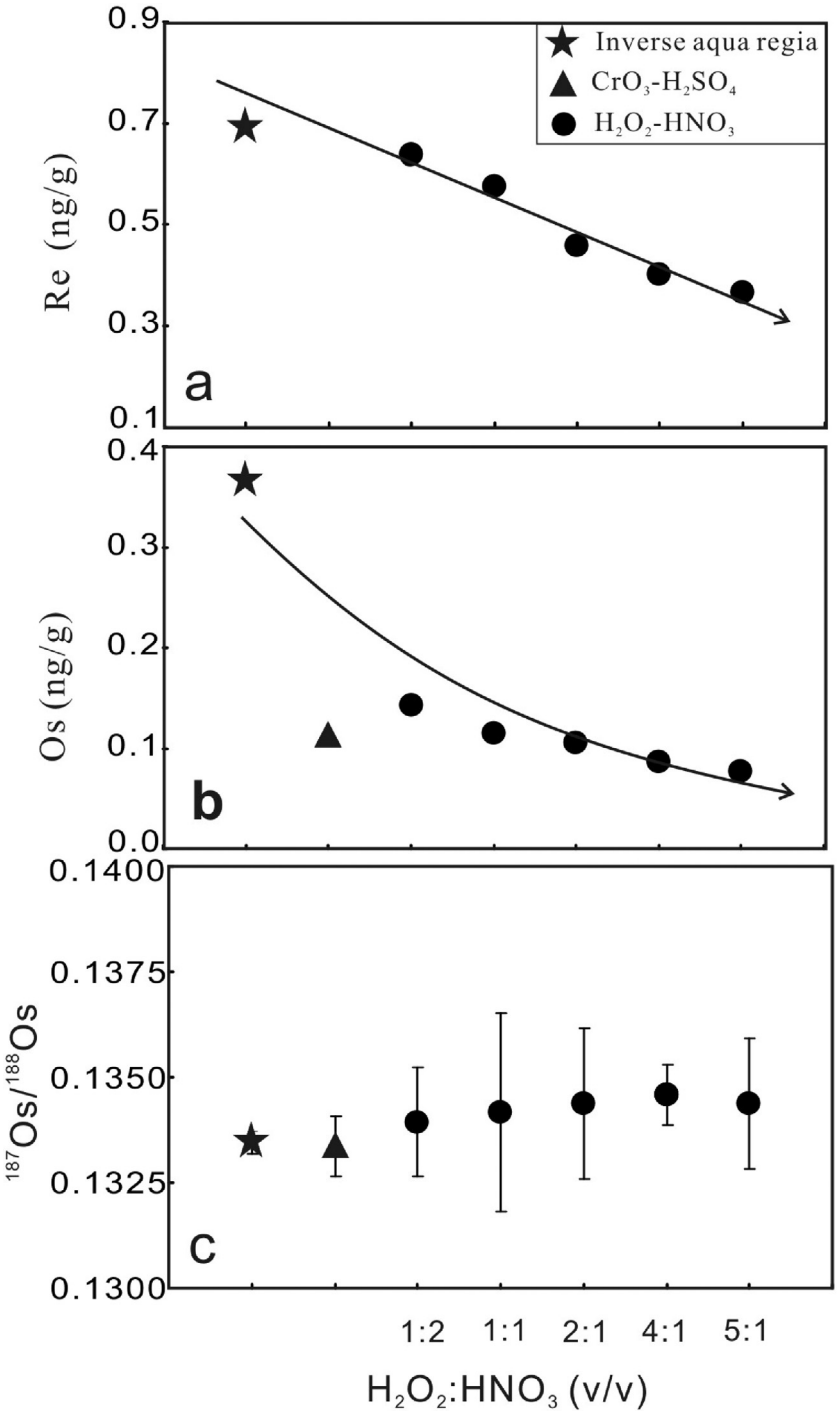

Fig. 2. (a) Average Re concentrations, (b) Os concentrations, and (c) $^{187}Os/^{188}Os$ values of BIR-1a digested at varying volumetric ratios of H_2O_2 and HNO_3. Data for digestion by inverse *aqua regia* and CrO_3–H_2SO_4 are shown for comparison.

(0.59 ± 0.14) for data obtained using inverse *aqua regia* than those obtained by H_2O_2–HNO_3 digestion (211 ± 11 Ma, 2σ; MSWD = 11; $^{187}Os/^{188}Os_i$ = 0.67 ± 0.09). Similar phenomena were observed in previous studies comparing inverse *aqua regia* and CrO_3–H_2SO_4 digestion for ORS samples [4,6,13]. We could not systematically compare the H_2O_2–HNO_3 and CrO_3–H_2SO_4 methods because of the high Re blanks produced by our CrO_3–H_2SO_4 solutions. The greater leaching of detrital Re and Os by this method may cause significant scatter on Re–Os isochrons. Thus, our experiments demonstrate that the 5:1 H_2O_2–HNO_3 analytical method may be superior in determining precise and accurate Re–Os depositional ages of organic-rich sedimentary systems.

4. Summary and conclusions

We have developed a new digestion method for the determination of Re–Os ages of organic-rich sedimentary rocks, using a solution of H_2O_2 and HNO_3 as the digestion medium. Experiments performed at different volumetric ratios of H_2O_2–HNO_3 indicate that a H_2O_2:HNO_3 value of 5 is optimal in achieving complete spike–sample equilibrium and minimizing the effects of detrital Re and Os. The analysis of oil shale SGR-1b shows that inverse *aqua regia* and CrO_3–H_2SO_4 digestion yield indistinguishable Re–Os values, and spike–sample equilibrium is achieved by the conventional techniques studied, as well as our new method. Moreover, our new

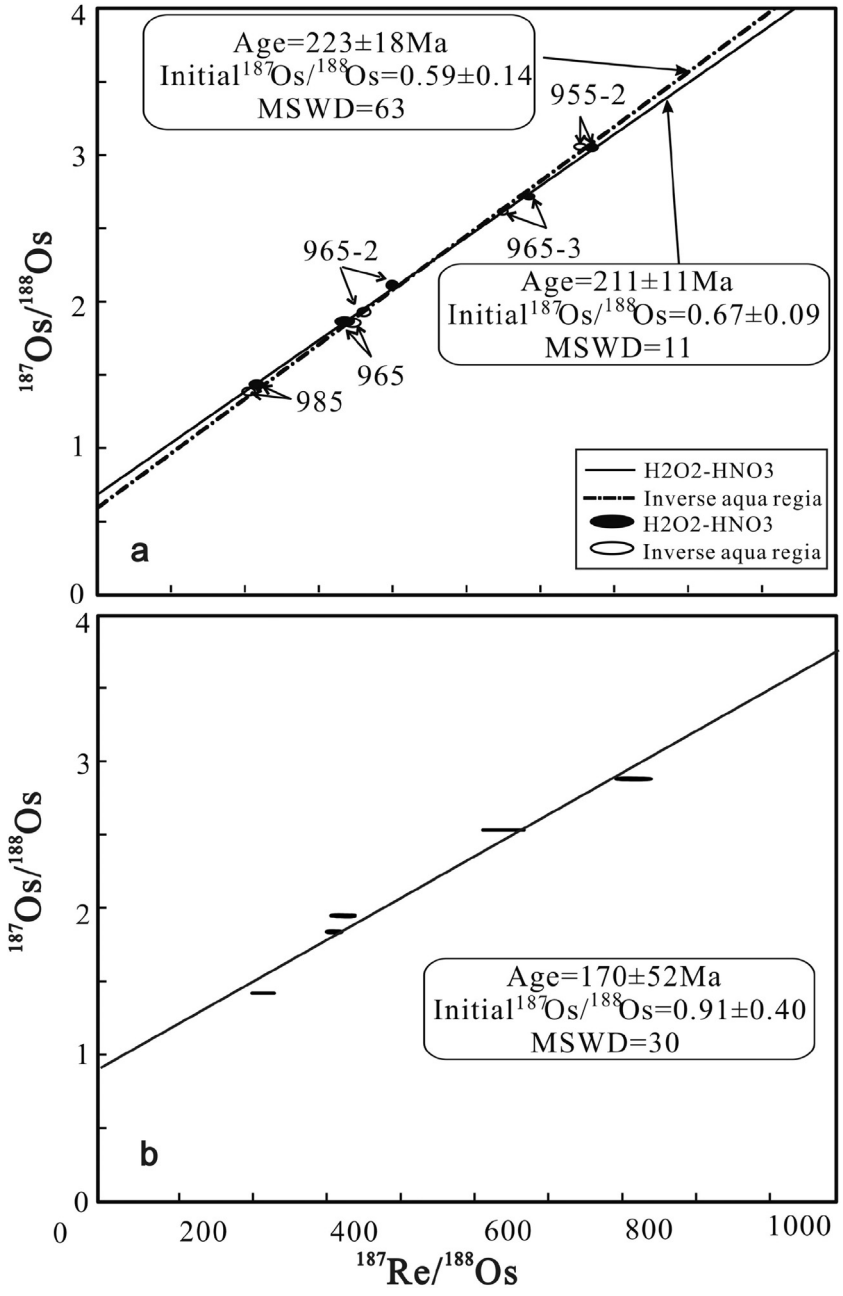

Fig. 3. Re–Os isochron of the Dabaoshan black shales. (Fig. a) Data obtained by inverse *aqua regia* digestion are represented by open ellipses, their regression is indicated by the dashed isochron, data obtained by H_2O_2–HNO_3 digestion are represented by filled ellipses, and their regression by the solid isochron. (Fig. b) Data obtained by CrO_3–H_2SO_4, digestion methods, and the Re–Os isochron ages were calculated using Isoplot 3.0 (Ludwig [17]).

method leaches less detrital Re and Os than the conventional methods, as demonstrated by analyses of natural samples (Dabaoshan black shales). The inverse *aqua regia* method yields greater scatter, older Re–Os isochron ages (223 ± 18 Ma, 2σ; MSWD = 63), and lower $^{187}Os/^{188}Os_i$ values (0.59 ± 0.14) than H_2O_2–HNO_3 digestion (211 ± 11Ma, 2σ; MSWD = 11; $^{187}Os/^{188}Os_i$ = 0.67 ± 0.09), as it liberates a greater amount of stable detrital Os, with a low Re/Os value. Because of the high Re blank of our CrO_3–H_2SO_4 solution, we could not systematically compare the Re–Os results obtained by H_2O_2–HNO_3 and CrO_3–H_2SO_4. The greater leaching of detrital Re and Os by CrO_3–H_2SO_4 may cause significant scatter on relative Re–Os isochrons. We propose that H_2O_2–HNO_3 digestion increases the precision and accuracy of Re–Os geochronology for organic-rich sedimentary systems, and may thus complement or replace conventional techniques.

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Table 3
Re and Os concentrations, and Os isotopic ratios of the Dabaoshan black shale.

Sample	Re (ng/g)	2SE	Os (ng/g)	2SE	$^{187}Os/^{188}Os$	2SE	$^{187}Re/^{188}Os$	2SE
5810-965 hp	4.87	0.03	0.0815	0.0007	1.8545	0.0043	337	4
5810-965 ar	4.82	0.04	0.0819	0.0001	1.8476	0.0029	347	3
5810-965 cr	4.46	0.11	0.0818	0.0002	1.8365	0.0058	321	8
5810-965-2 hp	3.40	0.01	0.0517	0.0002	2.0978	0.0082	399	2
5810-965-2 ar	3.38	0.01	0.0558	0.0001	1.9264	0.0034	361	1
5810-965-2 cr	3.03	0.12	0.0543	0.0001	1.9505	0.0030	333	13
5810-965-3 hp	5.94	0.02	0.0640	0.0003	2.7093	0.0062	586	4
5810-965-3 ar	5.80	0.02	0.0674	0.0001	2.6109	0.0042	549	2
5810-965-3 cr	5.78	0.24	0.0666	0.0001	2.5295	0.0061	548	23
5810-985 hp	3.21	0.03	0.0840	0.0006	1.4308	0.0097	215	2
5810-985 ar	3.12	0.02	0.0856	0.0001	1.3841	0.0020	204	1
5810-985 cr	3.40	0.19	0.0850	0.0004	1.4212	0.0038	225	13
5810-955-2 hp	7.68	0.04	0.0763	0.0001	3.0466	0.0079	669	3
5810-955-2 ar	7.60	0.03	0.0773	0.0001	3.0529	0.0041	654	3
5810-955-2 cr	8.73	0.22	0.0790	0.0001	2.8795	0.0047	724	18

"ar" denotes inverse *aqua regia* digestion, "hp"denotes H_2O_2-HNO_3 digestion (H_2O_2; HNO_3 = 5:1), "cr" denotes CrO_3-H_2SO_4 digestion.
Uncertainties on each digestion in this study all are estimated by error propagation of uncertainties in N-TIMS (Os and $^{187}Os/^{188}Os$) and ICP-QMS (for Re) measurements (2SE).

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