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**Precise Re-Os ages of organic-rich mudrocks and the Os isotope
composition of Jurassic seawater**

by

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Abstract

Rhenium and osmium isotope and abundance data have been obtained on precisely-located samples from three suites of immature, organic-rich mudrocks from Jurassic coastal outcrops in England. The data provide precise and accurate whole-rock ages of 207 ± 12 Ma, 181 ± 13 Ma and 155 ± 4.3 Ma for suites of Hettangian, Toarcian (*exeratum* Subzone) and Kimmeridgian (*sensu anglico*, *wheatleyensis* Subzone) samples. These new Re-Os ages are indistinguishable, within the assigned analytical uncertainties, from interpolated depositional ages estimated from published geological timescales, and establish the importance of the Re-Os dating technique for chronostratigraphic studies. Early-diagenetic pyrite nodules possess levels of Re and Os which are ~1–2 orders of magnitude lower than in the enclosing organic-rich mudrocks, indicating that these elements had already been removed from sediment pore waters at the time of nodule formation. Thus the Re-Os isotope system in these organic-rich mudrocks has been closed since, or from very soon after, the time of sediment deposition. Because most of the Re (98%+) and Os (95–99.8%+) in the mudrocks is shown to be hydrogenous, the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of the samples is interpreted to be that of contemporaneous seawater. The data thereby provide the first estimates of the Os isotope composition of Jurassic seawater. During the earliest Jurassic (Hettangian), the seawater $^{187}\text{Os}/^{188}\text{Os}$ ratio was extremely unradiogenic (~0.15); it had increased to ~0.8 at the end of the Early Jurassic (Toarcian) ~20 Ma later, while in the Late Jurassic (Kimmeridgian) the seawater $^{187}\text{Os}/^{188}\text{Os}$ ratio was ~0.59. The most likely explanation for the unradiogenic Os isotope composition of Hettangian seawater is that the contribution of unradiogenic Os to the oceans from the hydrothermal alteration of oceanic crust greatly exceeded the input of radiogenic Os from the continents at that time. This interpretation is in line with observations suggesting that global weathering rates were low in the Hettangian, and that increased hydrothermal and volcanic activity preceded the break-up of Pangea. The Re/Os ratios of Hettangian mudrocks (and by inference, of contemporaneous seawater) are similar to those of mudrocks deposited at later times during the Jurassic, and argues against the unradiogenic Os in Hettangian seawater being derived from extraterrestrial meteoritic sources.

Keywords: rhenium; osmium; dating; stratigraphy; mudrocks; Jurassic; seawater

1. Introduction

The chemical and isotopic compositions of marine sediments and chemical precipitates reflect the changing composition and physical condition of the seawater in which they accumulated. Marine sediments and precipitates therefore preserve a record of the changes that have occurred in the global inputs to the oceans, and by inference provide information about the varying environmental conditions that have caused the balance of these inputs to alter. Over geological time, marine sediments which are lithified to sedimentary rocks may in principle also be used to study earlier episodes of environmental change in Earth history.

The present study examines the potential of well-characterised, immature organic-rich mudrocks (ORM) for providing (1) precise Re-Os depositional ages for ORM, which are common in the geological record and yet are extremely difficult to date radiometrically, and (2) an estimate of the Os isotope composition of contemporaneous seawater. Three well-preserved whole-rock sample suites were collected from Jurassic coastal sections in Dorset (Hettangian–Sinemurian and Kimmeridgian (*sensu anglico*)), and in Yorkshire (Toarcian). In all three sample suites, levels of Re and Os and Re/Os ratios are much higher than average crustal values but are broadly similar to values reported previously for ORM [1–3]. The data for each sample suite define accurate Re-Os ages for marine ORM, demonstrating that the Re-Os isotope system closes at or soon after the time of sediment deposition in well-preserved, immature samples of these rocks. The calculated ages correspond closely to the interpolated timescale ages for the ammonite zones from which the ORM were obtained [4] while the initial $^{187}\text{Os}/^{188}\text{Os}$ ratios provide the first estimates of the Os isotope composition of Jurassic seawater.

2. Scientific background

The isotopic composition of Os in the Earth has changed over time as a result of the β -decay of ^{187}Re to ^{187}Os ; this property invests the Re-Os system with its use as a geochronometer and isotopic tracer. It is now well-established that the Os isotope composition of seawater, expressed as $^{187}\text{Os}/^{188}\text{Os}$, has varied during the Cenozoic in a manner analogous to that for Sr [5–9]. These variations have been attributed to processes similar to those responsible for

the increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater over the same period, and reflect the changing balance between the major inputs to the oceans from continental weathering, carbonate dissolution, and hydrothermal activity at mid-ocean ridges. Thus the particularly sharp increase in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater from ~ 0.7078 ca. 40 Ma ago to the present-day maximum of ~ 0.70916 [10,11] is thought to result from the release of relatively large quantities of radiogenic Sr from the erosion and weathering of the Himalaya. The $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater is a balance between the input of radiogenic from continental weathering and unradiogenic Os from the hydrothermal alteration of juvenile oceanic crust and the dissolution of meteoritic material. Release of radiogenic Os during Himalayan weathering has also been cited as the cause of the rise in the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater during the Cenozoic [6,12]. However, the geochemistry and marine behaviour of Os and Sr differ widely, and thus the Os and Sr isotope systems can convey different information. For example, because the residence time of Os is ~ 40 ka [13,14] and some 2 orders of magnitude shorter than that of Sr, the Os isotope record will in principle record changes in marine chemistry which have occurred on much shorter timescales than can Sr. Thus the Os isotope composition of seawater may reflect glacial-interglacial variations [15] whereas the Sr record does not [16]. Furthermore, the relative distribution of Os and Sr in the Earth and in meteorites is very different reflecting the siderophile/chalcophile characteristics of Os and the lithophile characteristics of Sr. At the Cretaceous–Tertiary (K–T) boundary the marine Os isotope record shows a dramatic minimum due to the input of relatively large amounts of unradiogenic Os from the impactor [5, 7], whereas the change in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio across the K–T boundary is very small at 28×10^{-6} [17].

The Os isotope record for Cenozoic seawater has been recovered from a number of marine materials, including deep-sea pelagic sediments [5], metalliferous coatings on carbonate-rich sediments [6,7,9], and hydrogenous Fe-Mn crusts [8]. However, significant discrepancies exist between Os isotope records obtained from different materials (e.g. Fe-Mn crusts and metalliferous carbonate-rich sediments) of apparently similar age from the same oceans [6,8], and also between records obtained from the same materials (Fe-Mn crusts) from different oceans [8]. Many of the deep-sea core samples used for Os isotope analysis have been leached, a consequence being that the differences between the leached and unleached data do

not allow for any reliable estimate of the accuracy of the results. Furthermore, apart from 3 analyses of samples marginally older than the K–T boundary [7], the record before the Cenozoic has remained undefined because marine material of known age suitable for Os isotope analysis had not been identified before this study.

ORM are a widespread and important class of marine sedimentary rock containing elevated levels of organic carbon which with burial and heating may produce hydrocarbons. ORM also contain relatively high abundances of certain inorganic elements (e.g. Ni, V, U, Mo, Re and the platinum group elements (PGE)) which are incorporated into organic-rich sediments either through their sequestration from seawater by organic species or as a result of redox changes [2,18–20]. At certain times in the past, large-scale deposition and preservation of organic-rich sediments took place over extensive areas of epicontinental seas [21,22]; such seas covered large areas of N. Europe during much of the Jurassic and have given rise to large quantities of ORM. Palaeogeographic reconstruction together with sedimentologic evidence (e.g. [23]) indicate that these European epicontinental seas were not landlocked, but were open to free circulation with the Tethyan ocean, suggesting that both the Sr and Os isotope compositions of the hydrogenous components in the sediments at the time of deposition should reflect that of the open ocean. Previous work [1,3] has indicated the potential for obtaining geochronological information from the Re-Os system in ancient ORM but results were constrained by reconnaissance sample selection and early analytical techniques.

3. Sample selection and analytical procedures

Three suites of ORM were collected with reference to published stratigraphical logs [24–28] from sections which are biostratigraphically well-dated by ammonites. Hettangian and Sinemurian (Lower Jurassic) laminated mudrocks were sampled at Lyme Regis and Charmouth in Dorset; Toarcian (Lower Jurassic) laminated mudrocks at Port Mulgrave, Yorkshire; while Upper Jurassic ORM samples were obtained from the Kimmeridgian (*sensu anglico*) near Kimmeridge, Dorset; (note that the Kimmeridgian of England is equivalent to all of the Kimmeridgian and part of the Tithonian elsewhere). Lower Jurassic samples

(Hettangian/Sinemurian, deposited ~206–196 Ma ago [4]) were obtained from the *Psiloceras planorbis*, *Alsatites liasicus*, *Schlotheimia angulata*, *Arietites bucklandi*, *Caenisites turneri* and *Asteroceras obtusum* ammonite biozones, while the Kimmeridgian samples were from the *Aulacostephanus eudoxus*, *A. autissiodorensis*, *Pectinatites wheatleyensis*, *P. huddlestoni* and *P. pectinatus* zones which were deposited ~150 Ma ago [4]. The samples collected from the Toarcian (uppermost Lower Jurassic, ~183 Ma ago) section in Yorkshire were from the *Harpoceras exeratum* Subzone and the top 35 cm of the underlying *Dactylioceras semicelatum* Subzone. Precise sample locations are shown in Fig. 1. Based on a rough calculation of the ratio of ammonite zones to section thickness, the Hettangian section sampled is thought to be condensed compared with the other Jurassic sections sampled, and probably represents a depositional interval of ~4 Ma. In contrast, the samples collected for the Kimmeridgian and Toarcian Re-Os regressions were from relatively expanded intervals representing no more than ~200–500 ka. Sample positions were recorded with a vertical uncertainty of ± 2 cm and a lateral uncertainty of ± 5 cm. In an attempt to ensure that Re and Os had remained in reduced oxidation states thus limiting their mobility after sediment deposition, and to target material with a high proportion of hydrogenous Re and Os, only those lithologies which were judged to contain greater than ~5% TOC (total organic carbon) were sampled.

The time resolution potentially available from mudrock sections is very high; for example, the vertical sampling uncertainty of ± 2 cm corresponds to a time interval in the Kimmeridgian sections of ± 1250 a, assuming that ~8 m compacted ORM of the *wheatleyensis* Subzone represents ~500 ka. In comparison, the accumulation rates of those materials which have been used previously for recovering the Os isotope compositions of seawater—Fe-Mn crusts and nodules, and deep-sea sediment—may be as much as 3–4 orders of magnitude lower, with the result that the time resolution available from such samples is often greatly reduced.

Sample preparation and the chemical separation of Re and Os broadly followed procedures published previously [29,30] involving Carius tube digestion and solvent extraction prior to isotope ratio and abundance determinations by N-TIMS. However, some modifications were introduced to accommodate the relatively large amounts of sulphide and organic carbon

which require full oxidation to sulphate and carbon dioxide, respectively. In brief, 0.3–0.5 g sample aliquots containing up to ~20% TOC were digested at temperatures up to ~240°C, using 12 ml of inverted (Le Fort) aqua regia in sealed pyrex Carius tubes with an overall capacity of ~30 ml. Proportionally smaller aliquots were used for samples with >20% TOC. Because the resulting carbon dioxide dissolves in the digest solution and pressurises the Carius tubes, extra care is needed during and after digestion. Subsequent tube opening was carried out only after the tube and contents had been chilled thoroughly in dry ice. Thereafter, chemical procedures follow those published previously [30].

4. Results

The measured Re and Os abundances and $^{187}\text{Os}/^{188}\text{Os}$ ratios of 46 Jurassic ORM samples, and of 2 pyrite nodules, together with the TOC and S contents of most of the samples, are presented in Table 1. Overall, Re and Os abundances in the ORM samples are highly variable, ranging from ~10–456 ppb (Re) and ~0.17–3.17 ppb (Os). While these levels are generally similar to values published previously for ORM [1,3] they are very much greater than average crustal abundances of 0.39 ppb for Re and 0.05 ppb for Os [31]. Re and Os abundances in the Toarcian samples are generally lower than are their abundances in Hettangian–Sinemurian and Kimmeridgian samples from Dorset and occupy a much more restricted range from 9.8–19.4 ppb and 0.196–0.271 ppb, respectively. Re and Os abundances in an early-diagenetic pyrite nodule (Kwh 96-34) of 2.65 ppb and 0.11 ppb, respectively, are much lower than those in the adjacent ORM sample Kwh 96-35, with 69.6 ppb Re and 0.833 ppb Os. The TOC and S data for the Hettangian, Toarcian and Kimmeridgian ORM define distinct fields (Fig. 2a). There is no clear relationship between TOC and S in any of the groups, except for the Kimmeridgian samples which show a bimodal distribution because 5 of the Kimmeridgian samples have unusually high TOC of 45–55%. The TOC of most ORM samples analysed here are in the range ~5–16%.

Covariations between the S, TOC, Re and Os abundances of the samples are shown in Fig. 2b–f. There is a broad, positive correlation between the abundances of Re and ^{192}Os (the unradiogenic or 'common' Os component (Fig. 2b)), but no simple relationships exist

between S and Re, S and ^{192}Os , TOC and Re, or TOC and ^{192}Os (Fig. 2c–f). However, the relatively high Re and ^{192}Os abundances found in all the Hettangian samples distinguish these from the other samples.

The calculated $^{187}\text{Re}/^{188}\text{Os}$ ratios of the samples vary from 212 to 1571, and are all greater than the ratio of ~42–48 for average continental crust [31]). Their present-day $^{187}\text{Os}/^{188}\text{Os}$ ratios vary between 0.72 and 5.52 and are generally higher than the average continental crustal value of ~1.26 [31] despite their relatively young depositional ages of ~150–200 Ma. The Re-Os isotope data for samples from the Hettangian (n=13), the Toarcian *exeratum* Subzone (n=9, including 2 samples from 8 cm and 35 cm below the base of the subzone) and the Kimmeridgian *wheatleyensis* Subzone (n=11, including 1 sample from 10 cm below the base of the subzone) define whole-rock ages (Fig. 3a–c) of 207 ± 12 Ma (MSWD=88), 181 ± 13 Ma (MSWD=17) and 155 ± 4.3 Ma (MSWD=11), as calculated using *Isoplot* [32]. All the ORM samples from the 3 selected stratigraphic intervals were used for the regression calculations, except for Toarcian sample Tex 97-38 which has an anomalously low $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ (Table 1). These new Re-Os ages are indistinguishable within the assigned analytical uncertainties from the interpolated depositional ages for these rocks taken from the timescale of Gradstein et al. [4].

5. Discussion

The Re-Os isotope results from the 3 sample suites (Table 1) and their sub-groups, as summarised above, provide the first direct, absolute age determinations for Jurassic ORM and highlight the potential for obtaining precise and accurate ages for marine mudrocks. The significance of the Re-Os data presented here is four-fold: (1) the results demonstrate that the Re-Os isotope system can provide direct age information from well-preserved, immature ORM and that their Re-Os ages are indistinguishable from the interpolated depositional age of the sediments. (2) The Re-Os isotope system in ORM must have remained closed since or soon after sediment deposition in order for the observed isotopic relationships to have been preserved. (3) It is argued below that the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios of ORM from appropriate settings reflect the Os isotope composition of contemporaneous seawater, thus providing a

means of establishing the pre-Cenozoic seawater Os isotope curve and of correlating it with other indices of palaeoenvironmental change. (4) The Re-Os data for the Jurassic ORM, and their co-variations with TOC and S abundances, illuminate the processes whereby these elements are removed from seawater into anoxic sediments.

5.1 Significance of the Re-Os whole-rock ages

There are 3 criteria which must be met if Re-Os isotope data from ORM are to provide reliable estimates of the age of sediment deposition. These are: (1) the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios of contemporaneous samples must be similar, (2) the Re-Os system must have closed at or soon after the time of sediment deposition, and (3) the samples must possess a range in Re/Os ratio in order to generate a range in present-day $^{187}\text{Os}/^{188}\text{Os}$ ratios. The principles underlying these criteria are essentially the same as those for obtaining reliable isotope ages from igneous and metamorphic rocks (e.g. [33,34]). In the present case the MSWD of each Re-Os regression is greater than unity, and so either criteria (1) or (2) has not been strictly fulfilled. Thus in the ORM analysed here either the Re-Os system has been slightly perturbed, or $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios of broadly contemporaneous samples were not identical, or both. Nevertheless, the first-order observations from the new Re-Os isotope data are: (1) that the Re-Os age estimates overlap the interpolated stratigraphic ages for these rocks taken from the published timescale, which is based on a few radiometric ages of volcanic horizons and correlation with geomagnetic polarity measurements and biostratigraphy (i.e. [4]). (2) The $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ for samples from similar stratigraphic horizons are remarkably similar (Fig. 1 and Table 1). (3) All the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ are lower than the present-day $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater. These observations indicate that, despite the high MSWD of the Re-Os regressions, the Jurassic ORM analysed here retain valuable Re-Os information recording the age of deposition and their $^{187}\text{Os}/^{188}\text{Os}_{(i)}$.

Although its MSWD is 11, it is noteworthy that the Re-Os whole-rock age of 155 ± 4.3 Ma as defined by all 11 Kimmeridgian *wheatleyensis* Subzone samples is the most precise date yet obtained for this period (J. G. Ogg, *pers. comm.* and [4]). The relative uncertainties on the Re-Os ages reported here are an order of magnitude lower than those obtained on Devonian

ORM by Ravizza and Turekian [1] when the Devonian data are calculated using *Isoplot* [32], reflecting advances in analytical techniques and careful sample selection. For example, only well-preserved, immature ORM have been used in the present study. This was considered to be very important as the results of Barre et al. [35] suggest that Re and Os are strongly partitioned into crude oil following source-rock maturation. It is probable that the Re-Os system will have been disturbed in ORM which have been heated at or above the modest temperatures required for hydrocarbon production, and thus it is unlikely that ORM would retain meaningful Re-Os age information under such conditions.

It is the relatively high MSWD of the three Re-Os regression analyses reported here which impose the major limitations on the precision of the Re-Os age estimates for the Jurassic ORM, reflecting ‘geological scatter’ in excess of the assigned analytical uncertainties. The data show that Re/Os ratios can vary by factors of ~2–3 over vertical length-scales of a few cm., although usually the Re/Os ratio of laterally adjacent samples is similar and the factors controlling this ratio in ORM remain unclear. Because the rate of sediment accumulation during the Hettangian was relatively low, giving rise to a condensed stratigraphic succession, a suitable spread in Re/Os ratio has been obtained by taking samples from a longer depositional interval of ~4 Ma. The most precise Re-Os age for the 3 sample suites (that of the Kimmeridgian samples) was obtained using samples from a relatively short depositional interval of ~500 ka. However, it is clear that not all the Re-Os data from the ORM analysed here provide precise chronological information, either because of an insufficient spread in Re/Os ratio of the samples analysed or because of small-scale disturbance of the Re-Os system in apparently pristine ORM.

Despite these constraints, the new data establish the great potential of the Re-Os method for dating ORM. ORM are much more common in the sedimentary record than are dateable ash layers and this is particularly so for much of the Jurassic. Furthermore, a major advantage of Re-Os age determinations from ORM is that they are made directly on the mudrocks themselves, thus eliminating any errors introduced through lateral correlation.

5.2 Mechanism and timing of Re and Os uptake by ORM

Certain trace elements such as Cd, Zn, Ni, Mo and U are highly concentrated in organic-rich sediments and ORM [18,21,22,36]. These elevated abundances occur as a result either of their scavenging by organic components (for Cd, Zn and Ni) or their direct reduction from seawater (for Mo and U) [20,37,38]. It is likely that the behaviour of Re mirrors that of Mo [38–41], and that the elevated levels of Re (and perhaps Os also) in marine ORM, as reported here and previously [1,3], result from their direct reduction from seawater or sediment porewaters. The lack of any clear correlation between TOC and either Re or Os abundance (Fig. 2b–f) is in line with the suggestion that Re and Os are incorporated into organic-rich sedimentary deposits as a result of redox reactions, rather than from organic scavenging or complexation [20,37,38]. Partial decarbonation after stabilisation of Re and Os within the sediment would corrupt any original relationship between TOC and trace element abundances.

Despite high PGE abundances in the Kimmeridgian ORM, the distribution of these elements appears to be uniform within hand specimens, and neither PGE-rich phases nor regions of high PGE concentration have been observed by SEM (H. M. Pritchard, *pers. comm.*). Furthermore, the extremely low levels of both Re and Os in the sample taken from the large (~5 cm dia.) pyrite nodule Kwh 96-34 suggests that these elements were not abundant in the pore fluids from which the pyrite formed. Had they been so, the expectation would be that the Re and Os would have been concentrated in the pyrite. Because sedimentary layering is observed to deform around nodules such as Kwh 96-34, they are known to have formed soon after sediment deposition while the sediment was still uncompact [42]. This observation suggests that Re and Os are likely to have been removed from seawater or pore fluids during or very soon after sediment deposition.

5.3 Sources of Re and Os in Jurassic ORM

Direct comparison between the very high Re abundances in the Jurassic ORM samples (10–456 ppb) and average levels in upper continental crust (~390 ppt [31]) indicates that the terrigenous contribution must be extremely small and that at least 96–99.9+% of the Re in these samples is hydrogenous in origin. The measured Os abundances of the Jurassic ORM

samples also greatly exceed levels estimated for average continental crust, although to a lesser extent than for Re. Contributions to the Os budgets of ORM, in addition to the dominant hydrogenous component, come from a relatively radiogenic terrigenous component, and a relatively unradiogenic micrometeorite component [1,3,43]. The reducing conditions within the ORM are likely to ensure that extraterrestrial Os will have remained immobile since incorporation within the sediment, and thus this extraterrestrial Os will have contributed to the measured Os budget of the samples. Although the meteorite flux to the Earth during the Jurassic is unknown, a recent estimate suggests that the flux during the Cenozoic has remained constant at $\sim 3.7 \times 10^4$ T/a [43]. Using this value, together with a chondritic Os abundance of 486 ppb [44], and assuming an evenly distributed global meteorite flux together with an accumulation rate of 50 m/Ma for compacted ORM, the extraterrestrial Os contribution amounts to $\sim 0.28 \times 10^{-12}$ g Os/g ORM. The extraterrestrial contribution thus forms an insignificant proportion (~ 0.01 – 0.1%) of the overall Os budget in ORM, and it has been ignored in the following discussion.

The magnitude of the Os contribution from the terrigenous component of ORM is, perhaps surprisingly, as or more difficult to assess than is the extraterrestrial contribution. Previously, the Os contribution from the terrigenous component has been estimated with the assumption that its abundance and isotopic composition is similar to that of average continental crust [31,45]. It is probable, although difficult to prove, that such an assumption is largely incorrect, since the distribution of Os and the other PGE within the crust is far from uniform. These elements tend to be concentrated in relatively dense sulphides, in PGE-bearing minerals in ultramafic rocks and in ORM, which on weathering either dissolve in oxygenated river- or sea-water, or are deposited in estuaries and nearshore sediments. Clay and silt particles predominate in the terrigenous component of ORM and their geochemistry is such that they are unlikely to host significant quantities of continental-derived PGE. Moreover, any Os adsorbed onto clay minerals—should this occur—is likely to equilibrate with Os dissolved in oxygenated seawater during transport and settling, and so the terrigenous component of ORM is more likely to reflect the Os isotope composition of seawater (i.e. the hydrogenous component) than that of the continents. Assuming, therefore, that the terrigenous component of ORM contains 10 ppt Os (i.e. 20% of the average crustal

abundance of ~50 ppt Os [31]), the hydrogenous contribution will account for 95+% of the Os in the Toarcian samples (i.e. those with the lowest Os abundances of the samples analysed here), and 99.8+% for many of the other samples. Because the Os contribution from the terrigenous component is very small and because its isotope composition is unknown, no attempt has been made to correct for it.

5.4 Accumulation rates of Re and Os in Jurassic ORM

As noted in previous studies, organic-rich sediments and ORM act as major repositories of Re and Os in the Earth's crust [1,38,40,46,47]. Thus significant proportions of the global marine budgets of these elements may be removed from seawater during times of widespread sediment deposition under suboxic or anoxic conditions. The following calculation shows that the burial rates of Re and Os in ORM may at times have equalled or even exceeded the annual global riverine input of these elements to the oceans (based on present-day estimates of riverine fluxes), possibly leading to a reduction in their seawater abundances. An important corollary of this observation is that the estimates for Re and Os accumulation rates in ORM during much of the Jurassic are sufficiently high so as to preclude an Os isotope bias from local river systems, simply because these are incapable of delivering sufficiently large quantities of Os to the accumulating organic-rich sediments. For this reason, the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of the ORM studied here reflect that of the open ocean at the time of sediment deposition.

Consider an area of seafloor accumulating sediment at a rate which gives a thickness of compacted ORM of 1 cm/200 a (i.e. 50 m ORM/Ma). If the ORM has a density of 2.5 g/cm³ and contains 0.4 ppb Os, and assuming that all of the Os is hydrogenous in origin, the mass of Os accumulating per cm² is 5×10^{-12} g/a. Thus 50 kg Os accumulates annually within a relatively modest area of organic-rich sedimentation of 10⁶ km², which is approximately 0.3% of the total present-day area of the ocean floor. (It is noteworthy that preserved Kimmeridgian organic-rich sedimentary deposits are estimated to have covered at least 3% of the ocean floor [48]). This quantity of Os is broadly similar to the annual present-day global riverine flux of Os to the oceans, estimated at 48 kg [49] and 70 kg [45]. It is also instructive

to calculate the volume of seawater required to provide the hydrogenous Os budget during the accumulation of organic-rich sediment. The Os abundance of present-day seawater has recently been determined at 0.004 ppt [13] and at 0.0109 ppt [14]. Taking the higher value of 0.0109 ppt, the annual quantity of Os accumulating per cm^2 (5×10^{-12} g) is contained in a column of seawater ~ 4.6 m by 1 cm^2 . Similar calculations for Re, assuming an ORM abundance of 100 ppb, yield an accumulation rate of $1.25 \times 10^4 \text{ kg/a}/10^6 \text{ km}^2$, which is close to the present-day mean annual riverine input of $1.54 \times 10^4 \text{ kg}$ [40]. Likewise, the quantity of Re accumulating annually per cm^2 (1.25×10^{-9} g), assuming a mean seawater Re concentration of 8 ppt [46], is contained in a water column 1.56 m by 1 cm^2 . The difference in water volume required to provide the hydrogenous Re and Os budgets of ORM reflects differences in their seawater concentrations and uptake rates in the accumulating organic-rich sediments. These calculations serve to show that the accumulation rates of Re and Os in ORM are sufficiently high to preclude bias from local rivers, and that the oceans acted as a large buffered reservoir which was able to provide ready replenishment of these elements in the vicinity of ORM deposition.

The possibility that the Re abundance of seawater—and hence its marine residence time—has varied in the past as a result of the extensive deposition of organic-rich sediments has been suggested by Colodner et al. [40] and it is likely that widespread deposition of organic-rich sediments would cause the marine abundance and residence time of Os also to vary. The very high Re and Os contents of the Hettangian ORM samples, which reach 456 ppb Re and 3.17 ppb Os in Hli 97-107c, suggest either that the seawater Re and Os abundance was unusually high at that time, or that sediment accumulation rates were relatively low. Using ages taken from the Mesozoic timescale of Gradstein et al. [4], a crude estimate suggests that rates of sediment accumulation at Lyme Regis were appreciably lower in the Hettangian (at around ~ 2 m/Ma) compared, for example, with rates during the Kimmeridgian (at around ~ 20 – 100 m/Ma). Thus the very high Re and Os abundances in the ORM samples from the lowermost Jurassic may be a simple consequence of low sediment accumulation rates.

5.5 Os isotope variations in Jurassic seawater

The $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios obtained from the 3 Re-Os whole-rock regressions, which are interpreted here to represent that of contemporaneous seawater, cover a wide range from 0.15 ± 0.16 (defined by the Hettangian data) to 0.80 ± 0.07 (defined by the Toarcian regression). All are lower than the $^{187}\text{Os}/^{188}\text{Os}$ ratio of present-day seawater of ~ 1.03 [5–8, 13–15]. The variations in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ from the regression calculations, and mean $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios from groups of individual samples from Table 1, are shown in Fig. 4, which represents the first attempt to define the changing Os isotope composition of Jurassic seawater. Of particular note is the unradiogenic Os isotope composition defined by all the Hettangian samples, and the very steep rise in $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ in the ~ 20 Ma period between the deposition of the Hettangian and Toarcian samples.

The consistently low $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios of the Hettangian ORM samples indicate that the input of radiogenic Os from continental weathering was greatly outweighed by a source of unradiogenic Os to the oceans at that time. The most likely source of this unradiogenic Os would have been through the hydrothermal alteration of juvenile oceanic rocks, or from the dissolution of meteoritic material. To obtain a seawater $^{187}\text{Os}/^{188}\text{Os}$ ratio in the range 0.15–0.31, assuming that the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the unradiogenic end-member was 0.127 (close to that of present-day mantle) and that the $^{187}\text{Os}/^{188}\text{Os}$ ratio of the radiogenic contribution from crustal weathering was 1.4, requires an input of crustal Os of just 2–13%. By comparison, the present-day radiogenic Os isotope composition of seawater requires a far greater crustal Os contribution of as much as 70% [43]. That the predominance of highly unradiogenic Os in the Hettangian might have been a consequence of meteorite impact(s) appears attractive at first sight because the low $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios occur in rocks which were deposited soon after a major geological boundary (the Triassic–Jurassic (T–J) boundary) close to which a number of large impacts are known to have taken place [50,51]. However, these Early Jurassic ORM also contain very high levels of Re and their $^{187}\text{Re}/^{188}\text{Os}$ ratios are not dissimilar to those of the younger Toarcian and Kimmeridgian samples; the abundances of Re and ^{192}Os (Fig. 2b) of all the ORM samples analysed here show a positive correlation. Because the Re/Os ratio of chondritic meteorites (0.075 [44]) is some 2 orders of magnitude lower than that of the continental crust, at ~ 8 [31], a meteoritic source would have been unable to account for the high levels of both Re and unradiogenic Os in Hettangian ORM.

Moreover, most of the Late Triassic impacts appear to have occurred ~5–20 Ma before the T–J boundary [50,51]; the short marine residence time of Os [13–15] would make it unlikely that unradiogenic Os of meteoritic origin would remain in seawater for this length of time.

Thus the Re and Os characteristics of the Hettangian ORM analysed here—very high Re and Os abundances, together with low $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ and $^{187}\text{Re}/^{188}\text{Os}$ ratios typical of ORM from later periods in the Jurassic—are more likely to reflect the relative effects of enhanced marine hydrothermal activity and diminished continental weathering in the earliest Jurassic as compared with the Toarcian, the Kimmeridgian or the present-day. Palaeogeographic reconstruction and palaeoclimate modelling (e.g. [52]) indicate that during the Late Triassic–Early Jurassic the mean relief over the supercontinent Pangea was low and that large ice sheets were absent; this time also marked the onset of a global sea-level rise. It is therefore probable that the rate of continental weathering was low with the consequence that relatively small amounts of radiogenic Os were released to the oceans. Thus the Os isotope composition of seawater would have been dominated by the unradiogenic Os input from hydrothermally-altered oceanic crust. The pronounced decline in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater, which started in the Early Sinemurian [53] immediately after the Hettangian, has also been attributed to the onset of accelerated hydrothermal activity in the Early Jurassic. The delay of ~3–4 Ma between the response shown by the Os and Sr isotope signals might reflect the buffering effect imposed by the long marine residence time of Sr (at 2–3 Ma) compared with the much shorter residence time of ~10–40 ka estimated for Os [13–15]. However, it is noteworthy that while the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater continued to fall for a protracted period of ~15 Ma until the Toarcian, the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater as indicated by the Toarcian ORM had risen to much higher values ($^{187}\text{Os}/^{188}\text{Os} \sim 0.8$) by that time. The low $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater appears to have lasted only for the duration of the Hettangian to the middle Sinemurian, as the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratio of the late Sinemurian sample Sob 96-14 is 0.55 (Fig. 4).

6. Conclusions

1. The Re-Os isotope system in well-preserved samples of contemporaneous, immature Jurassic ORM from England has yielded whole-rock ages of 207 ± 12 Ma, 181 ± 13 Ma and 155 ± 4.3 Ma for samples of Hettangian (n=13), Toarcian (n=9) and Kimmeridgian *sensu anglico* (n=11) age which are indistinguishable, within analytical uncertainty, from their interpolated stratigraphic ages. The Re-Os isotope system has thus been closed in these rocks since the time defined by the regressions, and it possesses great potential for stratigraphic dating and refining the geological timescale.
2. The abundances of Re and Os in early-formed diagenetic pyrite nodules are far lower than in the enclosing mudrocks, indicating that the incorporation of these elements into the sediments took place either during or soon after deposition.
3. Most of the Re and Os in ORM is shown to be hydrogenous in origin. The accumulation rates of these elements in Jurassic ORM were sufficiently high so as to preclude the Re and Os being derived predominantly from local continental run-off, with the important corollary that the Os isotope composition of the hydrogenous fraction was that of the open ocean. The contribution of Os to the ORM from micrometeorites is only 0.01–0.1% and may be ignored.
4. $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios, as defined by the Re-Os regression analyses and as calculated for individual samples, provide the first estimates of the Os isotope composition of contemporaneous Jurassic seawater. Seawater $^{187}\text{Os}/^{188}\text{Os}$ ratios were very low ($\sim 0.15\text{--}0.3$) at the start of the Jurassic, as defined by Hettangian ORM, and increased over the next ~ 20 Ma to a value of ~ 0.8 during the Toarcian. During the Kimmeridgian, the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater had fallen to ~ 0.59 .
5. The unradiogenic Os isotope composition of Hettangian seawater suggests that a relatively large, unradiogenic Os flux from the hydrothermal alteration of oceanic crust predominated over a relatively small, radiogenic Os flux from the continents at that time. This balance between the major Os inputs to the Hettangian oceans is quite unlike that at the present day, with seawater having a high $^{187}\text{Os}/^{188}\text{Os}$ ratio of ~ 1.03 as a consequence of high levels of continental weathering. The low $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater in the Hettangian is

consistent with evidence suggesting that low rates of continental weathering together with large amounts of volcanic and hydrothermal activity preceded the break-up of Pangea.

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Caption for Table 1

1. All Re and Os measurements were performed on a Finnegan MAT 261 instrument using a low-background SEM and peak-switching routines. Blanks during this study, 2–4 pg (Os) and 10–15 pg (Re), provided an insignificant contribution to the Os and Re analysed.
2. Within-run precision for the $^{187}\text{Os}/^{188}\text{Os}$ analyses was $\leq 0.2\%$ (2σ). The longer-term repeatability of $\sim 0.4\%$ (2 sd), as determined from standards, was used for the Re-Os regression calculations. The uncertainty on the $^{187}\text{Re}/^{188}\text{Os}$ ratios is 1.0% (2σ).
3. ^{187}Re decay constant is $1.666 \times 10^{-11} \text{ a}^{-1}$ [54].
4. $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ for individual samples were calculated as follows: (1) the Re-Os system is assumed to have been closed since sediment deposition; (2) depositional ages for the Kimmeridgian samples were based on the Re-Os whole-rock regression age of 155 Ma obtained for the *wheatleyensis* zone (wh) samples. The $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ for samples from the *eudoxus* (eu), *autissiodorensis* (au), *hudlestoni* (hu) and *pectinatus* (pe) zones were calculated relative to the 155 Ma *wheatleyensis* Subzone regression age at 158 Ma, 157 Ma, 154 Ma and 153 Ma, respectively. The age of the *exeratum* Zone (ex) samples was taken as that defined by the Re-Os data for the Toarcian samples (181 Ma), while the ages of the Sinemurian and Hettangian samples have been interpolated from the timescale of Gradstein et al. [4] and are: *obtusum* Zone (ob, 199 Ma), *turneri* Zone (tu, 200 Ma), *bucklandi* Zone (bu, 201 Ma), *angulata* Zone (an, 202 Ma), *liasicus* Zone (li, 203 Ma) and *planorbis* Zone (pl, 205 Ma).
5. n/a = not analysed.

Figure captions

Figure 1

Geographic and stratigraphic position of the samples analysed in this study. Graphic logs for the Kimmeridgian and Toarcian show the position of the samples used in the Re-Os age regressions (Fig. 3a, b). Height is given above the base of the relevant ammonite subzone or zone. Map of Great Britain showing the outcrop of the Jurassic and locations of the three principal sample localities. The Kimmeridgian samples were collected from the sea cliff and foreshore near Kimmeridge Dorset (SY 901789–SY 945773). Detailed stratigraphic logs and bed numbers in [26,27]. The Toarcian samples were collected from the foreshore at Port Mulgrave (NZ 79901755). Bed numbers and thicknesses from [24], ammonite zonation from [24,25]. The Hettangian and Sinemurian samples were collected from the foreshore and sea cliffs at Lyme Regis (SY 328910) and Charmouth (SY 364930 for sample Stu 96-11 and SY 375927 for samples Sob 96-12 and Sob 96-14). For detailed stratigraphic logs see [28].

Figure 2

Fig. 2 a–f. Variation diagrams showing relationships between the abundances of S, TOC, Re and Os within the ORM samples analysed in this study. Samples of different age are represented by the key shown in Fig. 2a, and this applies also to Fig. 2b–f. There is a broad positive correlation between the abundances of unradiogenic Os (^{192}Os) and Re, as seen in Fig. 2b. Importantly, no correlations are apparent in the other variation diagrams and, for example, neither the Re nor ^{192}Os abundance correlates with levels of TOC and/or S. However, samples of different age and those with atypical TOC define distinct regions within each figure. Thus the five high-TOC Kimmeridgian samples (45–55% TOC) form an obvious cluster in all the diagrams except Fig. 2b, while the Hettangian samples form a distinctive grouping in all six figures.

Figure 3

Re-Os evolution diagrams for ORM samples of Kimmeridgian age (Fig. 3a), Toarcian age (Fig. 3b) and Hettangian age (Fig. 3c). The 3 whole-rock sample suites define Re-Os ages of 155 ± 4.3 Ma, 181 ± 13 Ma and 207 ± 12 Ma which correspond to the depositional age of the sediments while the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ ratios, as defined by the regression data, reflect the Os isotope composition of contemporaneous seawater (see text for further details).

Figure 4

Variations in the Os isotope composition of Jurassic and Cenozoic seawater. Data for the Jurassic (solid squares and dotted lines) are from the ORM Re-Os isotope data of this study while the data for the Cenozoic (Peucker-Ehrenbrink et al. [7]) were obtained from leached metalliferous sediments from the Pacific (open circles and dotted lines). The solid squares marked K (Kimmeridgian) and To (Toarcian) represent the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ as defined by these 2 Re-Os regressions; the other Jurassic datapoints represent the mean $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of ORM samples from the *planorbis*, *liasicus*, *angulata*, *bucklandi-turneri*, *obtusum*, *eudoxus*, *hudlestoni* and *pectinatus* zones taken from Table 1. Both the Jurassic and Cenozoic datasets show pronounced minima in the vicinity of two major geological boundaries (the Cretaceous–Tertiary (K–T) and Triassic–Jurassic (T–J) boundaries). However, while the low $^{187}\text{Os}/^{188}\text{Os}$ ratios near the K–T boundary resulted from the release of large amounts of unradiogenic Os during the K–T impact event, the earlier minimum near the T–J boundary is probably unrelated to any impact and instead reflects the predominance at that time of unradiogenic Os released through the hydrothermal alteration of juvenile oceanic crust (see text).