

Nature and causes of Os isotope variations in late Triassic and Jurassic seawater

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Marine sediments which accumulate under suboxic or anoxic conditions contain certain elements, such as U, V, and Mo, at levels which greatly exceed average crustal abundances as a result of their concentration from seawater by scavenging, precipitation or redox reactions¹. Thus the chemical and isotopic compositions of well-preserved organic-rich mudrocks (ORM) can, in principle, reflect the composition of the seawater in which the sediments were deposited. At times during the Jurassic, much of Europe was covered by extensive areas of epicontinental sea with open-marine connections to the Tethyan ocean; the finely-laminated Jurassic ORM indicate that sub- or anoxic conditions pertained close to the sediment-water interface. On burial and heating, ORM mature to produce hydrocarbons into which some of the organophile elements of the ORM, notably Ni and V, may be partitioned. It is well established that Re and the platinum group elements (PGE) are also present at high concentration (compared with average crustal abundances) in ORM, while a recent preliminary study has shown that both Re and Os partition strongly into crude oil². Thus maturation and loss of a hydrocarbon phase is likely to perturb the Re-Os system in ORM.

We have recently demonstrated that the Re-Os isotope system is closed in well-preserved, immature ORM, because samples with a range in Re-Os ratios define precise and accurate isochron ages³ which are indistinguishable within the assigned uncertainties from the published depositional ages for these rocks⁴. Isochron ages and 2σ errors calculated for three suites of Jurassic ORM are 202 ± 28 , 183 ± 10 and 56 ± 7 Ma for samples of Hettangian–Sinemurian (n=4), Toarcian (n=9) and Tithonian (n=8) age, respectively, with $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of 0.40 ± 0.32 , 0.78 ± 0.06 and 0.58 ± 0.07 ³. Although the ORM are mixtures of hydrogenous, siliciclastic and carbonate components, most of the Os in the samples (90–99+%) is demonstrably hydrogenous in origin, while the high Os abundances preclude their compositions from being biased by local riverine input. Thus the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ as defined by

the three isochrons are interpreted to reflect the composition of contemporary Jurassic seawater. Furthermore, the actual timing of Re-Os isotopic closure is likely to have been very close to that of sediment deposition, because both Re and Os abundances in early-formed diagenetic pyrite, around which the ORM laminae are observed to have compacted, are ~2–3 orders of magnitude lower than in the enclosing mudrocks. Had Re and Os still been present in seawater or sediment porewater when the pyrite formed, then these chalcophile elements would have been strongly partitioned into the early diagenetic pyrite.

The present study was undertaken to investigate in detail the large apparent increase in the $^{187}\text{Os}/^{188}\text{Os}$ ratio of seawater over a ~20 Ma interval as suggested by the relatively unradiogenic $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of the early Jurassic Hettangian–Sinemurian samples, and the relatively radiogenic $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ as defined by the Toarcian samples. Detailed sampling of the lowermost Jurassic marine ORM (Hettangian *Psiloceras planorbis*, *Alsatites liasicus* and *Schlotheimia angulata* biozones) was carried out at coastal exposures 2–3 km to the west of Lyme Regis, Dorset, while samples across the Triassic–Jurassic (T–J) boundary section were collected from the coast at Watchet and from the proposed Global Stratotype Section and Point at St. Audrie's Bay in Somerset.

Results

The geochemical characteristics of the 10 Hettangian ORM samples analysed here differ markedly from those of the younger Toarcian ORM. For example, the Hettangian ORM have unusually high Re and Os abundances which reach 455 ppb and 3.2 ppb, respectively. These elevated abundances are ubiquitous in the Hettangian samples analysed, which span a depositional interval of 3–4 Ma, and suggest that 99+% of their Os and 99.9+% of their Re is hydrogenous in origin. By comparison, levels of Re and Os in Toarcian ORM from the Jet Rock in

Yorkshire are typically much lower at 8–20 ppb and 0.2–0.27 ppb, respectively³. Present-day $^{187}\text{Os}/^{188}\text{Os}$ ratios of the Hettangian samples are in the range 0.848–3.172, while $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ calculated assuming closed-system behaviour and depositional ages of 205–202 Ma vary from ~0.1–0.3. In contrast, the $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of the Toarcian samples are much higher, at 0.78 ± 0.06^3 . Samples of ORM from the Sinemurian, which are intermediate in age between the Hettangian and Toarcian ORM, possess an intermediate range of $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of 0.35–0.55; their Re and Os abundances also fall in between those of the Hettangian and Toarcian samples.

The Re and Os abundances of three ORM samples from the Rhaetic-age strata some 6 m below the T–J boundary in Somerset are in the range 0.6–3.2 ppb (Re) and 0.14–0.23 (Os); they possess relatively radiogenic $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of 0.5–0.7. These very low Re levels are atypical of ORM and may reflect their deposition in a restricted marine environment. In contrast, the characteristics of the youngest Triassic ORM sample analysed here, collected about 2.5 m below the T–J boundary, are similar to those of the overlying Hettangian samples, with high Os abundances and unradiogenic $^{187}\text{Os}/^{188}\text{Os}_{(i)}$; its Re concentration, at 18 ppb, is much greater than those of the underlying Rhaetic samples.

Discussion

Variations in the Os isotope composition of seawater reflect changes in the balance between the major inputs to the oceans – from rivers, MOR hydrothermal activity and meteorites⁵. Changes in the Os isotope composition of the riverine input can also cause the seawater ratio to vary and may be responsible for the relatively small, short-term glacial–interglacial variations reported recently (R. Oxburgh, pers. comm.). However, the magnitude of the seawater variations over the ~20 Ma interval in the Lower Jurassic, as indicated by the results presented here, is much greater than these recent glacial–interglacial variations and suggests that a substantial change between the balance of the three major ocean inputs occurred during the early Jurassic.

The unradiogenic $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ of the Hettangian samples require a dominant Os contribution either from MOR hydrothermal activity or from meteorites.

While an enhanced meteoritic input could provide the necessary unradiogenic Os, it is unlikely to have also resulted in elevated Re levels because the Re/Os ratio of chondritic meteorites is low. It appears more probable that the very high abundances of unradiogenic Os in the Hettangian ORM, together with their high Re levels, resulted from MOR hydrothermal activity predominating over the riverine (continental) input for an extended period of time. It is noteworthy that the early Jurassic marks the start of a pronounced decline in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater⁶, thought to be a consequence of accelerated hydrothermal activity associated with increased tectonic activity. Because the marine residence time of Os (~40 ka) is much shorter than that of Sr (~2–4 Ma), seawater Os will respond much more rapidly than will seawater Sr to changes in the isotopic composition of ocean inputs and can thus be used as a more precise indicator of the timing of palaeoenvironmental change. Our data demonstrate that the major shift in seawater Os precedes any decline in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio by the entire duration of the Hettangian, spanning some 3–4 Ma, as the decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio commences only during the subsequent Sinemurian stage. Thus, based on the similarity between the Os abundance and Os isotope patterns in the youngest Rhaetic ORM sample with those of samples from the Hettangian which follow immediately, it appears that the open marine conditions which characterize the early Jurassic were already established before the first known appearance of the ammonite *Psiloceras planorbis* in Somerset, which officially marks the T–J boundary in that section.

References

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