1 2 3	Opening of a trans- <u>Pangaea</u> n marine corridor during the Early Jurassic: Insights from osmium isotopes across the <u>Sinemurian–Pliensbachian</u> GSSP, Robin Hood's Bay, UK.
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13 14	Keywords: Osmium isotopes, Hispanic Corridor, <u>Sinemurian–Pliensbachian</u> , organic-rich sediments, ocean connectivity
15	
16	ABSTRACT
17	The Hispanic Corridor represents a significant phase of continental reorganisation of the Early
18	Jurassic that eventually provided connectivity between the western Tethyan and eastern Pacific
19	oceans along the Central Atlantic rift zone. Although the initiation of this marine corridor profoundly
20	impacted oceanic circulation and marine faunal exchange patterns, the timing of its formation
21	hitherto remains poorly constrained with estimates spanning both the Hettangian and Sinemurian.
22	The <u>Sinemurian–Pliensbachian</u> Global Stratotype Section and Point (GSSP) at Robin Hood's Bay, UK,
23	comprises a succession of well-exposed, immature organic-rich sediments, only previously
24	characterised by strontium, oxygen and carbon isotope geochemistry. New Re and Os isotope
25	profiling indicates substantial variation in seawater chemistry at this time. Initial osmium isotope
26	data become increasing unradiogenic (0.40 to 0.20) across the boundary, providing evidence for a
27	continual flux of unradiogenic Os into the oceans during the latest Sinemurian. The initial
28	unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os values indicate the occurrence of low-temperature hydrothermal activity
29	associated with the formation of the Hispanic Corridor during the breakup of Pangaea. Therefore,
30	combined with biogeography and faunal exchange patterns, the Os <u>isotope</u> data demonstrates that
31	connectivity between the Eastern Pacific and Tethyan oceans initiated during the latest Sinemurian.

As a result this study better constrains the timing of establishment of the Hispanic Corridor, which was previously limited to poorly defined biogeography.

1. Introduction

37	Marine sedimentary rocks hold the key to understanding past chemical changes and fluxes in
38	the oceans. Analysis of hydrogenous rhenium (Re) and osmium (Os) in organic-rich sediments allows
39	detailed evaluation of seawater chemistry at the time of sediment deposition. The Os isotope
40	system (¹⁸⁷ Os/ ¹⁸⁸ Os) is a particularly powerful tool for tracing temporal changes in the balance of
41	global inputs to the oceans (Ravizza et al., 1996; Levasseur et al., 1999; Cohen et al., 1999; Peucker-
42	Ehrenbrink and Ravizza, 2000), and as such it permits the evaluation of fluctuations in seawater
43	chemistry throughout geological time. Specifically, significant input from meteorite impact,
44	continental weathering and mantle-derived fluxes can be identified and distinguished.
45	The present-day seawater Os isotope composition may be relatively uniform (187 Os/ 188 Os
46	ratio of ~1.06; Levasseur et al., 1998; Peucker-Ehrenbrink and Ravizza, 2000), but it has varied
47	significantly throughout geological time. The short seawater residence time of Os of \sim 10–40 Ka
48	(Sharma et al., 1997; Oxburgh, 1998; Levasseur et al., 1998; Peucker-Ehrenbrink and Ravizza, 2000),
49	longer than the mixing time of the oceans (~2–4 Ka; Palmer et al., 1988), allows the Os isotope
50	composition to respond rapidly to any alterations in the composition and flux of these inputs
51	(Oxburgh, 1998; Cohen et al., 1999). This has been successfully exploited by past studies, where Os
52	has been used as a chemostratigraphic marker of significant volcanic events (eg., Cohen et al., 1999;
53	Ravizza and Peucker-Ehrenbrink, 2003).
54	Until now, isotope stratigraphy of the <u>Sinemurian–Pliensbachian</u> GSSP at <u>Robin Hood's Bay</u>
55	(Wine Haven, UK) has been limited to 87 Sr/ 86 Sr (Jones et al., 1994; Hesselbo et al., 2000), δ^{18} O and
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 δ^{13} C data (Hesselbo et al., 2000) from belemnites. Herein we compile these datasets with Re-Os

data, to provide new Os isotope characterisation of the Sinemurian-Pliensbachian GSSP. The longer

58	seawater residence time of Sr (~2.4 Ma; Jones and Jenkyns, 2001) relative to Os, slows the response
59	of Sr ratios to changes in the balances of inputs to the oceans (eg. Cohen and Coe, 2002). Therefore,
60	using Os isotopes provides improved resolution for changes in seawater chemistry across this
61	boundary section. Combined with data from previous studies this work has two significant
62	outcomes, by providing: (1) an increased geochemical understanding of an important GSSP, thereby
63	also enhancing <u>our</u> understanding of Lower Jurassic stratigraphy in the UK; and (2) a detailed
64	¹⁸⁷ Os/ ¹⁸⁸ Os profile for contemporaneous Jurassic seawater allowing insight into the contributions of
65	the various global inputs into the oceans at this time and therefore providing information regarding
66	ocean connectivity during the Early Jurassic.
67	Currently, the timing of development of oceanic seaways during Pangaean separation is
68	poorly constrained, with estimates that include both the Hettangian and Sinemurian. The Hispanic
69	Corridor, an initially epicontinental, but later fully oceanic seaway, connected the western Tethyan
70	and eastern Pacific oceans along the Central Atlantic rift zone (Smith and Tipper, 1986; Smith et al.,
71	1990; Riccardi, 1991; Hallam and Wignall, 1997; Aberhan, 2001). Formed through separation of the
72	Pangaean supercontinent, this proto-Atlantic seaway resulted from one of the most significant
73	pal <u>a</u> eogeographic reorganisations in Earth's history (Smith et al., 1990). Initially developing over
74	rifting continental crust (Smith et al., 1994), this marine corridor signified the tectonic transition
75	from rifting to drifting, prior to the formation of the Atlantic Ocean (Smith et al., 1990). In addition
76	to the profound impact on ocean circulation and equatorial distribution of marine organisms at this
77	time, the marine corridor acted as a filter during its early stages, preferentially allowing passage of
78	on-shore benthic species, whilst acting as an effective barrier for off-shore species (eg. Hallam and
79	Wignall, 1997; Smith et al., 1994; Aberhan, 2001). However, with no direct sedimentological or
80	geophysical evidence, determining the timing for the establishment of the corridor using
81	biogeography has been the subject of continuous debate. As such, the timing of seaway formation is
82	currently imprecise and suggested to have occurred within the Early Jurassic (eg. Damborenea, 2000;
83	Aberhan, 2001).

84	The ¹⁸⁷ Os/ ¹⁸⁸ Os values from the <u>Sinemurian–Pliensbachian</u> <u>GSSP</u> , Robin Hood's Bay, UK,
85	provide evidence for significant low-temperature hydrothermal activity that may have been
86	associated with the formation of the Hispanic Corridor during the breakup of Pangaea. Combined
87	with biogeography and faunal exchange patterns, the Os data herein suggests that connectivity
88	between the Eastern Pacific and Tethyan oceans initiated during the latest Sinemurian. Thus, this
89	study better constrains the timing of establishment of the Hispanic Corridor, previously limited to
90	poorly defined biogeography.
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93	2. Geology of the <u>Sinemurian–Pliensbachian</u> boundary GSSP
94	Our study focuses on the marine sediments at the Sinemurian–Pliensbachian Global
95	Boundary Stratotype Section and Point (GSSP) at Wine Haven, ~3 km S_SE of Robin Hood's Bay,
96	Yorkshire, UK (Grid ref. NZ9762 0230 eg., Hesselbo et al., 2000; Meister et al., 2006; Fig. 1). This
97	Lower Jurassic boundary occurs in the Pyritous Shales of the Redcar Mudstone Formation within the
98	l Lias Group (Powell, 1984). It has been the subject of scientific interest for many years, with the
99	earliest reference to the site being by Young and Bird (1822). Exposure at Robin Hood's Bay is
100	optimal, with lower beds exposed by a series of wave-cut platforms. The succession here is also
101	known for its well-preserved ammonite assemblages (eg. Tate and Blake, 1876; Dommergues and
102	Meister, 1992). <u>Using From-the biostratigraphy</u> , the base of the Pliensbachian Stage can be
103	unambiguously located at the bottom of the <u>taylori</u> Subzone of the <u>Uptonia i</u> amesoni Zone, marked
104	by the first occurrence of species of the genus Apoderoceras (Dean et al., 1961; Hesselbo et al.,
105	2000; Gradstein et al., 2004; Meister et al., 2006).
106	The age for the base of the Pliensbachian has been defined by the Geological Time Scale
107	(GTS) 2004 as 189.6 \pm 1.5 Ma (Gradstein et al., 2004), derived from cycle-scaled linear Sr trends and
108	ammonite occurrences (as noted above; also includes the lowest occurrence of Bifericeras donovani;
109	Gradstein et al., 2004). Herein, this age for the <u>Sinemurian–Pliensbachian</u> boundary is used. The

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110	Sinemurian-Pliensbachian boundary is placed very close to the base of Bed 73 (bed classification	
111	from Hesselbo and Jenkyns, 1995), ~6 cm above the midline of nodules forming the upper margin of	
112	Bed 72 in the Wine Haven section (Hesselbo et al., 2000).	
113	An epicontinental sea, positioned to the west of the deep Tethyan basin (Dera et al., 2009)	
114	covered most of Northern Europe, including Britain, during the Mesozoic (Sellwood and Jenkyns,	
115	1975; Fig. 1). Lithological evidence for sea level rise, combined with sedimentological evidence	
116	(Smith et al., 1994), indicates that the epicontinental sea during this time was not landlocked but	
117	free to circulate with the Tethyan ocean. The open ocean Os isotope composition across the	
118	boundary interval should therefore be echoed in the sampled sediments. Analysis of hydrogenous	
119	Re and Os from these samples instils certainty that the calculated initial Os isotope composition	
120	$(^{187}\text{Os}/^{188}\text{Os}_{(i)})$ reflects that of contemporaneous seawater (Cohen et al., 1999).	
121	Over a ~10 m interval, the lithology of the Wine Haven succession gradually progresses from	
122	pale siliceous and clay-rich mudrocks with intermittent coarser sand beds in the Upper Sinemurian	
123	(Aplanatum Subzone), to finer and much darker shales with less clay ~1.5 m above the boundary in	
124	the Lower Pliensbachian (<i>Tayloritaylori</i> Subzone; Meister et al., 2006; Hesselbo and Jenkyns, 1995,	
125	1998; this study). These facies changes indicate an overall relative increase in sea level of at least	
126	regional, but possibly global extent (Sellwood, 1972; <u>Hallam, 1981;</u> Hesselbo and Jenkyns 1995,	
127	1998; Hesselbo et al., 2000; Meister et al., 2006).	
128	Nodular beds of concretionary siderite (~10 cm in thickness) of both laterally continuous	
129	(Beds 70 and 72) and semi-continuous extent (Bed 74 and within Bed 71) are present throughout the	
130	Wine Haven section (Sellwood, 1972; Meister et al., 2006; this study). The origin of these nodules is	
131	uncertain, although they are suggested to represent non- or slow depositional phases based on their	
132	unique association with fauna found in life-position (Sellwood, 1972).	
133	Sedimentation rate across the Sinemurian-Pliensbachian boundary has been approximated	
134	here by taking \sim 64 Ma as the duration for the Jurassic period (Gradstein et al., 2004) and using mean	
135	thicknesses of ammonite zonal subdivisions estimated by Hallam and Sellwood (1976). This provides	

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136	a combined thickness for the Sinemurian and Pliensbachian of ~278 m, ~23 % of the total for the
137	Jurassic. By disregarding the uncertain effects of compaction (Hallam and Sellwood, 1976), a steady
138	sedimentation rate during this interval has been calculated at ~1.9 cm/Ka, in turn suggesting that the
139	interval sampled by this study (~6 m) spans ~320 Ka.
140	Although the ⁸⁷ Sr/ ⁸⁶ Sr profile (Hesselbo et al., 2000) shows a systematic decrease up-section
141	(~0.707487 to 0.707395 over a 10 m interval), a lack of any abrupt changes in the ⁸⁷ Sr/ ⁸⁶ Sr ratio
142	indicates that sedimentation was continuous (Jones et al., 1994; Hesselbo et al., 2000; Meister et al.,
143	2006). At the boundary level, a drop in 87 Sr/ 86 Sr value from ~0.707433 to 0.707418 (Hesselbo et al.,
144	2000) could allow the possibility of minor slowing or hiatus in sediment deposition (Hesselbo et al.,
145	2000; Meister et al., 2006). However, replicate analyses of belemnites from 1–4 cm above the
146	boundary give an average 87 Sr/ 86 Sr value of 0.707422 \pm 0.000012, well within uncertainty of the ratio
147	recorded for the boundary (0.707425 \pm 0.000004) (Hesselbo et al., 2000), suggesting a slowing
148	rather than break in deposition (Hesselbo et al., 2000; Meister et al., 2006). Further evidence for
149	continuous deposition is supported by a lack of lithological unconformities (Meister et al., 2006; this
150	study).
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153	3. Analytical methodology
154	3.1 Sampling
155	A set of 32 samples (SP7-09 to SP39-09) were collected from the Pyritous Shales Member of
156	the Redcar Mudstone Formation, along a 6 m vertical section bracketing the Sinemurian-
157	Pliensbachian boundary (sample SP22-09) at Robin Hood's Bay (Fig. 2). Sampling occurred at a
158	consistent interval of ~20 cm for 3 m above and 3 m below the boundary from Beds 69–75 except
159	within Bed 72, where a smaller sampling interval of \sim 15 cm was used (Fig. 2). Based on our
160	approximation above for the duration of sedimentation across this section, sampling at 20 cm
161	intervals allowed us to capture an estimated resolution of \sim 11 Ka per sample.

In preparation for geochemical analyses, the samples were cut and polished to expose fresh surfaces, and were then powdered in a Zr disc.

165 3.2 Re-Os analysis

166	Rhenium and osmium analyses of Robin Hood's Bay whole-rock powders were conducted at
167	the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) as part of the JSPS Summer
168	Fellowship Program 2010, following the CrO_3 - H_2SO_4 procedure outlined by Selby and Creaser (2003).
169	This digestion technique minimises removal of Re and Os from the nonhydrogenous (detrital)
170	component of the sample, allowing analysis and evaluation of the hydrogenous fraction (Selby and
171	Creaser, 2003). Sample powders of known quantities (500 mg for samples with >50 ppb Re or 1g for
172	samples with <50 ppb Re) were digested with a measured amount of 185 Re and 190 Os spike solution,
173	in 8 ml of CrO ₃ -H ₂ SO ₄ solution in Carius tubes at 240 $^{\circ}$ C for 48 hrs. After cooling, Os was removed
174	and purified from the solution by solvent extraction and micro-distillation.
175	Following Os removal, the remaining solution was prepared for anion exchange
176	chromatography to purify the Re fraction. To reduce Cr ⁶⁺ to Cr ³⁺ , necessary to avoid complications
177	during chromatography (Selby and Creaser, 2003), 1 ml of the remaining solution was removed and
178	reduced drop by drop (due to the violent exothermic reaction) using 3 ml of ethanol (gradual
179	addition of ethanol to the sample solution is advised to avoid loss of sample during the reduction
180	reaction). Once reduced, the solution was evaporated to dryness on a hotplate at ${\sim}80^{\circ}$ C.
181	The dried Re fraction was taken up in a 10 ml 0.5 N HCl loading solution, before being
182	purified by a two-stage HCl-HNO $_3$ anion chromatography procedure. The purified Re and Os was
183	loaded onto Ni and Pt filaments, respectively and the Re and Os isotope ratios were measured using
184	NTIMS (Creaser et al., 1991; Völkening et al., 1991) using Faraday collectors and the SEM,
185	respectively. The initial Os isotope composition (187 Os/ 188 Os(i)) was calculated using an independently
186	assumed sample age of ~189.6 Ma (Gradstein et al., 2004) and λ ¹⁸⁷ Re = 1.666 x 10 ⁻¹¹ a ⁻¹ (Smoliar et
187	al., 1996). During this study total procedural blanks were 14.1 \pm 0.2 pg and 3.56 \pm 0.52 pg (1 σ S.D., n

= 2) for Re and Os, respectively, with an average 187 Os/ 188 Os value of 0.19 ± 0.005 (n = 2). 188 189 Uncertainties presented in Table 1 include full error propagation of uncertainties in Re and Os mass 190 spectrometer measurements, blank abundances and isotopic compositions, spike calibrations and 191 reproducibility of standard Re and Os isotopic values. 192 193 194 4. Results 195 4.1 Re and Os abundance 196 The Re and Os abundances define a large range of values, from ~1.5–117 and ~0.12–1.9 ppb, 197 respectively (Table 1). These values are much greater than those of average continental crust: 0.39 198 ppb (Re) and 0.05 ppb (Os) (Sun et al., 2003 and references therein). Both Re and Os abundances 199 show an overall increase up-section that becomes more pronounced following the Sinemurian-200 Pliensbachian boundary. 201 202 4.2 Re-Os geochronology 203 In order to conduct Re-Os geochronology, the targeted samples should fulfil three criteria. Each sample must possess a similar initial Os isotope composition $({}^{187}Os/{}^{188}Os_{(i)})$ together with 204 variable ¹⁸⁷Re/¹⁸⁸Os ratios, and have experienced no disturbance to the isotope system since the 205 206 time of formation (Cohen et al., 1999). The Robin Hood's Bay section shows no evidence of post-207 depositional disturbance, e.g., no veining is evident and the section is thermally immature. Similar 208 Jurassic sections have been utilised for Re-Os geochronology (Cohen et al., 1999). For the Robin Hood Bay section the ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios vary from ~25–443 and 209 ~0.3–1.6, respectively. Both ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios decrease between 2.8 to 0.9 m below 210 the <u>Sinemurian–Pliensbachian</u> boundary (¹⁸⁷Re/¹⁸⁸Os, ~195–20; ¹⁸⁷Os/¹⁸⁸Os, ~1–0.3), before 211 212 systematically increasing across the boundary into the lowermost Pliensbachian. Although all the 187 Re/ 188 Os and 187 Os/ 188 Os ratios positively correlated (R² = 0.95), the Re-Os data yield model 3 age 213

214	of 179 \pm 16 Ma (2 σ , n = 32, MSWD = 473; Fig. 4a). Although within uncertainty of the calculated age
215	for the <u>Sinemurian–Pliensbachian</u> boundary (189.6 ± 1.5 Ma; Gradstein et al., 2004), the uncertainty
216	is large (~9%) and is accompanied by an extremely large MSWD, which indicates significant scatter
217	of the data about the isochron that relates to more than analytical uncertainty. We suggest that this
218	scatter relates to the sample set possessing variable initial ¹⁸⁷ Os/ ¹⁸⁸ Os values. The calculated initial
219	¹⁸⁷ Os/ ¹⁸⁸ Os (¹⁸⁷ Os/ ¹⁸⁸ Os _(i) at 189.6 Ma; Gradstein et al., 2004) values for this <u>Sinemurian</u>
220	Pliensbachian section are variable, but consistently unradiogenic for all samples, ranging from
221	\sim 0.20–0.48. Overall, with exceptions at 1.1 m below the boundary and at the boundary itself (sample
222	SP22-09, 187 Os/ 188 Os _(i) = ~0.48 and SP17-09 = ~0.44, respectively; Fig. 3; 4b), the 187 Os/ 188 Os _(i) values
223	become progressively less radiogenic up-section.
224	If we consider samples with similar 187 Os/ 188 Os _(i) values (~0.20–0.30) regression of the Re-Os
225	data produces a model 3 age of 183.4 \pm 3.3 Ma (2 σ , n = 17, MSWD = 20; Fig. 4c). This age is outside
226	of uncertainty of that given by Gradstein et al. (2004). Regression of Re-Os data for the top four
227	stratigraphic organic-rich samples in the section (SP34-09, SP35-09, SP36-09 and SP37-09) provides a
228	model 1 age of 194 \pm 4.8 Ma (2 σ , n = 4, MSWD = 0.04; Fig. 4d). These samples are ideally suited to
229	Re-Os geochronology because they possess extremely similar initial ¹⁸⁷ Os/ ¹⁸⁸ Os compositions (~0.20–
230	0.22) and variable ¹⁸⁷ Re/ ¹⁸⁸ Os ratios (~268–443). As such, the model age is within uncertainty of that
231	given by Gradstein et al. (2004). Although the Robin Hood bay section is not ideally suited for Re-Os
232	geochronology, the positive correlation of ¹⁸⁷ Re/ ¹⁸⁸ Os with ¹⁸⁷ Os/ ¹⁸⁸ Os that yields dates that are in
233	agreement with the Geological Time Scale 2004 (Gradstein et al., 2004), suggests that the Re-Os
234	systematics have not been disturbed and that calculated initial 187 Os/ 188 Os values can be used to
235	discuss Early Jurassic ocean chemistry.
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5. Discussion

241	The Jurassic was a dynamic period that hosted major geological events of Earth's history;
242	notably the full-scale tectonic plate reorganisation associated with the break-up of Pangaea. Ocean
243	chemistry was therefore subject to fluctuations as the balance of inputs changed, and as such the
244	seawater Os isotope composition was highly variable. In order to look critically at the data herein
245	and to determine the potential source of the Os isotope signal observed across the Sinemurian-
246	Pliensbachian boundary, there needs to be an understanding of the background seawater Os isotope
247	composition at this time. However, at present no studies conclusively document background
248	seawater Os for the Early Jurassic. The first estimation of stable, steady-state ¹⁸⁷ Os/ ¹⁸⁸ Os values for
249	the Sinemurian is proposed to be ~ 0.47 (Kuroda et al., 2010). The sampled section (Triassic_Jurassic
250	chert succession from Kurusu, Japan; Kuroda et al., 2010) was positioned to the east of the
251	separating supercontinent, in an intra-ocean setting. The recorded Os isotope composition would
252	therefore not have been directly affected by nearby continental flux, and would have been a good
253	representation of open ocean chemistry at this time. For this investigation, we will assume that this
254	value represents the best estimation of background seawater Os isotope composition at the
255	Sinemurian–Pliensbachian transition.
256	
257	5.1 Origin of the Sinemurian–Pliensbachian seawater Os isotope composition
258	The Os data from Robin Hoods Bay show that the calculated seawater initial ¹⁸⁷ Os/ ¹⁸⁸ Os
259	value becomes progressively more unradiogenic from the latest Sinemurian into the Pliensbachian.
260	Although there is some fluctuation, this trend to unradiogenic values can be broadly separated into
261	three groups, with average 187 Os/ 188 Os _(i) values of ~0.38, 0.28 and 0.21 (Fig. 3). These results indicate
262	that there was a marked and progressive increase of unradiogenic Os input into the global ocean
263	during the transition from the Sinemurian to the Pliensbachian.
264	A peak towards a relatively radiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os value of 0.48 is coincident with the

265 boundary. This is also matched by an increase in the ¹⁸⁷Re/¹⁸⁸Os ratio (from ~31 to 100) and a

decrease in ¹⁹²Os (from ~208 to 102 ppb). Assuming a background seawater Os isotope composition
of ~0.47 (Kuroda et al., 2010), this peak may reflect a period of hiatus in the input of unradiogenic Os
to the oceans.

There are three major inputs of Os that directly control the seawater ¹⁸⁷Os/¹⁸⁸Os value: (1)
 radiogenic input from weathering of continental crust; (2) unradiogenic contribution from

271 meteorites; (3) an unradiogenic signal from igneous and hydrothermal activity (eg. Peucker-

272 Ehrenbrink and Ravizza, 2000).

273

274 5.1.1 Why is the signal not induced by continental weathering?

275 The gradual trend towards unradiogenic Os isotope values observed in this study indicates that 276 continental weathering is unlikely to be the cause of the Os isotopic signal shown over Sinemurian-277 Pliensbachian boundary. Belemnite oxygen stable isotope data displays a marked increase of ~1 ‰ 278 over 10 m across the boundary (Hesselbo et al., 2000; Fig. 3). This 1 ‰ change is equivalent to a 279 substantial temperature decrease of ~5°C (Hesselbo et al., 2000; Meister et al., 2006). Such 280 considerable lowering of temperature, coupled with evidence for low mean land relief and absence 281 of ice sheets during the Early Jurassic (Golonka et al., 1994), would favour reduced rates of regional 282 and global continental weathering. 283 The Os isotope signal resulting from continental weathering is also significantly more radiogenic ($^{187}Os/^{188}Os = \sim 1.4$; Peucker-Ehrenbrink and Jahn, 2001) than that observed in this study.

radiogenic (¹⁸⁷Os/¹⁸⁸Os = ~1.4; Peucker-Ehrenbrink and Jahn, 2001) than that observed in this study.
This indicates that the seawater Os isotope composition was dominated by an unradiogenic source
that outweighed the input of radiogenic Os from continental weathering. It is extremely difficult to
constrain the exact continental ¹⁸⁷Os/¹⁸⁸Os input to the oceans during the <u>Early Jurassic</u>. However,
following Cohen et al. (1999), we can attempt to quantify the approximate contribution of crustal Os
into the ocean. Assuming an average ¹⁸⁷Os/¹⁸⁸Os value of ~1.4 for weathering of ancient continental
crust (Peucker-Ehrenbrink and Jahn, 2001), and a ¹⁸⁷Os/¹⁸⁸Os value of ~0.13 for an unradiogenic
mantle-derived source (Allègre and Luck, 1980; Esser and Turekian, 1993; Sharma et al., 1997;

292	Levasseur et al., 1998), an input of crustal-sourced Os of 5–22 % is required to obtain seawater
293	¹⁸⁷ Os/ ¹⁸⁸ Os ratios of ~0.44–0.20, respectively. This is small in contrast to the present-day radiogenic
294	contribution to the oceans from the continental crust, of between \sim 70 and 80 % (Peucker-
295	Ehrenbrink, 1996; Sharma et al. 1997), respectively. Given the geographical location of Robin Hood's
296	Bay in close-proximity to continental landmasses (Fig. 5), and the absence of ice sheets, there would
297	almost certainly be radiogenic continental input regardless of land-relief and climate. Further,
298	although challenging to quantify, the epicontinental setting would mean increased sensitivity to
299	continental input. There is no evidence for the weathering of unradiogenic lithologies, e.g., mafic
300	and ultramafic units, thus the decrease in seawater ¹⁸⁷ Os/ ¹⁸⁸ Os composition during the earliest
301	Pliensbachian therefore indicates that input of Os into the ocean at this time was dominated by an
302	unradiogenic source, not accounted for by the continental weathering flux.
303	
304	5.1.2 Why is the unradiogenic Os not from an extraterrestrial source?
305	Extraterrestrial and mantle-derived influxes are the dominant unradiogenic sources of Os to
306	the global oceans. The calculated 187 Os/ 188 Os values of these sources (~0.13) are indistinguishable
307	(Allègre and Luck, 1980; Esser and Turekian, 1993; Sharma et al., 1997; Levasseur et al., 1998). It is
308	therefore necessary to examine the structure of the Os isotope profiles from each source to
309	determine which was responsible for the declining unradiogenic Os signal into the Pliensbachian.
310	Fluctuations in the seawater Os isotope record during the Cenozoic were not induced by
311	extraterrestrial Os influx to the oceans, as the cosmic Os flux was continuous relative to the variable
312	ocean Os record (with the exception of the $K_{-}T$ boundary; Peucker-Ehrenbrink and Ravizza, 2000).
313	Although the extraterrestrial flux to Earth during the Jurassic is poorly constrained, the possibility of
314	meteorite impact at the Sinemurian-Pliensbachian boundary does not reconcile the gradual decline
315	in ¹⁸⁷ Os/ ¹⁸⁸ Os ratios. Following an impact, the Os isotope system should recover quickly due to the
316	relatively short seawater residence time of Os (Peucker-Ehrenbrink and Ravizza, 2000). Therefore,
317	although impacts have been documented ~5–20 Ma prior to the Triassic – Jurassic boundary (Hallam

318	and Wignall, 1997), it would be unlikely to find evidence of meteoritic unradiogenic Os during the
319	Pliensbachian. This is further supported by a study of the Os isotope excursion due to meteorite
320	impact across the K-T boundary (Ravizza and Peucker-Ehrenbrink, 2003), that shows relatively rapid
321	recovery of the Os isotope system to a steady state following impact (¹⁸⁷ Os/ ¹⁸⁸ Os value increases
322	from ~0.16 to 0.40 in a maximum of ~200 Ka).
323	
324	5.1.3 Unradiogenic Os from a mantle-derived source
325	The unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os values are therefore most likely to be mantle-derived. Unlike
326	the other potential sources of oceanic Os discussed above, increased input from a mantle source at
327	the time of the <u>Sinemurian–Pliensbachian</u> boundary can explain the observed isotope profiles.
328	Rifting of the Pangaean Supercontinent began during the latest Triassic (Marzoli et al., 1999;
329	Hames et al., 2000). The initial stages of continental break-up were focused along the 6000 km
330	lineament that would eventually form the continental margins of the Central North Atlantic Ocean
331	(Hames et al., 2000). Consequently, there is evidence for substantial magmatism during the Late
332	Triassic–Early Jurassic (Marzoli et al., 1999; Hames et al., 2000), defined by extensive continental
333	basalts in North America, Europe, Africa and South America (Wilson, 1997; Marzoli et al., 1999). This
334	formed what is termed as the Central Atlantic Magmatic Province (CAMP). The scale of the CAMP
335	has been postulated to exceed that of the Karoo-Ferrar, the Deccan Traps and the Siberian
336	continental flood basalt provinces (Hames et al., 2000), with a total areal extent and volume of at
337	least 7 x 10^{6} Km ² and 2 x 10^{6} km ³ , respectively (Marzoli et al., 1999; Hames et al., 2000).
338	High-precision ⁴⁰ Ar/ ³⁹ Ar geochronology of the oldest CAMP volcanic rocks, indicate that
339	emplacement occurred during the transition from Late Triassic to Early Jurassic (ca. 200 Ma) with a
340	brief duration of \sim < 2 Ma (Marzoli et al., 1999; Hames et al., 2000). A volcanic event of this
341	magnitude, considering both its sizeable magmatic and hydrothermal outputs, would have had a
342	considerable impact on ocean chemistry, regardless of its exceptionally brief duration (Ravizza and
343	Peucker-Ehrenbrink, 2003). This has been documented by several Os isotope studies of seawater at

344	the Triassic_Jurassic boundary and during the Hettangian (Cohen et al., 1999; Cohen and Coe, 2002;
345	Cohen, 2004). Prior to and immediately following the Triassic-Jurassic boundary, there was a
346	significant unradiogenic contribution of Os to the oceans that persisted into the Hettangian (Cohen
347	et al., 1999; Cohen and Coe, 2002; Cohen, 2004). This has been attributed to seawater interaction
348	and alteration of recently emplaced CAMP lavas, together with enhanced hydrothermal activity
349	(Cohen et al., 1999; Cohen and Coe, 2002; Cohen, 2004). High chemical weathering rates of juvenile
350	basalts (Louvat and Allègre, 1997) characteristically promote relatively rapid release of unradiogenic
351	Os, which can be seen in the Triassic–Jurassic and Hettangian sample suites (Cohen et al., 1999;
352	Cohen and Coe, 2002; Cohen, 2004). The seawater Os isotopic composition then becomes
353	increasingly unradiogenic across the <u>Sinemurian–Pliensbachian</u> boundary, to ¹⁸⁷ Os/ ¹⁸⁸ Os ratios of
354	~0.20. Using estimates for Early Jurassic stage durations from Gradstein et al. (2004), this boundary
355	occurred \sim 10 Ma after the Triassic–Jurassic boundary and at least \sim 8 Ma after emplacement of
356	CAMP. Further, the total duration of weathering of CAMP basalts is estimated at \sim 3.5 Ma (Cohen
357	and Coe, 2007), producing a seawater 187 Os/ 188 Os value of ~0.30. It is therefore difficult to reconcile
358	the observed Sinemurian-Pliensbachian seawater Os isotope composition with the CAMP
359	emplacement event (ca. 200 Ma) or weathering of the continental flood basalts, given a date for the
360	Sinemurian–Pliensbachian stage boundary of 189.6 ± 1.5 Ma (Gradstein et al., 2004).
361	However, when considering palaeogeographic and biogeographic evidence, it is possible to
362	determine a mantle-derived origin for the unradiogenic seawater Os isotope composition that does
363	not rely on emplacement of CAMP lavas. Hydrothermal activity would have been prevalent in this
364	tectonic setting, and low temperature hydrothermal fluids have a characteristically unradiogenic Os
365	isotope composition of ~0.12 (Cohen et al., 1999; Sharma et al., 2000).
366	
367	

369 5.2 Os isotope evidence for oceanic connectivity via the 'Hispanic Corridor' during the Early

370 Pliensbachian

371 The separation of Pangaea and onset of a global sea level rise established a number of 372 epeiric seaways, including the Hispanic Corridor (Aberhan, 2001). This initially epicontinental, but 373 later fully oceanic seaway was established along the Central Atlantic rift zone, between the areas of 374 North America, South America and Africa (Smith and Tipper, 1986), eventually connecting the 375 western Tethyan and eastern Pacific oceans (eg. Smith and Tipper, 1986; Smith et al., 1990; Riccardi, 376 1991; Aberhan, 2001; Fig. 5). 377 No connectivity existed between these oceans during the Hettangian or Sinemurian, 378 providing an effective barrier to oceanic circulation and thus to faunal exchange (eg. Smith and 379 Tipper, 1986; Riccardi, 1991; Aberhan, 2001). In addition, biogeographic and sedimentological 380 evidence indicates that an oceanic corridor did not develop before the Middle Jurassic (Aberhan, 381 2001). Whilst some studies, based on benthic faunas, postulate an opening time for the corridor of Late Triassic (Sandy and Stanley, 1993) and early Hettangian (Sha, 2002), substantial evidence for 382 sudden low levels of faunal exchange between the eastern Pacific and western Tethyan oceans 383 384 exists in the earliest Pliensbachian (Damborenea and Manceñido, 1979; Smith and Tipper, 1986; 385 Smith et al., 1990). This suggests establishment of the Hispanic Corridor as a shallow but continuous 386 seaway by the start of the Pliensbachian. Schootbrugge et al. (2005) also suggest that short bursts in 387 the diversification of dinoflagellates during the latest Sinemurian are consistent with the opening of 388 this seaway. The decline of seawater ¹⁸⁷Os/¹⁸⁸Os ratios and the rise in sea level evident across the 389 390 Sinemurian-Pliensbachian boundary section at Wine Haven, are therefore coincident with the onset 391 of flooding of the Hispanic Corridor. Furthermore, this study suggests that the isotopic signals 392 observed at the boundary reflect increasing hydrothermal activity associated with the opening of the 393 Hispanic Corridor.

394	The Hispanic Corridor developed across rifting continental crust (Smith et al., 1994), with
395	significant crustal stretching and attenuation occurring before creation of the oceanic strait (Hallam
396	and Wignall, 1997). Growing evidence also indicates that substantial off-axis hydrothermal venting
397	may occur in cooler crustal regions away from the immediate rift zone, driven by exothermic
398	reactions between seawater and mantle-derived rocks (Kelley et al., 2001). This is evident at the
399	Mid-Atlantic and Juan de Fuca ridges, respectively (Kelley et al., 2001; Sharma et al., 2000),. Off-axis
400	fluids are typically cool ($^40-75^{\circ}$ C) with high Os concentrations (500 femtomol/kg) and
401	unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os ratios of ~0.12 (Sharma et al., 2000). Mantle-derived material (basalt) was
402	prevalent in this Central Atlantic region (eg. Wilson, 1997; Marzoli et al., 1999), allowing seawater-
403	rock interaction to ensue following the initial flooding event. This would have driven extensive low-
404	temperature hydrothermal fluid circulation, promoting an increase in the release of unradiogenic Os
405	into the seawater (Sharma et al., 2000).
406	
407	
407 408	6. Conclusions
407 408 409	6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to
407 408 409 410	6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic.
407 408 409 410 411	 6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic. Further, understanding changes in ocean chemistry during this time has the potential to yield
407 408 409 410 411 412	 6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic. Further, understanding changes in ocean chemistry during this time has the potential to yield valuable insight into ocean connectivity during <u>Pangaea</u>n separation.
407 408 409 410 411 412 413	 6. Conclusions The Sinemurian–Pliensbachian boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic. Further, understanding changes in ocean chemistry during this time has the potential to yield valuable insight into ocean connectivity during Pangaean separation. Seawater during the Sinemurian–Pliensbachian transition became dominated by an
407 408 409 410 411 412 413 414	6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic. Further, understanding changes in ocean chemistry during this time has the potential to yield valuable insight into ocean connectivity during <u>Pangaean</u> separation. Seawater during the <u>Sinemurian–Pliensbachian</u> transition became dominated by an unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os signal that is not resolvable by influxes from continental weathering or
407 408 409 410 411 412 413 414 415	6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic. Further, understanding changes in ocean chemistry during this time has the potential to yield valuable insight into ocean connectivity during <u>Pangaea</u> n separation. Seawater during the <u>Sinemurian–Pliensbachian</u> transition became dominated by an unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os signal that is not resolvable by influxes from continental weathering or meteorite impact. The break-up of <u>Pangaea</u> was of fundamental importance to this observed
407 408 409 410 411 412 413 414 415	6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic. Further, understanding changes in ocean chemistry during this time has the potential to yield valuable insight into ocean connectivity during <u>Pangaea</u> n separation. Seawater during the <u>Sinemurian–Pliensbachian</u> transition became dominated by an unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os signal that is not resolvable by influxes from continental weathering or meteorite impact. The break-up of <u>Pangaea</u> was of fundamental importance to this observed isotopic trend, and a mantle-derived source favours the constructed Os isotope profile.
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407 408 409 410 411 412 413 414 415 416 417 418	6. Conclusions The <u>Sinemurian–Pliensbachian</u> boundary GSSP at Robin Hood's Bay, UK, has the potential to provide a significantly increased understanding of seawater chemistry during the Early Jurassic. Further, understanding changes in ocean chemistry during this time has the potential to yield valuable insight into ocean connectivity during <u>Pangaean</u> separation. Seawater during the <u>Sinemurian–Pliensbachian</u> transition became dominated by an unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os signal that is not resolvable by influxes from continental weathering or meteorite impact. The break-up of <u>Pangaea</u> was of fundamental importance to this observed isotopic trend, and a mantle-derived source favours the constructed Os isotope profile. The <u>Triassic–Jurassic</u> boundary marks the onset of volcanism in the Central Atlantic Magmatic Province, directly associated with <u>Pangaea</u> n fragmentation. Following this there is strong

420	Tethyan and eastern Pacific oceans in the latest Sinemurian and the start of the Pliensbachian, via
421	the Hispanic Corridor (defining the rift zone between North America, South America and Africa). This
422	stage boundary therefore marks the initial flooding event of the Hispanic Corridor that also
423	corresponds to an on-going global sea level rise. Seawater inundation would have initiated seawater
424	interaction with, and circulation into, deep crustal fissures associated with rifting in this region, thus
425	driving extensive low-temperature hydrothermal activity. Such low-temperature hydrothermal fluids
426	are characterised by unradiogenic 187 Os/ 188 Os ratios of ~0.12 (Sharma et al., 2000; Kelley et al.,
427	2001). It is therefore possible that the unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os signal observed across the
428	Sinemurian–Pliensbachian boundary marks the onset of hydrothermal activity associated with
429	formation of the Hispanic Corridor.
430	
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435	
436	Figure captions
137	Fig. 1 Man showing the European encontinental sea and the geographical relationship between the
420	Historia Camidan Tathura Ocean and Bahis Head's Day Madified after Dara et al. (2000). A lapation
438	Hispanic Corridor, Tethyan Ocean and Robin Hood's Bay. Modified after Dera et al. (2009). <u>A location</u>
439	map of the Wine Haven section is also provided.
440	
441	Fig. 2. Graphic log showing the Sinemurian-Pliensbachian boundary GSSP and the relative locations
442	of the samples analysed in this study. Bed number classification taken from Hesselbo and Jenkyns
443	(1995).

Fig. 3. Re-Os isotope stratigraphy across the Sinemurian–Pliensbachian boundary GSSP, UK.
Strontium isotope (⁸⁷ Sr/ ⁸⁶ Sr) from Jones et al. (1994) and Hesselbo et al. (2000), and δ^{18} O data from
Hesselbo et al. (2000). Grey dashed line, A, reflects the three groups of $^{187}\text{Os}/^{188}\text{Os}_{(i)}$ values for
seawater across the Sinemurian-Pliensbachian boundary (~0.38, 0.28 and 0.21). Black dashed line,
B^{1} , represents the first estimation of stable steady-state ¹⁸⁷ Os/ ¹⁸⁸ Os values for Early Jurassic
seawater (~0.47; Kuroda et al., 2010). Bed number classification taken from Hesselbo and Jenkyns
(1995).
Fig. 4. a) Rhenium-osmium isochron for all Robin Hood's Bay samples (n = 32); b) Histogram showing
l the variability of the initial ¹⁸⁷ Os/ ¹⁸⁸ Os ratio in the Robin Hood's Bay sediments, calculated at 189.6
Ma; c) All Robin Hood's Bay samples with initial 187 Os/ 188 Os ratios between ~0.20 – 0.30 (n = 17); d)
The four samples at the top of the studied Robin Hood's Bay section, with variable 187 Re/ 188 Os ratios
(~268 – 443) and similar initial ¹⁸⁷ Os/ ¹⁸⁸ Os ratios (~0.20 – 0.22).
Fig. 5. Global reconstruction of Pangaea in the Early Jurassic. Map shows the relative locations of the
Central Atlantic Magmatic Province (CAMP), the Hispanic Corridor, the Tethyan and Pacific oceans
and Robin Hood's Bay. Modified after www.scotese.com.
Table 1_Re and Os isotope data for the Sinemurian–Pliensbachian boundary GSSP, UK.

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- 614 www.scotese.com (Figure 5: <u>Pangaea</u>n reconstruction in the Early Jurassic)

Opening of a trans-Pangean marine corridor during the Early Jurassic: Insights from osmium isotopes across the Sinemurian-Pliensbachian GSSP, Robin Hood's Bay, UK.

Highlights

- New Re-Os isotope data across the Sinemurian-Pliensbachian boundary GSSP
- Os isotope composition of seawater becomes increasingly unradiogenic at this time
- Osmium isotopes indicate significant hydrothermal contribution to global seawater
- Osmium data indicates ocean connectivity via Hispanic Corridor in Latest Sinemurian

1 Opening of a trans-Pangaean marine corridor during the Early Jurassic: Insights from 2 osmium isotopes across the Sinemurian–Pliensbachian GSSP, Robin Hood's Bay, UK. 3 4 Sarah J. Porter^{a,*}, David Selby^a, Katsuhiko Suzuki^b, Darren Gröcke^a 5 6 7 ^a Department of Earth Sciences, Durham University, Durham, DH1 3LE, UK. ^b Japan-Agency for Marine-Earth Science and Technology, Yokosuka, 237-0061, Japan. 8 9 Corresponding author (S. J. Porter). Tel.: +44 (0)191 334 2300; fax: +44 (0191) 334 2301; E-mail: 10 sporter@eos.ubc.ca 11 12 13 Keywords: Osmium isotopes, Hispanic Corridor, Sinemurian–Pliensbachian, organic-rich sediments, 14 ocean connectivity 15 ABSTRACT 16 17 The Hispanic Corridor represents a significant phase of continental reorganisation of the Early Jurassic that eventually provided connectivity between the western Tethyan and eastern Pacific 18 19 oceans along the Central Atlantic rift zone. Although the initiation of this marine corridor profoundly 20 impacted oceanic circulation and marine faunal exchange patterns, the timing of its formation hitherto remains poorly constrained with estimates spanning both the Hettangian and Sinemurian. 21 22 The Sinemurian–Pliensbachian Global Stratotype Section and Point (GSSP) at Robin Hood's Bay, UK, comprises a succession of well-exposed, immature organic-rich sediments, only previously 23 characterised by strontium, oxygen and carbon isotope geochemistry. New Re and Os isotope 24 25 profiling indicates substantial variation in seawater chemistry at this time. Initial osmium isotope 26 data become increasing unradiogenic (0.40 to 0.20) across the boundary, providing evidence for a 27 continual flux of unradiogenic Os into the oceans during the latest Sinemurian. The initial unradiogenic ¹⁸⁷Os/¹⁸⁸Os values indicate the occurrence of low-temperature hydrothermal activity 28 29 associated with the formation of the Hispanic Corridor during the breakup of Pangaea. Therefore, 30 combined with biogeography and faunal exchange patterns, the Os isotope data demonstrates that 31 connectivity between the Eastern Pacific and Tethyan oceans initiated during the latest Sinemurian.

As a result this study better constrains the timing of establishment of the Hispanic Corridor, which
was previously limited to poorly defined biogeography.

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36 1. Introduction

37 Marine sedimentary rocks hold the key to understanding past chemical changes and fluxes in the oceans. Analysis of hydrogenous rhenium (Re) and osmium (Os) in organic-rich sediments allows 38 39 detailed evaluation of seawater chemistry at the time of sediment deposition. The Os isotope system (¹⁸⁷Os/¹⁸⁸Os) is a particularly powerful tool for tracing temporal changes in the balance of 40 41 global inputs to the oceans (Ravizza et al., 1996; Levasseur et al., 1999; Cohen et al., 1999; Peucker-42 Ehrenbrink and Ravizza, 2000), and as such it permits the evaluation of fluctuations in seawater 43 chemistry throughout geological time. Specifically, significant input from meteorite impact, 44 continental weathering and mantle-derived fluxes can be identified and distinguished.

The present-day seawater Os isotope composition may be relatively uniform (¹⁸⁷Os/¹⁸⁸Os 45 46 ratio of ~1.06; Levasseur et al., 1998; Peucker-Ehrenbrink and Ravizza, 2000), but it has varied 47 significantly throughout geological time. The short seawater residence time of Os of ~10-40 Ka (Sharma et al., 1997; Oxburgh, 1998; Levasseur et al., 1998; Peucker-Ehrenbrink and Ravizza, 2000), 48 49 longer than the mixing time of the oceans (~2-4 Ka; Palmer et al., 1988), allows the Os isotope 50 composition to respond rapidly to any alterations in the composition and flux of these inputs 51 (Oxburgh, 1998; Cohen et al., 1999). This has been successfully exploited by past studies, where Os 52 has been used as a chemostratigraphic marker of significant volcanic events (eg., Cohen et al., 1999; 53 Ravizza and Peucker-Ehrenbrink, 2003).

54 Until now, isotope stratigraphy of the Sinemurian–Pliensbachian GSSP at Robin Hood's Bay 55 (Wine Haven, UK) has been limited to 87 Sr/ 86 Sr (Jones et al., 1994; Hesselbo et al., 2000), δ^{18} O and 56 δ^{13} C data (Hesselbo et al., 2000) from belemnites. Herein we compile these datasets with Re-Os 57 data, to provide new Os isotope characterisation of the Sinemurian–Pliensbachian GSSP. The longer

58 seawater residence time of Sr (~2.4 Ma; Jones and Jenkyns, 2001) relative to Os, slows the response 59 of Sr ratios to changes in the balances of inputs to the oceans (eg. Cohen and Coe, 2002). Therefore, 60 using Os isotopes provides improved resolution for changes in seawater chemistry across this 61 boundary section. Combined with data from previous studies this work has two significant 62 outcomes, by providing: (1) an increased geochemical understanding of an important GSSP, thereby 63 also enhancing our understanding of Lower Jurassic stratigraphy in the UK; and (2) a detailed ¹⁸⁷Os/¹⁸⁸Os profile for contemporaneous Jurassic seawater allowing insight into the contributions of 64 65 the various global inputs into the oceans at this time and therefore providing information regarding 66 ocean connectivity during the Early Jurassic.

67 Currently, the timing of development of oceanic seaways during Pangaean separation is 68 poorly constrained, with estimates that include both the Hettangian and Sinemurian. The Hispanic 69 Corridor, an initially epicontinental, but later fully oceanic seaway, connected the western Tethyan 70 and eastern Pacific oceans along the Central Atlantic rift zone (Smith and Tipper, 1986; Smith et al., 71 1990; Riccardi, 1991; Hallam and Wignall, 1997; Aberhan, 2001). Formed through separation of the 72 Pangaean supercontinent, this proto-Atlantic seaway resulted from one of the most significant 73 palaeogeographic reorganisations in Earth's history (Smith et al., 1990). Initially developing over 74 rifting continental crust (Smith et al., 1994), this marine corridor signified the tectonic transition 75 from rifting to drifting, prior to the formation of the Atlantic Ocean (Smith et al., 1990). In addition 76 to the profound impact on ocean circulation and equatorial distribution of marine organisms at this 77 time, the marine corridor acted as a filter during its early stages, preferentially allowing passage of 78 on-shore benthic species, whilst acting as an effective barrier for off-shore species (eg. Hallam and 79 Wignall, 1997; Smith et al., 1994; Aberhan, 2001). However, with no direct sedimentological or 80 geophysical evidence, determining the timing for the establishment of the corridor using 81 biogeography has been the subject of continuous debate. As such, the timing of seaway formation is 82 currently imprecise and suggested to have occurred within the Early Jurassic (eg. Damborenea, 2000; 83 Aberhan, 2001).

The ¹⁸⁷Os/¹⁸⁸Os values from the Sinemurian–Pliensbachian GSSP, Robin Hood's Bay, UK, provide evidence for significant low-temperature hydrothermal activity that may have been associated with the formation of the Hispanic Corridor during the breakup of Pangaea. Combined with biogeography and faunal exchange patterns, the Os data herein suggests that connectivity between the Eastern Pacific and Tethyan oceans initiated during the latest Sinemurian. Thus, this study better constrains the timing of establishment of the Hispanic Corridor, previously limited to poorly defined biogeography.

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93 2. Geology of the Sinemurian–Pliensbachian boundary GSSP

94 Our study focuses on the marine sediments at the Sinemurian–Pliensbachian Global 95 Boundary Stratotype Section and Point (GSSP) at Wine Haven, ~3 km S–SE of Robin Hood's Bay, 96 Yorkshire, UK (Grid ref. NZ9762 0230 eg, Hesselbo et al., 2000; Meister et al., 2006; Fig. 1). This 97 Lower Jurassic boundary occurs in the Pyritous Shales of the Redcar Mudstone Formation within the 98 Lias Group (Powell, 1984). It has been the subject of scientific interest for many years, with the 99 earliest reference to the site being by Young and Bird (1822). Exposure at Robin Hood's Bay is 100 optimal, with lower beds exposed by a series of wave-cut platforms. The succession here is also 101 known for its well-preserved ammonite assemblages (eg. Tate and Blake, 1876; Dommergues and 102 Meister, 1992). Using the biostratigraphy, the base of the Pliensbachian Stage can be unambiguously 103 located at the bottom of the taylori Subzone of the Uptonia jamesoni Zone, marked by the first 104 occurrence of species of the genus Apoderoceras (Dean et al., 1961; Hesselbo et al., 2000; Gradstein 105 et al., 2004; Meister et al., 2006).

The age for the base of the Pliensbachian has been defined by the Geological Time Scale (GTS) 2004 as 189.6 ± 1.5 Ma (Gradstein et al., 2004), derived from cycle-scaled linear Sr trends and ammonite occurrences (as noted above; also includes the lowest occurrence of *Bifericeras donovani*; Gradstein et al., 2004). Herein, this age for the Sinemurian–Pliensbachian boundary is used. The

Sinemurian–Pliensbachian boundary is placed very close to the base of Bed 73 (bed classification
from Hesselbo and Jenkyns, 1995), ~6 cm above the midline of nodules forming the upper margin of
Bed 72 in the Wine Haven section (Hesselbo et al., 2000).

113 An epicontinental sea, positioned to the west of the deep Tethyan basin (Dera et al., 2009) 114 covered most of Northern Europe, including Britain, during the Mesozoic (Sellwood and Jenkyns, 115 1975; Fig. 1). Lithological evidence for sea level rise, combined with sedimentological evidence 116 (Smith et al., 1994), indicates that the epicontinental sea during this time was not landlocked but 117 free to circulate with the Tethyan ocean. The open ocean Os isotope composition across the 118 boundary interval should therefore be echoed in the sampled sediments. Analysis of hydrogenous 119 Re and Os from these samples instils certainty that the calculated initial Os isotope composition $(^{187}Os/^{188}Os_{(i)})$ reflects that of contemporaneous seawater (Cohen et al., 1999). 120

Over a ~10 m interval, the lithology of the Wine Haven succession gradually progresses from pale siliceous and clay-rich mudrocks with intermittent coarser sand beds in the Upper Sinemurian (*aplanatum* Subzone), to finer and much darker shales with less clay ~1.5 m above the boundary in the Lower Pliensbachian (*taylori* Subzone; Meister et al., 2006; Hesselbo and Jenkyns, 1995, 1998; this study). These facies changes indicate an overall relative increase in sea level of at least regional, but possibly global extent (Sellwood, 1972; Hallam, 1981; Hesselbo and Jenkyns 1995, 1998;

127 Hesselbo et al., 2000; Meister et al., 2006).

Nodular beds of concretionary siderite (~10 cm in thickness) of both laterally continuous (Beds 70 and 72) and semi-continuous extent (Bed 74 and within Bed 71) are present throughout the Wine Haven section (Sellwood, 1972; Meister et al., 2006; this study). The origin of these nodules is uncertain, although they are suggested to represent non- or slow depositional phases based on their unique association with fauna found in life-position (Sellwood, 1972).

Sedimentation rate across the Sinemurian–Pliensbachian boundary has been approximated here by taking ~64 Ma as the duration for the Jurassic period (Gradstein et al., 2004) and using mean thicknesses of ammonite zonal subdivisions estimated by Hallam and Sellwood (1976). This provides

a combined thickness for the Sinemurian and Pliensbachian of ~278 m, ~23 % of the total for the
Jurassic. By disregarding the uncertain effects of compaction (Hallam and Sellwood, 1976), a steady
sedimentation rate during this interval has been calculated at ~1.9 cm/Ka, in turn suggesting that the
interval sampled by this study (~6 m) spans ~320 Ka.

Although the ⁸⁷Sr/⁸⁶Sr profile (Hesselbo et al., 2000) shows a systematic decrease up-section 140 (~0.707487 to 0.707395 over a 10 m interval), a lack of any abrupt changes in the ⁸⁷Sr/⁸⁶Sr ratio 141 142 indicates that sedimentation was continuous (Jones et al., 1994; Hesselbo et al., 2000; Meister et al., 2006). At the boundary level, a drop in ⁸⁷Sr/⁸⁶Sr value from ~0.707433 to 0.707418 (Hesselbo et al., 143 2000) could allow the possibility of minor slowing or hiatus in sediment deposition (Hesselbo et al., 144 145 2000; Meister et al., 2006). However, replicate analyses of belemnites from 1–4 cm above the boundary give an average ⁸⁷Sr/⁸⁶Sr value of 0.707422 ± 0.000012, well within uncertainty of the ratio 146 147 recorded for the boundary (0.707425 ± 0.000004) (Hesselbo et al., 2000), suggesting a slowing 148 rather than break in deposition (Hesselbo et al., 2000; Meister et al., 2006). Further evidence for 149 continuous deposition is supported by a lack of lithological unconformities (Meister et al., 2006; this 150 study).

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153 3. Analytical methodology

154 3.1 Sampling

A set of 32 samples (SP7-09 to SP39-09) were collected from the Pyritous Shales Member of the Redcar Mudstone Formation, along a 6 m vertical section bracketing the Sinemurian– Pliensbachian boundary (sample SP22-09) at Robin Hood's Bay (Fig. 2). Sampling occurred at a consistent interval of ~20 cm for 3 m above and 3 m below the boundary from Beds 69–75 except within Bed 72, where a smaller sampling interval of ~15 cm was used (Fig. 2). Based on our approximation above for the duration of sedimentation across this section, sampling at ~20 cm intervals allowed us to capture an estimated resolution of ~11 Ka per sample.

162 In preparation for geochemical analyses, the samples were cut and polished to expose fresh 163 surfaces, and were then powdered in a Zr disc.

164

165 *3.2 Re-Os analysis*

166 Rhenium and osmium analyses of Robin Hood's Bay whole-rock powders were conducted at 167 the Japan Agency for Marine-Earth Science and Technology (JAMSTEC) as part of the JSPS Summer 168 Fellowship Program 2010, following the CrO₃-H₂SO₄ procedure outlined by Selby and Creaser (2003). 169 This digestion technique minimises removal of Re and Os from the non-hydrogenous (detrital) 170 component of the sample, allowing analysis and evaluation of the hydrogenous fraction (Selby and Creaser, 2003). Sample powders of known quantities (500 mg for samples with >50 ppb Re or 1g for 171 samples with <50 ppb Re) were digested with a measured amount of ¹⁸⁵Re and ¹⁹⁰Os spike solution, 172 in 8 ml of CrO₃-H₂SO₄ solution in Carius tubes at 240 ^oC for 48 hrs. After cooling, Os was removed 173 174 and purified from the solution by solvent extraction and micro-distillation.

Following Os removal, the remaining solution was prepared for anion exchange 175 chromatography to purify the Re fraction. To reduce Cr^{6+} to Cr^{3+} , necessary to avoid complications 176 during chromatography (Selby and Creaser, 2003), 1 ml of the remaining solution was removed and 177 reduced drop by drop (due to the violent exothermic reaction) using 3 ml of ethanol (gradual 178 179 addition of ethanol to the sample solution is advised to avoid loss of sample during the reduction 180 reaction). Once reduced, the solution was evaporated to dryness on a hotplate at $\sim 80^{\circ}$ C. 181 The dried Re fraction was taken up in a 10 ml 0.5 N HCl loading solution, before being 182 purified by a two-stage HCI-HNO₃ anion chromatography procedure. The purified Re and Os was 183 loaded onto Ni and Pt filaments, respectively and the Re and Os isotope ratios were measured using NTIMS (Creaser et al., 1991; Völkening et al., 1991) using Faraday collectors and the SEM, 184 respectively. The initial Os isotope composition (¹⁸⁷Os/¹⁸⁸Os_(i)) was calculated using an independently 185 assumed sample age of ~189.6 Ma (Gradstein et al., 2004) and λ ¹⁸⁷Re = 1.666 x 10⁻¹¹ a⁻¹ (Smoliar et 186 187 al., 1996). During this study total procedural blanks were 14.1 ± 0.2 pg and 3.56 ± 0.52 pg (1σ S.D., n

188 = 2) for Re and Os, respectively, with an average 187 Os/ 188 Os value of 0.19 ± 0.005 (n = 2).

189 Uncertainties presented in Table 1 include full error propagation of uncertainties in Re and Os mass

190 spectrometer measurements, blank abundances and isotopic compositions, spike calibrations and

191 reproducibility of standard Re and Os isotopic values.

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193

194 **4. Results**

195 *4.1 Re and Os abundance*

The Re and Os abundances define a large range of values, from ~1.5–117 and ~0.12–1.9 ppb, respectively (Table 1). These values are much greater than those of average continental crust: 0.39 ppb (Re) and 0.05 ppb (Os) (Sun et al., 2003 and references therein). Both Re and Os abundances show an overall increase up-section that becomes more pronounced following the Sinemurian– Pliensbachian boundary.

201

202 4.2 Re-Os geochronology

In order to conduct Re-Os geochronology, the targeted samples should fulfil three criteria. Each sample must possess a similar initial Os isotope composition (¹⁸⁷Os/¹⁸⁸Os_(i)) together with variable ¹⁸⁷Re/¹⁸⁸Os ratios, and have experienced no disturbance to the isotope system since the time of formation (Cohen et al., 1999). The Robin Hood's Bay section shows no evidence of postdepositional disturbance, e.g., no veining is evident and the section is thermally immature. Similar Jurassic sections have been utilised for Re-Os geochronology (Cohen et al., 1999).

For the Robin Hood Bay section the ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios vary from ~25–443 and ~0.3–1.6, respectively. Both ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios decrease between 2.8 to 0.9 m below the Sinemurian–Pliensbachian boundary (¹⁸⁷Re/¹⁸⁸Os, ~195–20; ¹⁸⁷Os/¹⁸⁸Os, ~1–0.3), before systematically increasing across the boundary into the lowermost Pliensbachian. Although all the ¹⁸⁷Re/¹⁸⁸Os and ¹⁸⁷Os/¹⁸⁸Os ratios positively correlated (R² = 0.95), the Re-Os data yield model 3 age

214	of 179 \pm 16 Ma (2 σ , n = 32, MSWD = 473; Fig. 4a). Although within uncertainty of the calculated age
215	for the Sinemurian–Pliensbachian boundary (189.6 \pm 1.5 Ma; Gradstein et al., 2004), the uncertainty
216	is large (~9%) and is accompanied by an extremely large MSWD, which indicates significant scatter
217	of the data about the isochron that relates to more than analytical uncertainty. We suggest that this
218	scatter relates to the sample set possessing variable initial 187 Os/ 188 Os values. The calculated initial
219	187 Os/ 188 Os (187 Os/ 188 Os _(i) at 189.6 Ma; Gradstein et al., 2004) values for this Sinemurian–
220	Pliensbachian section are variable, but consistently unradiogenic for all samples, ranging from
221	$^{\circ}0.20$ – 0.48 . Overall, with exceptions at 1.1 m below the boundary and at the boundary itself (sample
222	SP22-09, 187 Os/ 188 Os _(i) = ~0.48 and SP17-09 = ~0.44, respectively; Fig. 3; 4b), the 187 Os/ 188 Os _(i) values
223	become progressively less radiogenic up-section.
224	If we consider samples with similar 187 Os/ 188 Os _(i) values (~0.20–0.30) regression of the Re-Os
225	data produces a model 3 age of 183.4 \pm 3.3 Ma (2 σ , n = 17, MSWD = 20; Fig. 4c). This age is outside
226	of uncertainty of that given by Gradstein et al. (2004). Regression of Re-Os data for the top four
227	stratigraphic organic-rich samples in the section (SP34-09, SP35-09, SP36-09 and SP37-09) provides a
228	model 1 age of 194 \pm 4.8 Ma (2 σ , n = 4, MSWD = 0.04; Fig. 4d). These samples are ideally suited to
229	Re-Os geochronology because they possess extremely similar initial ¹⁸⁷ Os/ ¹⁸⁸ Os compositions (~0.20-
230	0.22) and variable ¹⁸⁷ Re/ ¹⁸⁸ Os ratios (~268–443). As such, the model age is within uncertainty of that
231	given by Gradstein et al. (2004). Although the Robin Hood bay section is not ideally suited for Re-Os
232	geochronology, the positive correlation of 187 Re/ 188 Os with 187 Os/ 188 Os that yields dates that are in
233	agreement with the Geological Time Scale 2004 (Gradstein et al., 2004), suggests that the Re-Os
234	systematics have not been disturbed and that calculated initial 187 Os/ 188 Os values can be used to
235	discuss Early Jurassic ocean chemistry.
236	

240 **5. Discussion**

241 The Jurassic was a dynamic period that hosted major geological events of Earth's history; 242 notably the full-scale tectonic plate reorganisation associated with the break-up of Pangaea. Ocean 243 chemistry was therefore subject to fluctuations as the balance of inputs changed, and as such the 244 seawater Os isotope composition was highly variable. In order to look critically at the data herein 245 and to determine the potential source of the Os isotope signal observed across the Sinemurian-246 Pliensbachian boundary, there needs to be an understanding of the background seawater Os isotope 247 composition at this time. However, at present no studies conclusively document background seawater Os for the Early Jurassic. The first estimation of stable, steady-state ¹⁸⁷Os/¹⁸⁸Os values for 248 249 the Sinemurian is proposed to be ~ 0.47 (Kuroda et al., 2010). The sampled section (Triassic–Jurassic 250 chert succession from Kurusu, Japan; Kuroda et al., 2010) was positioned to the east of the 251 separating supercontinent, in an intra-ocean setting. The recorded Os isotope composition would 252 therefore not have been directly affected by nearby continental flux, and would have been a good 253 representation of open ocean chemistry at this time. For this investigation, we will assume that this 254 value represents the best estimation of background seawater Os isotope composition at the Sinemurian–Pliensbachian transition. 255

256

257 5.1 Origin of the Sinemurian–Pliensbachian seawater Os isotope composition

The Os data from Robin Hoods Bay show that the calculated seawater initial ¹⁸⁷Os/¹⁸⁸Os value becomes progressively more unradiogenic from the latest Sinemurian into the Pliensbachian. Although there is some fluctuation, this trend to unradiogenic values can be broadly separated into three groups, with average ¹⁸⁷Os/¹⁸⁸Os_(i) values of ~0.38, 0.28 and 0.21 (Fig. 3). These results indicate that there was a marked and progressive increase of unradiogenic Os input into the global ocean during the transition from the Sinemurian to the Pliensbachian.

A peak towards a relatively radiogenic 187 Os/ 188 Os value of 0.48 is coincident with the boundary. This is also matched by an increase in the 187 Re/ 188 Os ratio (from ~31 to 100) and a

decrease in ¹⁹²Os (from ~208 to 102 ppb). Assuming a background seawater Os isotope composition
of ~0.47 (Kuroda et al., 2010), this peak may reflect a period of hiatus in the input of unradiogenic Os
to the oceans.

There are three major inputs of Os that directly control the seawater ¹⁸⁷Os/¹⁸⁸Os value: (1) radiogenic input from weathering of continental crust; (2) unradiogenic contribution from meteorites; (3) an unradiogenic signal from igneous and hydrothermal activity (eg. Peucker-Ehrenbrink and Ravizza, 2000).

273

274 5.1.1 Why is the signal not induced by continental weathering?

275 The gradual trend towards unradiogenic Os isotope values observed in this study indicates that 276 continental weathering is unlikely to be the cause of the Os isotopic signal shown over Sinemurian-277 Pliensbachian boundary. Belemnite oxygen stable isotope data displays a marked increase of ~1 ‰ 278 over 10 m across the boundary (Hesselbo et al., 2000; Fig. 3). This 1 ‰ change is equivalent to a substantial temperature decrease of ~5°C (Hesselbo et al., 2000; Meister et al., 2006). Such 279 280 considerable lowering of temperature, coupled with evidence for low mean land relief and absence 281 of ice sheets during the Early Jurassic (Golonka et al., 1994), would favour reduced rates of regional 282 and global continental weathering.

283 The Os isotope signal resulting from continental weathering is also significantly more radiogenic (¹⁸⁷Os/¹⁸⁸Os = ~1.4; Peucker-Ehrenbrink and Jahn, 2001) than that observed in this study. 284 285 This indicates that the seawater Os isotope composition was dominated by an unradiogenic source 286 that outweighed the input of radiogenic Os from continental weathering. It is extremely difficult to constrain the exact continental ¹⁸⁷Os/¹⁸⁸Os input to the oceans during the Early Jurassic. However, 287 following Cohen et al. (1999), we can attempt to quantify the approximate contribution of crustal Os 288 into the ocean. Assuming an average ¹⁸⁷Os/¹⁸⁸Os value of ~1.4 for weathering of ancient continental 289 crust (Peucker-Ehrenbrink and Jahn, 2001), and a ¹⁸⁷Os/¹⁸⁸Os value of ~0.13 for an unradiogenic 290 291 mantle-derived source (Allègre and Luck, 1980; Esser and Turekian, 1993; Sharma et al., 1997;

292 Levasseur et al., 1998), an input of crustal-sourced Os of 5–22 % is required to obtain seawater 293 ¹⁸⁷Os/¹⁸⁸Os ratios of ~0.44–0.20, respectively. This is small in contrast to the present-day radiogenic 294 contribution to the oceans from the continental crust, of between ~ 70 and 80 % (Peucker-295 Ehrenbrink, 1996; Sharma et al. 1997), respectively. Given the geographical location of Robin Hood's 296 Bay in close-proximity to continental landmasses (Fig. 5), and the absence of ice sheets, there would 297 almost certainly be radiogenic continental input regardless of land-relief and climate. Further, 298 although challenging to quantify, the epicontinental setting would mean increased sensitivity to 299 continental input. There is no evidence for the weathering of unradiogenic lithologies, e.g., mafic and ultramafic units, thus the decrease in seawater ¹⁸⁷Os/¹⁸⁸Os composition during the earliest 300 301 Pliensbachian therefore indicates that input of Os into the ocean at this time was dominated by an 302 unradiogenic source, not accounted for by the continental weathering flux.

303

304 5.1.2 Why is the unradiogenic Os not from an extraterrestrial source?

305 Extraterrestrial and mantle-derived influxes are the dominant unradiogenic sources of Os to the global oceans. The calculated ¹⁸⁷Os/¹⁸⁸Os values of these sources (~0.13) are indistinguishable 306 (Allègre and Luck, 1980; Esser and Turekian, 1993; Sharma et al., 1997; Levasseur et al., 1998). It is 307 therefore necessary to examine the structure of the Os isotope profiles from each source to 308 309 determine which was responsible for the declining unradiogenic Os signal into the Pliensbachian. 310 Fluctuations in the seawater Os isotope record during the Cenozoic were not induced by 311 extraterrestrial Os influx to the oceans, as the cosmic Os flux was continuous relative to the variable 312 ocean Os record (with the exception of the K-T boundary; Peucker-Ehrenbrink and Ravizza, 2000). 313 Although the extraterrestrial flux to Earth during the Jurassic is poorly constrained, the possibility of meteorite impact at the Sinemurian–Pliensbachian boundary does not reconcile the gradual decline 314 in ¹⁸⁷Os/¹⁸⁸Os ratios. Following an impact, the Os isotope system should recover quickly due to the 315 316 relatively short seawater residence time of Os (Peucker-Ehrenbrink and Ravizza, 2000). Therefore, 317 although impacts have been documented ~5–20 Ma prior to the Triassic – Jurassic boundary (Hallam and Wignall, 1997), it would be unlikely to find evidence of meteoritic unradiogenic Os during the
Pliensbachian. This is further supported by a study of the Os isotope excursion due to meteorite
impact across the K–T boundary (Ravizza and Peucker-Ehrenbrink, 2003), that shows relatively rapid
recovery of the Os isotope system to a steady state following impact (¹⁸⁷Os/¹⁸⁸Os value increases
from ~0.16 to 0.40 in a maximum of ~200 Ka).

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340

324 5.1.3 Unradiogenic Os from a mantle-derived source

The unradiogenic ¹⁸⁷Os/¹⁸⁸Os values are therefore most likely to be mantle-derived. Unlike 325 the other potential sources of oceanic Os discussed above, increased input from a mantle source at 326 the time of the Sinemurian–Pliensbachian boundary can explain the observed isotope profiles. 327 328 Rifting of the Pangaean Supercontinent began during the latest Triassic (Marzoli et al., 1999; 329 Hames et al., 2000). The initial stages of continental break-up were focused along the 6000 km 330 lineament that would eventually form the continental margins of the Central North Atlantic Ocean 331 (Hames et al., 2000). Consequently, there is evidence for substantial magmatism during the Late 332 Triassic-Early Jurassic (Marzoli et al., 1999; Hames et al., 2000), defined by extensive continental 333 basalts in North America, Europe, Africa and South America (Wilson, 1997; Marzoli et al., 1999). This formed what is termed as the Central Atlantic Magmatic Province (CAMP). The scale of the CAMP 334 335 has been postulated to exceed that of the Karoo-Ferrar, the Deccan Traps and the Siberian 336 continental flood basalt provinces (Hames et al., 2000), with a total areal extent and volume of at 337 least 7 x 10⁶ Km² and 2 x 10⁶ km³, respectively (Marzoli et al., 1999; Hames et al., 2000). High-precision ⁴⁰Ar/³⁹Ar geochronology of the oldest CAMP volcanic rocks, indicate that 338 339 emplacement occurred during the transition from Late Triassic to Early Jurassic (ca. 200 Ma) with a

341 magnitude, considering both its sizeable magmatic and hydrothermal outputs, would have had a

342 considerable impact on ocean chemistry, regardless of its exceptionally brief duration (Ravizza and

brief duration of \sim < 2 Ma (Marzoli et al., 1999; Hames et al., 2000). A volcanic event of this

343 Peucker-Ehrenbrink, 2003). This has been documented by several Os isotope studies of seawater at

344 the Triassic–Jurassic boundary and during the Hettangian (Cohen et al., 1999; Cohen and Coe, 2002; 345 Cohen, 2004). Prior to and immediately following the Triassic–Jurassic boundary, there was a 346 significant unradiogenic contribution of Os to the oceans that persisted into the Hettangian (Cohen 347 et al., 1999; Cohen and Coe, 2002; Cohen, 2004). This has been attributed to seawater interaction 348 and alteration of recently emplaced CAMP lavas, together with enhanced hydrothermal activity 349 (Cohen et al., 1999; Cohen and Coe, 2002; Cohen, 2004). High chemical weathering rates of juvenile 350 basalts (Louvat and Allègre, 1997) characteristically promote relatively rapid release of unradiogenic 351 Os, which can be seen in the Triassic–Jurassic and Hettangian sample suites (Cohen et al., 1999; 352 Cohen and Coe, 2002; Cohen, 2004). The seawater Os isotopic composition then becomes increasingly unradiogenic across the Sinemurian–Pliensbachian boundary, to ¹⁸⁷Os/¹⁸⁸Os ratios of 353 354 $^{\circ}$ 0.20. Using estimates for Early Jurassic stage durations from Gradstein et al. (2004), this boundary 355 occurred ~ 10 Ma after the Triassic–Jurassic boundary and at least ~8 Ma after emplacement of 356 CAMP. Further, the total duration of weathering of CAMP basalts is estimated at ~3.5 Ma (Cohen and Coe, 2007), producing a seawater ¹⁸⁷Os/¹⁸⁸Os value of ~0.30. It is therefore difficult to reconcile 357 358 the observed Sinemurian-Pliensbachian seawater Os isotope composition with the CAMP 359 emplacement event (ca. 200 Ma) or weathering of the continental flood basalts, given a date for the 360 Sinemurian–Pliensbachian stage boundary of 189.6 ± 1.5 Ma (Gradstein et al., 2004). 361 However, when considering palaeogeographic and biogeographic evidence, it is possible to

determine a mantle-derived origin for the unradiogenic seawater Os isotope composition that does
not rely on emplacement of CAMP lavas. Hydrothermal activity would have been prevalent in this
tectonic setting, and low temperature hydrothermal fluids have a characteristically unradiogenic Os
isotope composition of ~0.12 (Cohen et al., 1999; Sharma et al., 2000).

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369 5.2 Os isotope evidence for oceanic connectivity via the 'Hispanic Corridor' during the Early
370 Pliensbachian

The separation of Pangaea and onset of a global sea level rise established a number of epeiric seaways, including the Hispanic Corridor (Aberhan, 2001). This initially epicontinental, but later fully oceanic seaway was established along the Central Atlantic rift zone, between the areas of North America, South America and Africa (Smith and Tipper, 1986), eventually connecting the western Tethyan and eastern Pacific oceans (eg. Smith and Tipper, 1986; Smith et al., 1990; Riccardi, 1991; Aberhan, 2001; Fig. 5).

377 No connectivity existed between these oceans during the Hettangian or Sinemurian, 378 providing an effective barrier to oceanic circulation and thus to faunal exchange (eg. Smith and 379 Tipper, 1986; Riccardi, 1991; Aberhan, 2001). In addition, biogeographic and sedimentological 380 evidence indicates that an oceanic corridor did not develop before the Middle Jurassic (Aberhan, 381 2001). Whilst some studies, based on benthic faunas, postulate an opening time for the corridor of 382 Late Triassic (Sandy and Stanley, 1993) and early Hettangian (Sha, 2002), substantial evidence for 383 sudden low levels of faunal exchange between the eastern Pacific and western Tethyan oceans 384 exists in the earliest Pliensbachian (Damborenea and Manceñido, 1979; Smith and Tipper, 1986; 385 Smith et al., 1990). This suggests establishment of the Hispanic Corridor as a shallow but continuous 386 seaway by the start of the Pliensbachian. Schootbrugge et al. (2005) also suggest that short bursts in 387 the diversification of dinoflagellates during the latest Sinemurian are consistent with the opening of 388 this seaway.

The decline of seawater ¹⁸⁷Os/¹⁸⁸Os ratios and the rise in sea level evident across the Sinemurian–Pliensbachian boundary section at Wine Haven, are therefore coincident with the onset of flooding of the Hispanic Corridor. Furthermore, this study suggests that the isotopic signals observed at the boundary reflect increasing hydrothermal activity associated with the opening of the Hispanic Corridor.

394	The Hispanic Corridor developed across rifting continental crust (Smith et al., 1994), with
395	significant crustal stretching and attenuation occurring before creation of the oceanic strait (Hallam
396	and Wignall, 1997). Growing evidence also indicates that substantial off-axis hydrothermal venting
397	may occur in cooler crustal regions away from the immediate rift zone, driven by exothermic
398	reactions between seawater and mantle-derived rocks (Kelley et al., 2001). This is evident at the
399	Mid-Atlantic and Juan de Fuca ridges, respectively (Kelley et al., 2001; Sharma et al., 2000),. Off-axis
400	fluids are typically cool (~40–75 $^{\circ}$ C) with high Os concentrations (~500 femtomol/kg) and
401	unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os ratios of ~0.12 (Sharma et al., 2000). Mantle-derived material (basalt) was
402	prevalent in this Central Atlantic region (eg. Wilson, 1997; Marzoli et al., 1999), allowing seawater-
403	rock interaction to ensue following the initial flooding event. This would have driven extensive low-
404	temperature hydrothermal fluid circulation, promoting an increase in the release of unradiogenic Os
405	into the seawater (Sharma et al., 2000).
406	
407	
408	6. Conclusions
409	The Sinemurian–Pliensbachian boundary GSSP at Robin Hood's Bay, UK, has the potential to
410	provide a significantly increased understanding of seawater chemistry during the Early Jurassic.
411	Further, understanding changes in ocean chemistry during this time has the potential to yield
412	valuable insight into ocean connectivity during Pangaean separation.
413	Seawater during the Sinemurian–Pliensbachian transition became dominated by an
414	unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os signal that is not resolvable by influxes from continental weathering or
415	meteorite impact. The break-up of Pangaea was of fundamental importance to this observed
416	isotopic trend, and a mantle-derived source favours the constructed Os isotope profile.
417	The Triassic–Jurassic boundary marks the onset of volcanism in the Central Atlantic
418	Magmatic Province, directly associated with Pangaean fragmentation. Following this there is strong
419	taxonomic evidence for sudden, albeit restricted levels, of faunal exchange between the western

420	Tethyan and eastern Pacific oceans in the latest Sinemurian and the start of the Pliensbachian, via
421	the Hispanic Corridor (defining the rift zone between North America, South America and Africa). This
422	stage boundary therefore marks the initial flooding event of the Hispanic Corridor that also
423	corresponds to an on-going global sea level rise. Seawater inundation would have initiated seawater
424	interaction with, and circulation into, deep crustal fissures associated with rifting in this region, thus
425	driving extensive low-temperature hydrothermal activity. Such low-temperature hydrothermal fluids
426	are characterised by unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os ratios of ~0.12 (Sharma et al., 2000; Kelley et al.,
427	2001). It is therefore possible that the unradiogenic ¹⁸⁷ Os/ ¹⁸⁸ Os signal observed across the
428	Sinemurian–Pliensbachian boundary marks the onset of hydrothermal activity associated with
429	formation of the Hispanic Corridor.
430	
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435	
436	Figure captions
437	Fig. 1. Map showing the European epicontinental sea and the geographical relationship between the
438	Hispanic Corridor, Tethyan Ocean and Robin Hood's Bay. Modified after Dera et al. (2009). A location
439	map of the Wine Haven section is also provided.
440	
441	Fig. 2. Graphic log showing the Sinemurian–Pliensbachian boundary GSSP and the relative locations
442	of the samples analysed in this study. Bed number classification taken from Hesselbo and Jenkyns
443	(1995).

Fig. 3. Re-Os isotope stratigraphy across the Sinemurian–Pliensbachian boundary GSSP, UK.

446 Strontium isotope (87 Sr/ 86 Sr) from Jones et al. (1994) and Hesselbo et al. (2000), and δ^{18} O data from

447 Hesselbo et al. (2000). Grey dashed line, A, reflects the three groups of ¹⁸⁷Os/¹⁸⁸Os_(i) values for

448 seawater across the Sinemurian–Pliensbachian boundary (~0.38, 0.28 and 0.21). Black dashed line,

 B^1 , represents the first estimation of stable steady-state 187 Os/ 188 Os values for Early Jurassic

450 seawater (~0.47; Kuroda et al., 2010). Bed number classification taken from Hesselbo and Jenkyns

451 (1995).

Fig. 4. a) Rhenium-osmium isochron for all Robin Hood's Bay samples (n = 32); b) Histogram showing
the variability of the initial ¹⁸⁷Os/¹⁸⁸Os ratio in the Robin Hood's Bay sediments, calculated at 189.6
Ma; c) All Robin Hood's Bay samples with initial ¹⁸⁷Os/¹⁸⁸Os ratios between ~0.20 – 0.30 (n = 17); d)
The four samples at the top of the studied Robin Hood's Bay section, with variable ¹⁸⁷Re/¹⁸⁸Os ratios
(~268 – 443) and similar initial ¹⁸⁷Os/¹⁸⁸Os ratios (~0.20 – 0.22).

Fig. 5. Global reconstruction of Pangaea in the Early Jurassic. Map shows the relative locations of the
Central Atlantic Magmatic Province (CAMP), the Hispanic Corridor, the Tethyan and Pacific oceans
and Robin Hood's Bay. Modified after www.scotese.com.

Table 1.Re and Os isotope data for the Sinemurian–Pliensbachian boundary GSSP, UK.

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- fossils occurring between the Humber and the Tees, from the German Ocean to the Plain ofYork. Whitby. 366.
- 613
- 614 www.scotese.com (Figure 5: Pangaean reconstruction in the Early Jurassic)











Monte Re (pp) Note Re (pp) Note Re (pp) Note Roy (10^{-10}) Note Note </th <th></th> <th>Distance from</th> <th>Bad</th> <th></th> <th></th> <th>102 Ue</th> <th></th> <th></th> <th></th> <th></th>		Distance from	Bad			102 Ue				
9770 30 75 86.46 ± 0.3 123756 ± 803 4332 4653 ± 432 1563 ± 0.018 650 022 9750 24 75 1176 ± 0.02 1254.46 ± 1126 $575.46 \pm 4332 \pm 432$ 11633 ± 0.0130 650 023 9740 24 75 6154 ± 0.23 123645 ± 126 4332 ± 215 11633 ± 0.0130 650 023 9740 17 57 5384 ± 0.53 10934 ± 12.126 70434 2137 ± 12.16 1004 ± 0.013 650 023 9710 17 57 5384 ± 0.53 10334 ± 12.16 7034 ± 12.16 1004 ± 0.012 650 023 9710 112 75 5354 ± 0.13 3373 1003 ± 0.012 650 023 9730 113 75 5114 ± 0.03 4334 ± 1160 66020 2354 ± 123 1003 ± 0.012 6603 0234 023 9730 1131 ± 103 1131 ± 1160 1502 ± 1012 1003 ± 0.012 </th <th>Sample</th> <th>(m)</th> <th>number</th> <th>Re (ppb)</th> <th>Os (ppt)</th> <th>(ppt)</th> <th>¹⁸⁷Re/¹⁸⁸Os</th> <th>187 Os/¹⁸⁸ Os</th> <th>Rho *</th> <th>9⁽¹⁾SO₈₈₇/SO₆₈₁</th>	Sample	(m)	number	Re (ppb)	Os (ppt)	(ppt)	¹⁸⁷ Re/ ¹⁸⁸ Os	187 Os/ ¹⁸⁸ Os	Rho *	9 ⁽¹⁾ SO ₈₈₇ /SO ₆₈₁
995<09 28 75 11736 ± 0.52 125448 ± 11.56 56.56 ± 66.35 568.65 ± 2.52 1058 ± 0.013 0.639 0.630 0.023 993-09 2.4 75 6.5.4 ± 0.02 1038 ± 1.058 ± 0.013 0.639 0.023 0.023 993-09 2.1 75 6.5.4 ± 0.02 1393.44 ± 8.71 46.35 268.65 ± 2.23 1058 ± 0.013 0.6.29 0.23 991-09 1.8 75 5.6.4 ± 0.02 1393.44 ± 8.71 493.46 213.31 ± 1.47 0.0139 0.629 0.23 991-09 1.8 75 5.6.71 ± 0.03 1393.44 ± 8.71 493.46 235.56 ± 1.23 237.31 ± 1.47 0.0139 0.629 0.23 991-09 1.1 75 5.054 ± 0.03 833.64 ± 1.23 130.54 ± 1.17 0.0134 ± 0.0126 0.639 0.639 0.23 973-09 1.1 75 5.054 ± 0.03 833.64 ± 1.23 130.54 ± 1.03 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 0.023 </td <td>5P37-09</td> <td>3.0</td> <td>75</td> <td>88,40 ± 0.39</td> <td>1237.56 ± 8,93</td> <td>433.22</td> <td>405.93 ± 3.96</td> <td>1.502 ± 0.0184</td> <td>0.630</td> <td>0.22</td>	5P37-09	3.0	75	88,40 ± 0.39	1237.56 ± 8,93	433.22	405.93 ± 3.96	1.502 ± 0.0184	0.630	0.22
995-00 25 62.97 ± 0.28 156.69 ± 8.25 466.35 266.51 ± 2.5 1006 ± 0.013 0.629 0.21 993-00 21 75 62.45 ± 0.28 192.3151 ± 8.16 641.34 259.32 ± 2.15 1008 ± 0.013 0.639 0.20 993-00 12 75 53.48 ± 0.35 192.341 ± 1.81 641.34 259.32 ± 1.31 0.639 0.539 0.239 991-00 18 75 52.64 ± 0.13 883.94 ± 51.3 340.30 153.16 ± 1.47 0.071 ± 0.006 0.539 0.23 973-09 11 75 50.51 ± 0.03 833.95 ± 513 340.30 153.34 ± 1.23 0.071 ± 0.006 0.539 0.23 973-09 11 75 170.24 ± 0.03 636.55 ± 3.68 245.55 133.20 133.44 ± 1.23 0.071 ± 0.008 0.639 0.23 973-09 10 75 170.24 ± 0.03 636.55 ± 3.68 245.55 133.20 133.44 ± 1.23 100.34 ± 0.016 0.639 0.23 973-0 10 75 10.51 ± 1.17	5P36-09	2.8	75	117.36 ± 0.52	1524.48 ± 11.26	526,64	443.32 ± 4.32	1.623 ± 0.0199	0.630	0.22
994400 2.4 75 6.2.5 10.23 10.33 10.33 10.34 10.34 10.34 0.00 0.00 0.00 991300 2.10 75 19.44 0.05 10.34 10.34 0.01 0.010 0.050 0.03 0.03 991300 1.8 75 58.41 0.05 133.44 8.11 49.48 134.64 10.05 0.650 0.03 0.03 0.03 0.03 0.03 0.03 0.03 99109 1.8 75 55.41 0.03 60.20 235.46 1.17 0.011 0.053 0.023 0.023 99209 1.1 75 55.41 0.03 12.23 12.23 12.23 12.23 <th12.24< th=""> 10.33 10.33 0.023<!--</td--><td>5P35-09</td><td>2.6</td><td>75</td><td>62.97 ± 0.28</td><td>1266.69 ± 8.25</td><td>466.35</td><td>268.63 ± 2.62</td><td>1.058 ± 0.0130</td><td>0.629</td><td>0.21</td></th12.24<>	5P35-09	2.6	75	62.97 ± 0.28	1266.69 ± 8.25	466.35	268.63 ± 2.62	1.058 ± 0.0130	0.629	0.21
993309 2.2 75 7538 ± 0.35 193.43 ± 1.26 704 ± 4 2.21.37 ± 2.16 1.014 ± 0.0125 0.630 0.21 993109 1.2 75 1.94.4 ± 0.05 1.32.43 ± 3.34 1.98.66 1.94.65 ± 3.00 1.93.44 ± 6.17 0.711 ± 0.0125 0.633 0.023 0.023 99309 1.4 75 5.05.4 ± 0.03 833.94 ± 5.13 3.10.00 1.93.4 ± 0.0136 0.633 0.003 0.633 0.023 972090 1.1 75 5.10.2 ± 0.03 5.35.65 ± 3.68 2.45.05 1.93.2 ± 1.21 0.711 ± 0.0136 0.633 0.023 0.023 97209 1.3 75 1.10.2 ± 0.013 0.633 ± 0.0076 0.633 0.023 0.023 97209 1.3 73 1.051 ± 0.013 1.065 ± 3.03 1.27.31 ± 1.124 0.023 ± 0.013 0.633 ± 0.0073 0.633 0.023 0.023 97209 0.3 73 1.015 ± 0.013 1.024 ± 0.0166 0.633 0.023 0.023 0.023 0.023 0.023 0.023	SP34-09	2.4	75	62,45 ± 0.28	1253.15 ± 8.16	461.36	269.28 ± 2.63	1.058 ± 0.0130	0.629	0.20
9912-09 210 75 9944 ± 000 57743 ± 344 193.46 194.69 ± 147 0.012 0.020 0.032 9791-09 11 75 5554 ± 0.12 133395 ± 4.13 313.66 ± 1.17 0.053 ± 0.0126 0.033 979-09 11 75 5554 ± 0.02 83397 ± 5.13 313.00 151.14 0.653 ± 0.0078 0.653 0.03 970-09 11 75 558.1 0.03 139.01 ± 1.150 0.633 0.03 0.03 975-09 13 75 57.31 ± 0.03 53.65.4 33 138.24 133 0.013 0.639 0.33 975-09 0.4 73 10.054 ± 0.03 53.65.91 ± 30 133.21 10.054 ± 0.03 0.639 0.23 972-09 0.4 73 10.054 ± 0.03 32.35.4 ± 0.013 0.633 0.639 0.23 972-09 0.4 73 10.054 ± 0.03 32.34.4 ± 1.27 0.0134 ± 0.013 0.639 0.23 972-09 0.4 73 10.054 ± 0.0	5P33-09	2.2	75	78.38 ± 0.35	1903.42 ± 12.26	704.34	221.37 ± 2.16	1.014 ± 0.0125	0.630	0.31
991409 18 75 58.1 ± 0.26 1339.4 ± 8.71 493.48 235.8 ± 2.30 105.2 ± 0.0129 0.629 0.20 9727-09 14 75 25.8 ± 0.12 855.9 ± 5.15 340.30 151.16 ± 1.47 0.701 ± 0.008 0.528 0.23 9727-09 11 75 75.8 ± 0.34 1790.11 ± 11.60 660.20 228.44 ± 2.23 1.043.4 ± 0.0128 0.528 0.23 9727-09 10 75 51.70 ± 0.08 656.5 ± 3.68 24.505 313.0 177.51 ± 1.47 0.751 ± 0.008 0.528 0.23 9726-09 0.6 73 10.154 ± 0.05 556.9 ± 3.07 217.32 10.205 ± 0.03 0.539 0.23 9727-09 0.0 73 10.154 ± 0.05 556.9 ± 3.07 217.32 10.205 ± 1.003 0.539 0.23 972409 0.0 73 10.154 ± 0.05 556.9 ± 3.07 217.32 10.205 ± 0.037 0.53 0.23 972409 0.1 73 10.55 ± 0.05 30.31 ± 0.012 0.53 ± 0.013 0.5	5P32-09	2.0	75	19.44 ± 0.09	527,43 ± 3,24	198,66	194.69 ± 1.90	0.864 ± 0.0106	0.630	0.25
990-09 15 75 2586 ± 0.12 885.97 ± 515 340.30 151.16 ± 1.47 0.701 ± 0.0086 0.628 0.23 9729.09 11 75 20.52 ± 0.03 833.95 ± 1.160 66.02.0 238.44 ± 7.3 120.013 0.623 0.23 972.09 11 75 17.02 ± 0.08 63.65 ± 3.68 245.05 138.0 ± 1.35 0.684 ± 0.0084 0.623 0.23 972.09 10 73b 10.11 ± 0.03 217.02 ± 1.03 127.31 102.31 0.334 ± 0.0034 0.623 0.25 972.09 0.4 73b 10.115 ± 0.05 555.61 ± 3.07 217.32 102.51 ± 1.07 0.564 ± 0.0034 0.623 0.25 972.09 0.4 73b 10.15 ± 0.05 555.61 ± 3.07 217.32 102.51 ± 1.07 0554 ± 0.073 0.623 0.25 972.09 0.1 71 126.31 127.31 102.51 ± 1.07 0554 ± 0.073 0.623 0.25 973.09 0.1 71 158.44 10.051 ± 1.07 0554 ± 0.073	SP31-09	1.8	75	58.51 ± 0.26	1339,44 ± 8,71	493,48	235,86 ± 2.30	1.052 ± 0.0129	0.629	0.30
\$\$\$\$25-0\$ 14 75 20.62 ± 0.03 83.36 ± 4.73 123.00 $1273 \pm 10.32 \pm 0.078$ 06.23 0.23 0.23 \$\$\$\$26-0 10 75 10.72 ± 0.03 190.33 ± 11.60 660.30 238.44 ± 2.23 10.43 ± 0.073 06.32 0.23 \$\$\$\$\$26-0 0.6 736 10.24 ± 0.03 412.56 ± 2.23 162.112 82.23 ± 0.073 0.633 0.632 0.23 \$	5P30-09	1.6	75	25.86 ± 0.12	885.97 ± 5.15	340.30	151.16 ± 1.47	0.701 ± 0.0086	0.628	0.22
SP28-09 11 75 75.81 ± 0.34 1790.13 ± 11.60 660.20 228.44 ± 2.23 10.63 ± 0.028 0.628 0.23 SP27-09 10 75 6.71 ± 0.03 636.65 ± 3.68 245.05 133.20 ± 1.35 0.654 0.629 0.23 SP24-09 0.8 730 11.15 ± 0.03 536.56 ± 3.07 217.32 102.55 ± 1.20 0.53 <	SP29-09	1.4	75	20.62 ± 0.09	833.96 ± 4.73	323.00	127.03 ± 1.24	0.633 ± 0.0078	0.629	0.23
SP2709 10 75 1702 ± 008 6565 ± 3.68 245.05 138.20 ± 1.35 0.684 ± 0.008 0.629 0.25 SP26-99 0.6 73 1069 ± 0.05 329.82 ± 301 121.31 120.51 ± 1003 0.629 0.25 SP24-99 0.4 736 11.15 ± 0.05 329.82 ± 2.03 121.31 107.51 ± 1.67 0.553 ± 0.0073 0.629 0.23 SP24-99 0.4 736 10.65 ± 0.05 329.82 ± 2.03 121.31 107.51 ± 1.67 0.553 ± 0.0073 0.653 0.23 SP22-09 0.1 SP bounding 519.2 ± 0.02 31.38 ± 0.44 0.366 ± 0.0073 0.53 0.23 SP30-90 0.1 SP bounding 518.2 ± 1.57 102.05 13.38 ± 0.44 0.366 ± 0.0073 0.53 0.24 SP10-90 0.1 SP bounding 518.2 ± 1.15 102.05 13.34 ± 1.17 11.75 13.34 ± 0.043 0.436 0.036 0.24 SP10-90 0.1 R11.44 112.55 110.515 12.32 ± 0.21 0.341 ± 0.003 <td>5P28-09</td> <td>1.2</td> <td>75</td> <td>75.81 ± 0.34</td> <td>1790.13 ± 11.60</td> <td>660.20</td> <td>228.44 ± 2.23</td> <td>1.043 ± 0.0128</td> <td>0.628</td> <td>0.32</td>	5P28-09	1.2	75	75.81 ± 0.34	1790.13 ± 11.60	660.20	228.44 ± 2.23	1.043 ± 0.0128	0.628	0.32
SP5-09 0.8 75 6.71 ± 0.03 412.56 ± 2.23 16.212 82.29 ± 0.81 0.515 ± 0.003 0.629 0.22 SP2-09 0.4 73b 110.69 ± 0.05 520.99\pm2.91 207.77 104.45 ± 1.02 0.559 ± 0.0073 0.629 0.24 SP2-09 0.4 73b 1115 ± 0.03 536.56 ± 3.03 237.747 ± 1.64 102.55 10070 0.629 0.23 SP2-09 0.0 S.P. boundary 519 ± 0.02 270.47 ± 1.64 102.65 100.74 ± 0.076 0.629 0.23 0.25 SP2-09 0.1 72 233 ± 0.04 012.65 100.52 0.747 0.736 0.25 SP10-09 0.1 72 233 ± 0.04 012.65 102.52 103.74 ± 1.64 102.52 103.74 ± 0.043 0.436 0.043 0.436 0.043 0.25 SP10-09 0.4 71 126.64 109.00 532.4 ± 0.006 0.25 0.25 SP10-09 0.4 71 <td< td=""><td>SP27-09</td><td>1.0</td><td>75</td><td>17.02 ± 0.08</td><td>636.65 ± 3.68</td><td>245.05</td><td>138.20 ± 1.35</td><td>0.684 ± 0.0084</td><td>0.629</td><td>0,25</td></td<>	SP27-09	1.0	75	17.02 ± 0.08	636.65 ± 3.68	245.05	138.20 ± 1.35	0.684 ± 0.0084	0.629	0,25
SP2509 0.6 73b 10.69 ± 0.05 5209 ± 2.91 20.77 104.85 ± 1.02 0.593 ± 0.0070 0.629 0.24 SP2409 0.4 73b 1115 ± 0.05 555.54 ± 307 217.32 102.05 ± 1.00 0.564 ± 0.0070 0.631 0.33 SP2309 0.1 SF pointeny 5.19 ± 0.02 27047 ± 1.64 102.55 100.55 ± 0.05 0.539 0.010 0.531 0.43 SP2109 0.1 SF pointeny 5.19 ± 0.01 27047 ± 1.64 102.55 107.51 0.539 0.416 0.31 SP109 0.1 72 2.81 ± 0.01 275.83 ± 1.46 109.00 51.34 ± 0.028 0.616 0.31 SP109 0.1 71 1.08 ± 0.01 493.24 ± 1.96 105.01 23.24 ± 0.03 0.596 0.026 0.24 SP109 0.7 71 1.08 ± 0.01 493.54 ± 1.96 105.01 0.346 ± 0.003 0.596 0.24 SP109 0.7 71 1.07 1.65.23 ± 0.27 205.24 ± 0.21 0.234	SP26-09	0.8	75	6.71 ± 0.03	412.56 ± 2.23	162.12	82.29 ± 0.81	0.515 ± 0.0063	0.628	0.25
SP2409 0.4 73b 11.15 ± 0.05 556.50 ± 3.07 217.32 102.05 ± 1.07 0.56.5 ± 0.070 0.629 0.24 SP2309 0.1 3.7 10.65 ± 0.05 535.50 ± 3.07 11.431 17051 ± 1.67 0.588 ± 0.016 0.631 0.23 SP3009 0.1 3.7 2.19 ± 0.02 270.87 ± 1.64 109.00 51.34 ± 0.019 0.629 0.631 0.32 SP3009 0.1 3.7 2.19 ± 0.01 275.83 ± 1.46 199.00 51.30 ± 0.52 0.436 ± 0.003 0.629 0.31 SP3009 0.1 72 2.19 ± 0.01 248.32 ± 2.37 195.01 2.232 ± 0.23 0.436 ± 0.003 0.616 0.31 SP3009 0.1 71 1.68 ± 0.01 494.32 ± 2.37 195.01 2.232 ± 0.27 0.321 ± 0.003 0.616 0.31 SP109 0.1 71 1.68 ± 0.01 493.32 ± 1.16 175.02 0.321 ± 1.003 0.616 0.616 0.31 SP109 0.1 71 1.68 ± 0.01 493.34 ± 1	SP25-09	0.6	735	10.69 ± 0.05	520.99 ± 2.91	202.77	104.85 ± 1.02	0.593 ± 0.0073	0.629	0.26
SP23-09 0.2 73b 10.65 ± 0.05 329.82 ± 2.03 12.431 17.051 ± 1.67 0.885 ± 0.0106 0.631 0.22 SP2209 0.0 S P boundary 519 ± 0.02 270.47 ± 1.64 102.65 100.56 ± 0.99 0.631 0.23 SP3809 0.1 72 328 ± 0.01 518.25 ± 2.57 208.02 31.38 ± 0.043 0.616 0.31 SP3909 0.3 72 21.91 ± 0.01 454.32 1.35 1.35 0.321 ± 0.043 0.616 0.31 SP3909 0.3 71 1.68 ± 0.01 464.32 1.35 1.35 0.31 ± 0.043 0.616 0.31 SP109 0.7 71 1.68 ± 0.01 403.24 ± 1.96 155.77 35.73 ± 0.21 0.314 ± 0.0038 0.590 0.25 SP1090 0.7 71 1.08 ± 0.01 403.24 ± 1.96 155.77 35.73 ± 0.21 0.314 ± 0.0038 0.590 0.25 SP1090 0.7 71 1.98 ± 0.01 403.24 ± 1.96 155.73 ± 0.21 0.314 ± 0.0038 <	SP24-09	0.4	73b	11.15 ± 0.05	556.50 ± 3.07	217.32	102.05 ± 1.00	0.566 ± 0.0070	0.629	0.24
SP2209 0.0 SP boundary 5.19 ± 0.02 270.47 ± 1.64 102.65 100.56 ± 0.99 0.801 ± 0.0099 0.629 0.48 SP38-09 -0.1 72 2.38 ± 0.04 518.25 ± 2.57 208.02 31.38 ± 0.44 0.346 ± 0.0043 0.456 0.25 SP20-09 -0.3 72 2.19 ± 0.01 278.23 ± 1.36 105.01 51.30 ± 0.23 0.310 ± 0.0038 0.616 0.31 SP20-09 -0.7 71 1.68 ± 0.01 483.32 ± 1.36 115.77 35.73 ± 0.21 0.310 ± 0.0038 0.506 0.25 SP10-09 -0.7 71 1.68 ± 0.01 403.24 ± 1.96 115.77 35.73 ± 0.21 0.310 ± 0.0038 0.506 0.25 SP10-09 -1.1 71 2.03 ± 0.01 130.74 ± 1.96 115.77 35.73 ± 0.21 0.305 0.045 0.25 0.27 SP10-09 -1.1 71 2.03 ± 0.01 130.74 ± 1.76 0.536 10.047 0.665 0.25 SP14-09 -1.1 711 2.058 ± 1.03 74.1	SP23-09	0.2	73b	10.65 ± 0.05	329.82 ± 2.03	124.31	170.51 ± 1.67	0.858 ± 0.0106	0.631	0.32
SP38-09 0.1 72 3.28 ± 0.04 518.25 ± 2.57 2.08.02 31.38 ± 0.44 0.346 ± 0.0043 0.436 0.25 SP31-09 0.3 72 2.81 ± 0.01 275.33 ± 1.46 109.00 51.30 ± 0.52 0.470 ± 0.0058 0.616 0.31 SP31-09 0.3 72 2.81 ± 0.01 275.33 ± 1.46 109.00 51.30 ± 0.52 0.470 ± 0.0058 0.616 0.31 SP30-09 0.7 71 1.68 ± 0.01 494.32 ± 2.37 195.01 22.33 ± 0.27 0.331 ± 0.0047 0.606 0.25 SP10-09 0.7 71 1.68 ± 0.01 493.34 ± 1.16 115.77 25.73 ± 0.27 0.335 ± 0.0047 0.605 0.25 SP10-09 0.13 71 1.28 ± 0.01 497.07 26.33 ± 1.27 0.331 ± 1.27 0.325 ± 0.017 0.655 0.24 SP10-09 -1.1 71 2.09 ± 0.01 407.07 ± 2.00 163.76 25.33 ± 0.27 0.336 ± 0.0013 0.655 0.44 SP14-09 -1.7 71 198 ± 1.47	SP22-09	0.0	S-P boundary	5.19 ± 0.02	270.47 ± 1.64	102.65	100.56 ± 0.99	0.801 ± 0.0099	0.629	0.48
SP11090372281 ± 0.01275.83 ± 1.46109.0051.30 ± 0.520.470 ± 0.00580.6160.31SP30090.4722.19 ± 0.01484.32 ± 2.37195.0122.32 ± 0.230.321 ± 0.00400.6060.25SP30090.5711.68 ± 0.01484.32 ± 2.37195.0122.32 ± 0.230.311 ± 0.00380.5900.25SP20090.7711.58 ± 0.01403.24 ± 1.96155.73 ± 0.370.310 ± 0.00380.5050.25SP10900.9711.79 ± 0.01107.09 ± 0.06155.73 ± 0.370.334 ± 0.00470.6050.24SP1709-0.1712.27 ± 0.01107.09 ± 0.06153.7625.33 ± 0.250.232 ± 0.0370.2350.24SP1509-13711.79 ± 0.01197.07 ± 2.00163.7625.33 ± 0.250.354 ± 0.00110.6590.24SP1509-13711.98 ± 0.01197.77 ± 2.00163.7625.33 ± 0.250.321 ± 0.00310.6590.42SP1509-13711.98 ± 0.01197.77 ± 2.00163.7655.33 ± 0.250.559 ± 0.00310.6590.42SP1509-13711.87 ± 0.01119.77 ± 1.0054.3374.3877.380.550 ± 0.00330.6590.33SP1409-17711.87 ± 0.01119.07 ± 1.0069.9657.31 ± 0.570.556 ± 0.00330.6590.33SP1409-17711.87 ± 0.01119.70 ± 1.0069.9574.1857.31 ± 0.57	5P38-09	-0.1	72	3.28 ± 0.04	518.25 ± 2.57	208.02	31.38 ± 0.44	0.346 ± 0.0043	0.436	0.25
SP39-09 0.4 72 2.19 ± 0.01 484.32 ± 2.37 195.01 2.23.2 ± 0.23 0.321 ± 0.0040 0.606 0.25 SP20-09 0.5 71 1.68 ± 0.01 403.324 ± 1.96 162.59 20.58 ± 0.21 0.310 ± 0.038 0.590 0.25 SP19-09 0.7 71 1.68 ± 0.01 403.34 ± 1.15 115.77 35.73 ± 0.37 0.356 ± 0.023 0.25 SP18-09 0.9 71 1.79 ± 0.01 436.18 ± 2.11 176.00 20.27 ± 0.21 0.356 ± 0.037 0.595 0.24 SP18-09 -11 71 2.09 ± 0.01 137.74 0.77 56.43 718 0.750 0.595 0.24 SP14-09 -1.1 71 2.09 ± 0.01 137.74 0.77 56.43 0.756 0.666 ± 0.605 0.24 SP14-09 -1.1 71 1.98 ± <	SP21-09	-0.3	72	2.81 ± 0.01	275.83 ± 1.46	109.00	51.30 ± 0.52	0.470 ± 0.0058	0.616	0.31
SP20-09 05 71 168 ± 0.01 403.24 ± 1.96 16.259 205.8 ± 0.21 0.310 ± 0.0038 0.590 0.25 SP19-09 0.7 71 2.08 ± 0.01 289.80 ± 1.47 115.77 35.73 ± 0.37 0.384 ± 0.0047 0.605 0.27 SP19-09 0.7 71 1.79 ± 0.01 289.80 ± 1.47 115.77 35.73 ± 0.37 0.384 ± 0.0047 0.605 0.27 SP17-09 -11 71 2.27 ± 0.01 107.09 ± 0.66 40.68 110.84 ± 1.17 0.794 ± 0.0101 0.605 0.24 SP17-09 -17 71 2.27 ± 0.01 107.09 ± 0.66 40.68 110.84 ± 1.17 0.794 ± 0.0101 0.629 0.24 SP16-09 -17 71 1.98 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.25 0.34 0.601 0.25 0.42 SP14-09 -17 71 1.87 ± 0.01 118.2.84 ± 1.03 74.18 56.94 ± 0.75 0.669 ± 0.0663 0.650 0.42 SP14-09 -17 1.87 ± 0.01 118.2.	60-6EdS	-0.4	72	2.19 ± 0.01	484.32 ± 2.37	195,01	22.32 ± 0.23	0.321 ± 0.0040	0.606	0.25
SP19-09 0.7 71 2.08 ± 0.01 289.80 ± 1.47 115.77 35.73 ± 0.37 0.384 ± 0.0047 0.605 0.27 SP18-09 0.9 71 1.79 ± 0.01 436.18 ± 2.11 176.00 2027 ± 0.21 0.305 ± 0.0037 0.595 0.24 SP17-09 -1.1 71 2.27 ± 0.01 107.09 ± 0.66 40.68 110.84 ± 1.17 0.794 ± 0.0101 0.629 0.44 SP16-09 -1.3 71 2.27 ± 0.01 107.09 ± 0.66 46.68 110.84 ± 1.17 0.794 ± 0.0101 0.629 0.44 SP16-09 -1.3 71 2.09 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.26 0.328 ± 0.0040 0.601 0.25 SP16-09 -1.7 71 198 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.28 0.669 ± 0.0081 0.601 0.24 SP14-09 -1.7 71 1.98 ± 0.01 118.28 ± 0.69 45.76 68.82 ± 0.75 0.662 ± 0.0081 0.615 0.42 SP14-09 -1.7 71 1.87 ± 0.01 118.28 ± 0.69 45.76 68.82 ± 0.75 0.669 ± 0.0081 0.611 0.42 SP12-09 -2.1 71 1.87 ± 0.01 118.28 ± 0.69 45.76 68.82 ± 0.75 0.569 ± 0.0073 0.603 0.603 SP12-09 -2.1 71 2.07 ± 0.01 118.249 ± 1.08 74.99 78.84 ± 0.80 0.569 ± 0.0073 0.603 0.603 SP209 -2.6 6.9 5.24 ± 0.02 199.32 ± 0.02 <	5P20-09	-0.5	11	1.68 ± 0.01	403.24 ± 1.96	162.59	20.58 ± 0.21	0.310 ± 0.0038	0.590	0,25
SP18-09 0.9 71 1.79 ± 0.01 436.18 ± 2.11 176.00 20.27 ± 0.21 0.305 ± 0.0037 0.595 0.24 SP17-09 -1.1 71 2.27 ± 0.01 107.09 ± 0.66 40.68 110.84 ± 1.17 0.794 ± 0.0101 0.629 0.44 SP15-09 -1.3 71 2.09 ± 0.01 107.09 ± 0.66 40.68 110.84 ± 1.17 0.794 ± 0.0101 0.629 0.44 SP15-09 -1.7 71 1.98 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.82 0.619 0.601 0.25 SP14-09 -1.7 71 1.58 ± 0.01 118.28 ± 0.69 45.76 68.82 ± 0.75 0.669 ± 0.0081 0.615 0.42 SP13-09 -1.7 71 1.87 ± 0.01 118.28 ± 0.69 57.81 ± 0.669 ± 0.601 0.503 0.42 SP12-09 -2.1	5P19-09	-0.7	1	2.08 ± 0.01	289.80 ± 1.47	115.77	35.73 ± 0.37	0.384 ± 0.0047	0.605	0.27
SP17-09 -L1 71 2.27 ± 0.01 107.09 ± 0.56 40.68 110.84 ± 1.17 0.794 ± 0.0101 0.629 0.44 SP16-09 -L3 71 2.09 ± 0.01 407.07 ± 2.00 163.76 25.33 ± 0.26 0.328 ± 0.0040 0.601 0.25 SP16-09 -L3 71 1.98 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.26 0.328 ± 0.0081 0.601 0.25 SP16-09 -L3 71 1.98 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.75 0.562 ± 0.0081 0.615 0.42 SP16-09 -L17 71 1.58 ± 0.01 118.28 ± 0.69 45.76 58.82 ± 0.75 0.569 ± 0.0081 0.595 0.42 SP14-09 -L1 71 1.58 ± 0.01 118.28 ± 1.03 74.18 50.21 ± 0.52 0.569 ± 0.0081 0.503 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.603 0.33 55.94 <t< td=""><td>SP18-09</td><td>6.0-</td><td>11</td><td>1.79 ± 0.01</td><td>436.18 ± 2.11</td><td>176.00</td><td>20.27 ± 0.21</td><td>0.305 ± 0.0037</td><td>0.595</td><td>0.24</td></t<>	SP18-09	6.0-	11	1.79 ± 0.01	436.18 ± 2.11	176.00	20.27 ± 0.21	0.305 ± 0.0037	0.595	0.24
SP16-09 -1.3 71 2.09 ± 0.01 407.07 ± 2.00 163.76 25.33 ± 0.26 0.328 ± 0.0040 0.601 0.25 SP15-09 -1.5 71 1.98 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.82 0.669 ± 0.0084 0.615 0.42 SP15-09 -1.7 71 1.98 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.82 0.669 ± 0.0081 0.505 0.425 0.42 SP13-09 -1.9 71 1.58 ± 0.01 118.28 ± 0.69 45.76 68.82 ± 0.75 0.664 ± 0.0081 0.595 0.42 SP13-09 -1.9 71 1.87 ± 0.01 118.28 ± 0.69 45.76 68.82 ± 0.75 0.669 ± 0.0081 0.595 0.42 SP12-09 -2.1 71 2.03 ± 0.01 179.00 ± 1.00 69.96 57.81 ± 0.50 0.503 ± 0.0070 0.603 0.33 SP12-09 -2.1 71 2.03 78.84 ± 0.80 0.585 ± 0.0070 0.603 0.33 SP9-09 -2.1 69 5.43 ± 0.20 78.84 ± 0.80 0.5	5P17-09	-1.1	1	2.27 ± 0.01	107.09 ± 0.66	40.68	110.84 ± 1.17	0.794 ± 0.0101	0.629	0.44
SP15-09 -1.5 71 1.98 ± 0.01 130.77 ± 0.77 50.43 78.30 ± 0.82 0.066 ± 0.0084 0.615 0.42 SP14-09 -1.7 71 1.58 ± 0.01 118.28 ± 0.69 45.76 58.82 ± 0.75 0.642 ± 0.081 0.595 0.42 SP13-09 -1.9 71 1.87 ± 0.01 118.28 ± 0.69 45.76 58.82 ± 0.75 0.642 ± 0.081 0.595 0.42 SP13-09 -1.9 71 1.87 ± 0.01 188.64 ± 1.00 69.96 57.81 ± 0.50 0.509 ± 0.003 0.603 0.35 SP12-09 -2.1 71 2.03 ± 0.01 179.00 ± 1.00 69.96 57.81 ± 0.50 0.505 ± 0.073 0.603 0.33 SP12-09 -2.3 69 2.97 ± 0.01 192.49 ± 1.08 74.99 78.84 ± 0.80 0.585 ± 0.073 0.613 0.33<	SP16-09	E.L-	12	2.09 ± 0.01	407,07 ± 2.00	163.76	25.33 ± 0.26	0.328 ± 0.0040	0.601	0.25
SP14-09 -1.7 71 1.58 ± 0.01 118.28 ± 0.69 45.76 6.882 ± 0.75 0.642 ± 0.0081 0.595 0.42 SP13-09 -1.9 71 1.87 ± 0.01 188.64 ± 1.03 74.18 50.21 ± 0.52 0.603 0.603 0.35 SP13-09 -1.9 71 1.87 ± 0.01 188.64 ± 1.03 74.18 50.21 ± 0.52 0.509 ± 0.603 0.35 0.35 SP12-09 -2.1 71 2.03 ± 0.01 179.00 ± 1.00 69.96 57.81 ± 0.60 0.560 ± 0.073 0.609 0.38 SP8-09 -2.3 69 5.26 ± 0.01 192.49 ± 1.08 74.99 78.84 ± 0.80 0.563 ± 0.613 0.33 SP9-09 -2.6 69 5.26 ± 0.02 164.12 ± 1.04 51.38 170.52 ± 1.71 0.923 ± 0.613 0.36 0.38 SP10-09	SP15-09	-1.5	11	1.98 ± 0.01	130.77 ± 0.77	50.43	78.30 ± 0.82	0,669 ± 0.0084	0.615	0.42
SP13-09 -1.9 71 1.87 ± 0.01 188.64 ± 1.03 74.18 50.21 ± 0.52 0.509 ± 0.0063 0.603 0.35 SP12-09 -2.1 71 2.03 ± 0.01 179.00 ± 1.00 69.96 57.81 ± 0.60 0.560 ± 0.0070 0.609 0.38 SP12-09 -2.1 71 2.03 ± 0.01 179.00 ± 1.00 69.96 57.81 ± 0.60 0.560 ± 0.0070 0.609 0.38 SP8-09 -2.3 69 2.97 ± 0.01 192.49 ± 1.08 74.99 78.84 ± 0.80 0.565 ± 0.0073 0.622 0.33 SP9-09 -2.8 69 5.26 ± 0.02 164.12 ± 1.04 61.38 17052 ± 1.71 0.923 ± 0.0115 0.636 0.38 SP10-09 -2.8 69 5.43 ± 0.02 149.32 ± 0.97 55.48 194.57 ± 1.95 0.980 ± 0.0122 0.636 0.36 SP10-09 -3.0 69 5.29 ± 0.02 152.90 ± 0.98 56.94 184.94 ± 1.86 0.960 ± 0.0120 0.637 0.36 SP11-09 -3.0 69 5.29 ± 0.02	SP14-09	-1.7	11	1.58 ± 0.01	118.28 ± 0.69	45.76	68.82 ± 0.75	0.642 ± 0.0081	0.595	0.42
SP12-09 -2.1 71 2.03 ± 0.01 179.00 ± 1.00 69.96 57.81 ± 0.60 0.560 ± 0.070 0.609 0.38 SP8-09 -2.3 69 2.97 ± 0.01 192.49 ± 1.08 74.99 78.84 ± 0.80 0.555 ± 0.073 0.622 0.33 SP9-09 -2.6 69 5.26 ± 0.02 164.12 ± 1.04 61.38 170.52 ± 1.71 0.923 ± 0.0115 0.636 0.33 SP9-09 -2.8 69 5.43 ± 0.02 164.12 ± 1.04 61.38 170.52 ± 1.71 0.923 ± 0.0115 0.636 0.38 SP10-09 -2.8 69 5.43 ± 0.02 149.32 ± 0.97 55.48 194.57 ± 1.95 0.920 ± 0.0122 0.636 0.36 SP11-09 -3.0 69 5.29 ± 0.02 152.90 ± 0.98 56.94 184.94 ± 1.86 0.960 ± 0.0120 0.637 0.37	SP13-09	-1.9	11	1.87 ± 0.01	I88.64 ± 1.03	74.18	50.21 ± 0.52	0.509 ± 0.0063	0.603	0.35
SP8-09 -2.3 69 2.97 ± 0.01 192.49 ± 1.08 74.99 78.84 ± 0.80 0.585 ± 0.0073 0.622 0.33 SP9-09 -2.6 69 5.26 ± 0.02 164.12 ± 1.04 61.38 170.52 ± 1.71 0.923 ± 0.0115 0.636 0.38 SP10-09 -2.8 69 5.43 ± 0.02 149.32 ± 0.97 55.48 194.57 ± 1.95 0.923 ± 0.0122 0.638 0.36 SP11-09 -3.0 69 5.43 ± 0.02 152.90 ± 0.97 55.48 194.57 ± 1.95 0.980 ± 0.0122 0.638 0.36 SP11-09 -3.0 69 5.29 ± 0.02 152.90 ± 0.98 56.94 184.94 ± 1.86 0.960 ± 0.0120 0.637 0.37	SP12-09	-2.1	11	2.03 ± 0.01	179.00 ± 1.00	69,96	57.81 ± 0.60	0.560 ± 0.0070	0.609	0.38
SP9-09 -2.6 69 5.26 ± 0.02 164.12 ± 1.04 61.38 170.52 ± 1.71 0.923 ± 0.0115 0.636 0.38 SP10-09 -2.8 69 5.43 ± 0.02 149.32 ± 0.97 55.48 194.57 ± 1.95 0.980 ± 0.0122 0.638 0.36 SP11-09 -3.0 69 5.43 ± 0.02 152.90 ± 0.98 56.94 184.94 ± 1.86 0.960 ± 0.0120 0.637 0.37	5P8-09	-2.3	69	2.97 ± 0.01	192.49 ± 1.08	74.99	78.84 ± 0.80	0.585 ± 0.0073	0.622	0.33
SP10-09 -2.8 69 5.43 ± 0.02 149.32 ± 0.97 55.48 194.57 ± 1.95 0.980 ± 0.0122 0.638 0.36 SP11-09 -3.0 69 5.29 ± 0.02 152.90 ± 0.98 56.94 184.94 ± 1.86 0.960 ± 0.0120 0.637 0.37	60-6dS	-2.6	69	5.26 ± 0.02	164.12 ± 1.04	61.38	170.52 ± 1.71	0.923 ± 0.0115	0.636	0.38
SP11-09 -3.0 69 5.29 ± 0.02 152.90 ± 0.98 56.94 184.94 ± 1.86 0.960 ± 0.0120 0.637 0.37	SP10-09	+2.8	69	5,43 ± 0.02	149.32 ± 0.97	55.48	194.57 ± 1.95	0.980 ± 0.0122	0.638	0.36
	SP11-09	-3,0	69	5,29 ± 0,02	152.90 ± 0.98	56.94	184.94 ± 1.86	0.960 ± 0.0120	0.637	0.37

* Rho is the associated error correlation (Ludwig, 1980)

^b The initial ¹⁸⁷ Os/¹⁸⁸ Os isotope ratio calculated at 189.6 Ma

Ages calculated using the $\lambda^{11} R_{\bullet} \star 1.668 \times 10^{-71} \mu^{-1}$