- 1 Regional chronostratigraphic synthesis of the Cenomanian-Turonian OAE2 interval,
- 2 Western Interior Basin (USA): New Re-Os chemostratigraphy and <sup>40</sup>Ar/<sup>39</sup>Ar
- 3 geochronology
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- 17 Highlights:
- 18 New bentonite <sup>40</sup>Ar/<sup>39</sup>Ar dates yield revised Cenomanian-Turonian Boundary (CTB) age
- New rhenium-osmium geochemistry of Angus and SH#1 cores in Western Interior Basin
- Rapid pre-OAE2 initial Os isotope excursions mark large igneous province volcanism
- 59±10 kyr lag between LIP volcanism and global net organic C burial at OAE2 onset
- Quantified duration of basal OAE2 hiatus in the Base Turonian GSSP section at Pueblo, CO

## 23 Keywords:

- Ocean Anoxic Event 2, geochronology, Cenomanian-Turonian stage boundary, large igneous
- 25 province volcanism, osmium chemostratigraphy, Western Interior Seaway

#### 26 Abstract

Fluctuations in depositional conditions during the onset of severe climate events in Earth history 27 28 predispose stratigraphic archives to hiatuses, often hindering complete reconstructions of 29 paleoclimate events and their triggers. Several studies have proposed that a hiatus of unknown duration exists at the base of Oceanic Anoxic Event 2 (OAE2) in the North American Western 30 31 Interior Basin (WIB) at the Base Turonian Global Boundary Stratotype Section and Point (GSSP) in Pueblo, Colorado, potentially influencing integrated radioisotopic, biostratigraphic, and 32 astrochronologic age models of the Cenomanian-Turonian boundary (CTB) interval. To quantify 33 the duration of this hiatus, refine the chronology of OAE2, and assess marine geochemical 34 perturbations associated with the onset of the event, we present new <sup>40</sup>Ar/<sup>39</sup>Ar dates from regional 35 CTB interval bentonites along with a new proximal-distal chemostratigraphic transect of the 36 epeiric WIB, including rhenium-osmium and stable carbon isotope data. The new <sup>40</sup>Ar/<sup>39</sup>Ar age 37 determinations confirm and further constrain previous estimates of CTB timing. Initial osmium 38 isotope ratio (Osi) studies of OAE2 at globally distributed sites record prolific large igneous 39 province (LIP) volcanic activity 10's of kyr prior to the carbon isotope ( $\delta^{13}$ C) excursion of OAE2. 40 However, a recent chemostratigraphic study observed minimal stratigraphic offset between Osi 41 and  $\delta^{13}$ C excursions in a Re-Os record near the Base Turonian GSSP in the central WIB, 42 confirming a hiatus. In contrast, the new Os<sub>i</sub> chemostratigraphy of the Angus Core (Denver Basin) 43 and SH#1 Core (S. Utah) exhibit more characteristic stratigraphic lags between Os<sub>i</sub> and  $\delta^{13}$ C 44 excursions, indicating stratigraphic expansion and conformability across the onset of the event at 45 other sites in the WIB. An existing astronomical time scale for the Angus Core quantifies the 46 temporal lag between LIP volcanism and the beginning of OAE2 (59±10 kyr) and constrains the 47 duration of the hiatus in the Portland Core as geologically brief, indicating that the stratigraphic 48

record at the GSSP locality is largely conformable through OAE2. This astronomically-tuned 49 conformable Osi record across the onset of OAE2 captures a geologically rapid onset of LIP 50 volcanism, consistent with other records, such that the addition of CO<sub>2</sub> to the ocean-atmosphere 51 system may have driven changes in marine carbonate chemistry. Additionally, the refined 52 chronostratigraphy of OAE2 and the CTB in the central WIB improves correlation with other 53 records, such as those in the Eagle Ford Group, Texas. The correlations highlight that discrepancies 54 among OAE2 age models from globally distributed sections commonly stem from differing 55 definitions of the event and uncertainties associated with astronomical tuning, in addition to 56 57 stratigraphic preservation.

## 58

#### INTRODUCTION AND BACKGROUND

Resolving the causal mechanisms of major paleoclimate and paleobiotic events in Earth 59 history is critical to understanding the vulnerabilities of modern and ancient ecosystems. However, 60 the extreme changes in depositional environments associated with the onset of many mass 61 extinction events and carbon cycle perturbations, such as sea level fluctuations or ocean 62 63 acidification, may result in hiatal surfaces that obscure geological evidence of the processes initiating such events (Smith et al., 2001; Holland and Patzkowsky, 2015; Baresel et al., 2017). 64 Expanded, or at least relatively continuous, stratigraphic successions with robust time control are, 65 therefore, key to reconstructing climate change in the geologic record. This study investigates the 66 onset of Oceanic Anoxic Event 2 (OAE2, ~94 Ma), a significant Late Cretaceous carbon cycle 67 perturbation lasting over half a million years, through a proximal-distal chemostratigraphic 68 transect of the shallow marine Western Interior Basin (WIB) of North America. It assesses 69 stratigraphic conformability at reference sites such as the Base Turonian Stage Global Boundary 70 71 Stratotype Section and Point (GSSP) in Pueblo, Colorado, and refines the timing of changes in volcanic activity, global geochemical cycles, and sea level spanning the onset of OAE2. 72

Episodes of voluminous volcanism emplacing large igneous provinces (LIPs) commonly 73 74 precede, or are broadly contemporaneous with, carbon cycle perturbations and mass extinctions through geologic time (Wignall, 2001; Turgeon and Creaser, 2008; Kidder and Worsley, 2010). 75 As a result, elemental and isotopic paleoceanographic proxies sensitive to volcanic fluxes may 76 identify the initiation of such events, as well as elucidate a causal linkage between LIPs and 77 perturbation of the carbon cycle. Moreover, they provide potential chemostratigraphic markers to 78 define the relative expansion or condensation of stratigraphic intervals during the onset of such 79 events, arguably the critical phase for determination of causal factors. This is especially the case 80

for isotopic systems with short marine residence times  $(\tau)$  that capture rapid changes in 81 geochemical fluxes (e.g., Kuroda et al., 2007; Percival et al., 2018). The osmium reservoir of the 82 global ocean mixes over geologically brief time scales ( $\tau < 30$  kyr, Oxburgh, 2001; Rooney et al., 83 2016) and, at the time of deposition, initial marine osmium isotope ratios ( $^{188}Os/^{187}Os(initial) = Osi$ ) 84 principally record changes in the relative fluxes of osmium from two isotopically distinct end 85 members, continental weathering ( $Os_i = -1.4$ ) and hydrothermal inputs ( $Os_i = 0.13$ ) (Peucker-86 Ehrenbrink and Ravizza, 2000). Consequently, the Osi proxy has resolved anomalous increases in 87 volcanic activity across many Mesozoic climate transitions, including OAEs, the Triassic-Jurassic 88 Boundary, and the Cretaceous-Paleogene Boundary (Ravizza and Peucker-Ehrenbrink, 2003; 89 Kuroda et al., 2010; Bottini et al., 2012). 90

For OAE2, the discovery of an abrupt unradiogenic Osi excursion at the base of the event 91 (Turgeon and Creaser, 2008) provides strong evidence for the hypothesis that hydrothermal inputs, 92 likely emanating from the Caribbean LIP and potentially the High Arctic LIP, triggered an Earth 93 94 system response that ultimately led to expanded bottom water anoxia and elevated organic carbon burial (Sinton and Duncan, 1997; Kerr, 1998; Snow et al., 2005; Adams et al., 2010; Barclay et 95 al., 2010; Owens et al., 2013). The OAE2 Osi excursion is also recorded in numerous disparate 96 basins, confirming the proxy as a globally correlative marine chemostratigraphic marker and 97 highlighting a temporal lag, on the order of tens of kiloyears, between the onset of the Osi excursion 98 and the younger carbon isotope ( $\delta^{13}$ C) excursion (Turgeon and Creaser, 2008; Du Vivier et al., 99 100 2014; Du Vivier et al., 2015b; Schröder-Adams et al., 2019; Sullivan et al., in press). This lag likely reflects the fundamental response time of the Earth's carbon cycle to a massive pulse of CO<sub>2</sub> 101 102 to the ocean-atmosphere system from LIP volcanism.

To assess the potential explanations and implications of this lag, and to quantify its 103 duration, this study presents new Osi chemostratigraphic records of the OAE2 onset interval in the 104 WIB from the Angus Core in north-central Colorado and the SH#1 Core in southern Utah (Fig. 1). 105 New <sup>40</sup>Ar/<sup>39</sup>Ar dating of regionally correlated bentonites, along with existing radioisotopic ages, 106 astrochronology, and  $\delta^{13}$ C chemostratigraphy (Meyers et al., 2012b; Ma et al., 2014; Jones et al., 107 108 2019), provide tight age control at these locales for comparison with the Base Turonian GSSP in Pueblo, Colorado, as well as refine the timing and sequence of marine geochemical events through 109 the onset of OAE2. A previous Os<sub>i</sub> chemostratigraphy of the Portland Core, near the GSSP locality, 110 does not exhibit the full characteristic lag between Os<sub>i</sub> and  $\delta^{13}$ Corg preserved in many other records 111 globally (Du Vivier et al., 2014). This chemostratigraphic feature suggests that a hiatus exists at 112 the base of OAE2 in the GSSP. As a result, some recent studies have questioned the stratigraphic 113 completeness of the CTB records from the mid-latitudes of the WIB and suggested that critical 114 time intervals of OAE2 may be missing at the GSSP (Eldrett et al., 2017; Li et al., 2017; Scott et 115 116 al., 2018). Thus, the new Osi chemostratigraphic transect of the WIB presents an opportunity to constrain the spatial extent, origin, and duration of this stratigraphic gap and to evaluate the 117 hypothesis that a crucial interval of time is missing from sedimentary records of OAE2 in the 118 119 central WIB, including at the GSSP locality.

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#### 121 GEOLOGIC SETTING AND MATERIALS

#### 122 Cenomanian-Turonian Stratigraphy in the Western Interior Basin

123 The Late Cretaceous Greenhorn Cyclothem of the foreland Western Interior Basin 124 preserves a ~10-Myr succession of shallow marine facies; OAE2 spans the CTB and occurs just 125 prior to the Early Turonian peak highstand (maximum transgression) of the cyclothem (Kauffman

and Caldwell, 1993). This highstand of the seaway inundated the North American craton and 126 linked the proto-Gulf of Mexico to the arctic Boreal Sea, ranging longitudinally from present-day 127 Iowa to central Utah (Fig. 1). Uplift along the Sevier thrust belt generated maximum subsidence 128 in the proximal western foredeep of the basin, providing accommodation space and sediment 129 supply that produced relatively expanded records of OAE2, such as in the Tropic Shale of the 130 131 SH#1 Core near Big Water, Utah (Jones et al., 2019). Further east, in the more distal "axial basin" of Colorado and the "stable craton" of the central plains (sensu Kauffman, 1984), the hemipelagic 132 sediments of the Bridge Creek Limestone accumulated more slowly and are more carbonate-rich. 133 This is the case in the Angus Core of the Denver Basin, studied here, and in the Portland Core, 134 near the Base Turonian GSSP at the Rock Canyon Anticline in Pueblo, Colorado (Figs. 1-2). A 135 chronostratigraphic framework to correlate these proximal-distal mid-latitude regions of the WIB 136 comprises: areally expansive and radioisotopically dated bentonites ("bentonites A-D"; Elder, 137 1988; Obradovich, 1993; Meyers et al., 2012b), ammonite, inoceramid, and microfossil 138 biostratigraphy (Leckie, 1985; Bralower, 1988; Elder, 1989; Elder, 1991; Kauffman et al., 1993; 139 Kennedy et al., 2005; Corbett and Watkins, 2013), astrochronology from climatically sensitive 140 lithologic patterns (Sageman et al., 1997; Meyers et al., 2001; Ma et al., 2014; Jones et al., 2019), 141 142 lithostratigraphy (Hattin, 1971; Cobban and Scott, 1972; Elder et al., 1994; Elderbak and Leckie, 2016), and carbon isotope chemostratigraphy (Pratt and Threlkeld, 1984; Pratt et al., 1993; 143 Sageman et al., 2006; Joo and Sageman, 2014). 144

Prior to OAE2, during deposition of the late Cenomanian Hartland Shale in the axial basin,
the seaway was relatively oxygen-depleted, restricted, and conducive to organic carbon burial
(Eicher and Worstell, 1970; Sageman, 1985; Sageman, 1989; Meyers et al., 2001; Sageman et al.,
2014a; Eldrett et al., 2017). The lower Bridge Creek Limestone overlies the Hartland Shale in the

Angus and Portland cores (Fig. 2) of the axial basin and preserves the carbon isotope excursion 149 (CIE) that defines OAE2 globally (Pratt et al., 1993). The shift to more calcareous, rhythmically 150 bedded lithologies above the basal contact of the Bridge Creek follows a transgression and 151 pronounced backstepping of the basin's shoreline along the seaway's western margin in southern 152 Utah (Kauffman, 1977; Laurin and Sageman, 2007). This deepening is associated with 153 154 development of a more oxic watermass in the seaway during early OAE2 deposition in the lower Bridge Creek (Eicher and Worstell, 1970; Eicher and Diner, 1985, 1989; Arthur and Sageman, 155 1994; Savrda and Bottjer, 1994; Sageman et al., 1997; Eldrett et al., 2017), contrasting with anoxic 156 conditions in many proto-Atlantic and Tethyan sites during the event (Schlanger et al., 1987). 157

Along the western paleo-margin of the seaway in southern Utah, the fossiliferous Tropic 158 Shale overlies the Naturita Sandstone (Young, 1965; Peterson, 1969; Uličný, 1999), a unit that 159 was, until recently, designated the Dakota Sandstone following standard lithostratigraphic 160 convention for the WIB (Carpenter, 2014). The SH#1 Core, drilled near Big Water, UT on the 161 Kaiparowits Plateau, records an apparently continuous succession of proximal calcareous shales 162 through OAE2 and the CTB (Jones et al., 2019). Thin traceable carbonate-rich beds also occur 163 within the OAE2 interval of the lower Tropic Shale in SH#1 and nearby outcrops, such as the 164 Nipple Creek outcrop section sampled in this study for <sup>40</sup>Ar/<sup>39</sup>Ar bentonite dating. The carbonate 165 beds preserve evidence of partial diagenetic alteration within the expanded  $\delta^{13}$ C chemostratigraphy 166 of the SH#1 Core. This diagenesis relates to eccentricity paced relative sea level cycles and 167 168 flooding surfaces (Jones et al., 2019), which grade westward to shoreface parasequences (Laurin et al., 2019) and eastward to the rhythmically bedded marlstone-limestone couplets of the Bridge 169 170 Creek in the axial basin (Elder et al., 1994). The combined astrochronology, microfossil datums, bentonite A-D stratigraphy, expanded  $\delta^{13}$ C chemostratigraphy (Jones et al., 2019), and ammonite 171

biostratigraphy from outcrops on the Kaiparowits Plateau region (Elder, 1989) form a chronostratigraphic framework for the SH#1 Core within which our new Os<sub>i</sub> chemostratigraphy and  ${}^{40}$ Ar/ ${}^{39}$ Ar geochronologic data are incorporated.

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## 176 OAE2 Hiatuses in the Central Western Interior Basin

177 The Bridge Creek and uppermost Hartland Shale in the Portland Core and GSSP exhibit evidence for hiatal surfaces at two horizons (Fig. 5). The first hiatal surface, identified by spectral 178 analyses and quantified to be <20 kyr, occurs near the base of the ammonite Neocardioceras juddi 179 Biozone (Meyers and Sageman, 2004). The second hiatus, a focus of this study, is associated with 180 a phosphatic bone bed at the base of the CIE and 55 cm below the thick lowermost Bridge Creek 181 limestone bed (Bed 63 or LS1) (Pratt, 1984; Eicher and Diner, 1989), which defines the members' 182 contact (Cobban and Scott, 1972; Elder and Kirkland, 1985). This unquantified hiatus (Du Vivier 183 et al., 2014) falls at the critical OAE2 onset interval (Fig. DR4 in the GSA Data Repository<sup>1</sup>). 184

185

#### 186 **METHODS**

## 187 **Re-Os Geochemistry**

Existing  $\delta^{13}$ C chemostratigraphic profiles guided high-resolution sampling for rheniumosmium geochemical analyses through the onset of OAE2 from the SH#1 Core (n=20, median spacing = 50 cm) and the Angus Core (n=15, median spacing = 30 cm). See Data Repository for details on sample collection and alignment of the Angus Core depth scale with previous studies. Prior to analysis at Durham University, samples were powdered in ceramic containers using highpurity crushing techniques (Ottawa sand pre-clean) at Northwestern University. Following the

methodology of Selby and Creaser (2003), sample powders were spiked with a <sup>185</sup>Re+<sup>190</sup>Os tracer 194 solution and digested in sealed Carius tubes with 8 mL of 0.25 g/g CrO<sub>3</sub> in 4N H<sub>2</sub>SO<sub>4</sub> for ~48 195 hours at 220°C, principally leaching hydrogenous Re and Os (i.e., carbonates and organic matter). 196 The Re fraction was isolated via NaOH-acetone extraction and anion chromatography. The Os 197 fraction was isolated and purified via chloroform extraction with back reduction into HBr and 198 CrO<sub>3</sub>·H<sub>2</sub>SO<sub>4</sub>-HBr microdistillation. Isotopic ratios of samples and standards were measured on a 199 Triton TIMS in negative ionization mode. The average  $2\sigma$  precision for Os<sub>i</sub> values was  $\pm 0.014$ 200 (max =  $\pm$  0.057). Present-day measured <sup>187</sup>Os/<sup>188</sup>Os values of samples were corrected to initial 201 osmium ratios (Os<sub>i</sub>) by accounting for post-depositional beta decay of  $^{187}$ Re ( $\lambda = 1.666 \times 10^{-11} \text{yr}^{-1}$ ; 202 Smoliar et al., 1996) using an age of 94.4 Ma for the onset of OAE2. 203

## 204 <sup>40</sup>Ar/<sup>39</sup>Ar Geochronology

Bulk samples of regional bentonites B, C, and D of (Elder, 1988) were collected from the 205 206 Nipple Creek (NC) outcrop section in southern Utah 13 km WSW of the SH#1 Core (Fig. DR3 in the Data Repository). Bentonites were identified via the local lithostratigraphy of the CTB interval 207 (Elder, 1991) and an impression of ammonite N. juddi confirmed the Bentonite B horizon. Two 208 additional <sup>40</sup>Ar/<sup>39</sup>Ar dates were obtained from samples of bentonites C and D previously collected 209 and analyzed from Pueblo, Colorado (K-07-01C) and Lohali Point, Arizona (90-O-34) 210 (Obradovich, 1993; Meyers et al., 2012b). Sanidine was isolated via magnetic and density sorting 211 techniques and its composition verified using a variable pressure scanning electron microscope. 212 Sanidine separates were irradiated for 65 hours along with the 28.201 Ma Fish Canyon Tuff 213 sanidine (Kuiper et al., 2008) in the CLICIT facility of the Oregon State University TRIGA reactor. 214 In the WiscAr Laboratory at the University of Wisconsin-Madison, individual sanidine crystals 215

from each of the Nipple Creek bentonites were incrementally heated using a 50W CO<sub>2</sub> laser and the extracted gas analyzed using a Nu Instruments Noblesse multi-collector mass spectrometer following Jicha et al. (2016). Single crystal total fusion experiments were performed for samples K-07-01C and 90-O-34. Dates were calculated using the decay constants of Min et al. (2000) and reported with uncertainties as  $\pm X/Y$  at the 95% confidence level with: (X) analytical sources of uncertainty including the *J* uncertainty and (Y) full external sources of uncertainty, including standard age and decay constants.

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#### 224 **RESULTS**

#### 225 **Re-Os Geochemistry**

The new records from the Angus and SH#1 cores reproduce an abrupt, unradiogenic Osi 226 excursion that spans the onset of OAE2, similar to the Portland Core Osi record (Du Vivier et al., 227 2014). Unlike the Portland Core record, however, both the SH#1 and Angus cores preserve strata 228 between the bases of the Os<sub>i</sub> and  $\delta^{13}$ C excursions, as is documented in other conformable records 229 of the OAE2 onset, such as the expanded Pont'd Issole section of southern France (Du Vivier et 230 al., 2014). The  $O_{s_i}$  excursion occurs below the base of the carbon isotope excursion (CIE) by 231 131±22 cm in the SH#1 Core at 122.29 m and by 80±25 cm in the Angus Core at 2279.98 m (Figs. 232 3-4 and Fig. DR4). The unradiogenic Osi shift occurs in the SH#1 Core at a flooding surface 233 ("fs2a" of Elder et al., 1994) (Fig. 4) and in the Angus Core in the uppermost calcareous shales of 234 the Hartland Member. 235

Minimum values of Os<sub>i</sub> at each Western Interior locality (SH#1 =  $0.149 \pm 0.006$ , Angus = 0.167  $\pm$  0.002, Portland = 0.156  $\pm$  0.003) approach the hydrothermal end member of the osmium isotope system (<sup>187</sup>Os/<sup>188</sup>Os<sub>hydrothermal</sub> = 0.13; Peucker-Ehrenbrink and Ravizza, 2000). However, the magnitude of the Os<sub>i</sub> excursion is significantly larger in the proximal SH#1 Core ( $\Delta$ Os<sub>i</sub> = 1.30) than in the Portland Core ( $\Delta$ Os<sub>i</sub> = 0.78; Du Vivier et al., 2014) and the Angus Core ( $\Delta$ Os<sub>i</sub> = 0.74), due to more radiogenic Os<sub>i</sub> values preceding the event (max. Os<sub>i</sub> in SH#1 = 1.446  $\pm$  0.039 vs. Angus = 0.910  $\pm$  0.027) (Fig. 5).

The astronomical time scale for the Angus Core (Ma et al., 2014) constrains the duration 243 of the temporal lag between the Osi excursion and the base of the OAE2 CIE to 2.9  $\pm$  0.5 244 precessional cycles, equivalent to  $59 \pm 10$  kiloyears (Fig. 5). The Os<sub>i</sub> and  $\delta^{13}$ C excursions are nearly 245 superimposed in the Portland Core, whereas initiation of the  $\delta^{13}$ C shift lags the Os shift at the two 246 other WIB sites. This observation supports the hypothesis of a hiatus in the Pueblo area and permits 247 the duration of missing time to be quantified. Equivalent to the duration of the lag, the hiatus 248 249 represents ~60 kyr (see Discussion). Based on the established astrochronology of the Angus Core, values of Osi remain unradiogenic for 172-257 kiloyears spanning the ammonite Sciponoceras 250 gracile Biozone at the beginning of OAE2 (Fig. 6). 251

Broadly correlative enrichments of Os, best represented by <sup>192</sup>Os concentration data, occur through the onset of OAE2 in all WIB sites (Figs. 2-3). Concentrations of <sup>192</sup>Os in the Angus Core are significantly enriched (max [<sup>192</sup>Os] = 1183.9 ± 4.3 ppt) by roughly an order of magnitude compared to the SH#1 Core (max [<sup>192</sup>Os] = 162.3 ± 0.9 ppt) (Table 1). Elevated <sup>192</sup>Os concentrations occur throughout the duration of the unradiogenic Os<sub>i</sub> excursion.

257 Concentrations of Re in the Angus Core are highest in the uppermost Hartland Shale (max 258  $[Re] = 89.31 \pm 0.22$  ppb) in the ~60 kiloyears prior to OAE2 and exceed the background levels of 259 ~50 ppb (Table 1; Figs. 4, 6). Similar to records from the Portland Core (Du Vivier et al., 2014), 260 Re concentrations in the Angus Core decrease markedly above the Hartland Shale-Bridge Creek 261 Limestone contact and during the main body of the OAE2 CIE. Like <sup>192</sup>Os, concentrations of Re 262 are elevated in the central axial basin localities compared to the SH#1 core where Re 263 concentrations do not exceed 14 ppb despite enrichment during the Os<sub>i</sub> excursion.

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## 265 <sup>40</sup>Ar/<sup>39</sup>Ar Geochronology

The <sup>40</sup>Ar/<sup>39</sup>Ar analyses yield five new precise sanidine <sup>40</sup>Ar/<sup>39</sup>Ar dates for bentonites B, C and D (Table 2; Fig. 7). Incremental heating experiments produce plateau dates in most cases, with only one being markedly older than the population of plateau dates for a given sample. The weighted mean ages for each bentonite obey superposition and the ages for the B and C bentonites from different localities are indistinguishable (Table 2). Full analytical results and Ar plots can be found in the Data Repository (Tables DR4-5).

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#### 273 DISCUSSION AND IMPLICATIONS

### 274 Assessing Conformability of the Base Turonian GSSP

An integrated chronostratigraphic framework of radioisotopic age dates, astrochronology, chemostratigraphy, and biostratigraphy spans the Cenomanian-Turonian boundary (CTB) interval at the Base Turonian GSSP at Rock Canyon Anticline in Pueblo, Colorado, constraining rates of change in geochemical and paleobiologic datasets from the Western Interior Seaway during OAE2 (Kennedy et al., 2005; Sageman et al., 2006 and refs therein). This high-resolution age control has

aided in quantifying a cryptic 17 kyr hiatus above the LS5 bed of Elder et al. (1994) in the Bridge 280 Creek Limestone Member (Meyers and Sageman, 2004) and has also indicated the presence of a 281 second hiatus at the base of OAE2 at the GSSP section, assessed in this study (Fig. 5). This basal 282 OAE2 hiatus occurs as a distinct 0.5 cm "thin wavy-bedded layer" in the uppermost Hartland Shale 283 with phosphatized bones and scoured quartz sand at the GSSP (Pratt, 1984). These 284 285 sedimentological characteristics, along with a sharp influx of benthic foraminifera with Tethyan affinity in the overlying uppermost marlstone bed of the Hartland Shale, allude to a marked shift 286 in paleoenvironmental conditions which Eicher and Diner (1989) hypothesized to represent a 287 hiatus. More recently, Osi chemostratigraphy of the nearby Portland Core (Fig. 5) detected that the 288 unradiogenic Os<sub>i</sub> excursion preceding OAE2 directly underlies the base of the event's CIE and 289 lacks the characteristic stratigraphic lag between Os<sub>i</sub> and  $\delta^{13}$ C excursions of the event globally(Du 290 Vivier et al., 2014). This chemostratigraphic feature confirmed the presence of a hiatus (Fig. DR4 291 in Data Repository) that has the potential to impact geochemical reconstructions of the critical 292 OAE2 onset interval and precise Earth system responses to the event's trigger (see discussion in 293 Du Vivier et al., 2015a; Eldrett et al., 2017). However, the duration of the hiatus at the base of the 294 OAE2 CIE at the GSSP section and Portland Core remained unquantified prior to this study. 295

Lithostratigraphic correlations of the hemipelagic marlstone-limestone couplets of the CTB interval in the central WIB reveal that the LS1 bed of the Bridge Creek at the GSSP and Portland Core is condensed (Ma et al., 2014). The bed expands into multiple couplets south and north of Pueblo, at the Greenhorn Creek outcrop and in the Angus Core of the Denver Basin, respectively (Fig. 5). Additionally, the new Os<sub>i</sub> chemostratigraphy of the CTB interval from both the SH#1 Core and the astronomically-tuned Angus Core exhibit an expanded stratigraphic interval between the Os<sub>i</sub> excursion and base of the OAE2 CIE (Figs. 3-5). These observations signify that more continuous sedimentation existed elsewhere in the region across the onset of OAE2 compared to the GSSP locality and, further, they constrain the duration of the hiatus at the GSSP section to  $59\pm10$  kyr (Fig. 5). Summing the quantified hiatuses above LS5 and at the base of OAE2, we estimate that the GSSP section is missing  $82\pm10$  kiloyears in detectable hiatal surfaces (i.e., hiatuses of  $\geq 10$ s kiloyears in duration). This suggests that the GSSP section preserves ~90% of the temporal duration of the broader OAE2 interval from the Os<sub>i</sub> excursion to CIE termination.

Although the GSSP section is conformable spanning the Cenomanian-Turonian stage boundary, adhering to criteria for GSSPs, the hiatus at the onset of OAE2 in this site omits a brief time interval. This interval, however, is represented in other sections within the basin that can be readily correlated to the GSSP site, such as the Angus and SH#1 cores.

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#### 315 OAE2 Time Scale Comparisons

Oceanic Anoxic Event 2, which was first identified as a black shale succession spanning 316 the Cenomanian-Turonian boundary at many marine sites (Schlanger and Jenkyns, 1976; Arthur 317 et al., 1987), can be recognized globally by a prominent positive carbon isotope excursion (CIE) 318 (Scholle and Arthur, 1980). Defining OAE2 from the base of this CIE to a return to stable 319 background  $\delta^{13}$ C values at the top of the event (the "long" definition, as compared to the shorter 320 "end of CIE plateau" definition: Tsikos et al., 2004; Sageman et al., 2006), recent studies from the 321 Iona-1 Core in the Maverick Basin of Texas and in Gongzha, Tibet found comparatively expanded 322 durations of OAE2 of 920±170 kyr and 820±25 kyr, respectively (Eldrett et al., 2015; Li et al., 323 2017). Compared to syntheses from the Western Interior Basin, these recent findings are 324

equivalent in duration to the long definition values of 866±19 kyr (Sageman et al., 2006). 325 However, to reconcile the nominal offsets in mean durations, authors have noted the occurrence 326 of pre-cursor isotopic events in the Iona-1 Core of Texas and stratigraphic expansion in Tibet, 327 proposing that hiatuses at the base of the OAE2 CIE in the central WIB sites account for the 328 discrepancies (Eldrett et al., 2017; Li et al., 2017). With our new quantification of the hiatus at the 329 330 base of the OAE2 CIE in the Portland Core and the addition of more continuous Osi records in the Angus and SH#1 cores, it is possible to assess this hypothesis more critically. Additionally, a 331 recent Os<sub>i</sub> chemostratigraphy of the CTB succession in the Iona-1 Core (Sullivan et al., in press) 332 provides another distinct profile to correlate and compare records from Utah and Colorado to 333 Texas. 334

When the records from the central WIB and the Iona-1 cores are aligned and correlated 335 using  $\delta^{13}$ C and Os<sub>i</sub> excursions, there is strong overlap between the floating eccentricity bandpass 336 astronomical time scales of OAE2 (Fig. DR5). Bandpass filtering of the short eccentricity (E2-3) 337 spectral peak in both the central WIB (Meyers et al., 2001; Jones et al., 2019) and Texas (Eldrett 338 et al., 2015) detect approximately six E<sub>2-3</sub> cycles from the CIE base to the top of the CIE plateau 339 (i.e., short definition ~600 kyr) and seven to eight E<sub>2-3</sub> cycles from the CIE base to the return to 340 stable  $\delta^{13}$ C values (i.e. long definition) (Fig. 5). Most other sites with relatively conformable 341 records of OAE2 globally preserve a similar number of cycles (see figure 9 of Charbonnier et al., 342 2018). However, discrepancies in timing of the CIE emerge when comparing the central WIB 343 sites to the traced short obliquity cycle (O1: ~50 kyr) time scale for the Iona-1 Core preferred by 344 Eldrett et al. (2015), which reports a longer duration for OAE2 (Fig. DR5). Thus, since 345 eccentricity-based time scales correspond well among the sites, it is likely that the reported 346 discrepancy between the Texas and central WIB durations for OAE2 primarily arises not from 347

hiatuses, but from the usage of the less common O1 cycle to tune the Iona-1 Core record. This 348 finding suggests that, despite the increased amplitude of obliquity forcing during the CTB (Meyers 349 et al., 2012a; Charbonnier et al., 2018), the O1 cycle is less reliable for astronomical tuning of 350 mid-Cretaceous stratigraphic datasets given markedly lower power in the La2004 and La2010 351 solutions than other astronomical terms (Laskar et al., 2004; Laskar et al., 2011; Wu et al., 2013). 352 353 The hypothesis that minor offsets in durations of OAE2 records in the Eagle Ford, Tibet, and the central WIB originate from cyclostratigraphic techniques, as opposed to hiatuses or significant 354 differences in local stratigraphic preservation of the event, is consistent with the presented finding 355 of a relatively short-lived hiatus at the base of the OAE2 CIE in the Portland Core and GSSP 356 locality. 357

In addition, the Eagle Ford record from the Iona-1 Core preserves two ~+1-2‰  $\delta^{13}$ C 358 excursions underlying the main body of OAE2 (Fig. 5) labelled as pre-cursor isotope events 359 (PCEs). These PCE do not appear in the Portland Core  $\delta^{13}$ C record, a feature that has been 360 attributed to hiatuses in the central WIB (Eldrett et al., 2015; 2017). However, the Osi excursion 361 of OAE2 occurs below the PCEs in the Iona-1 Core (Sullivan et al., in press). When compared to 362 the Osi records of the central WIB, this chemostratigraphic relationship indicates another 363 possibility: that the PCEs in the Iona-1 Core correspond to the "A"  $\delta^{13}$ C peak for OAE2 of Pratt 364 (1985) in the central WIB. The position of biostratigraphic markers in the last occurrence (LO) 365 datums of the foraminifera Rotalipora cushmani and nannofossil marker Axopodorhabdus 366 albianus, as well as equivalent durations for OAE2 from eccentricity bandpasses, support this 367 scenario (Fig. 5). The Iona-1 Core may preserve two  $\delta^{13}$ C peaks within the "A" interval due to a 368 more stratigraphically expanded record compared to the Portland Core and Pueblo GSSP. 369 Nonetheless, additional high-resolution  $\delta^{13}$ C chemostratigraphic studies of the onset of OAE2 in 370

the WIB, such as in the conformable Angus Core (Fig. 3), are needed to further test the hypothesisthat the PCEs correlate to the "A" CIE peak.

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#### 374 Radioisotope Geochronology of the Cenomanian-Turonian Boundary

The five new <sup>40</sup>Ar/<sup>39</sup>Ar ages (Fig. 7) for bentonites B, C, and D from Nipple Creek, UT, 375 Lohali Point, Arizona, and Pueblo, Colorado all overlap with recent <sup>40</sup>Ar/<sup>39</sup>Ar ages from the WIB 376 (Meyers et al., 2012b; Jicha et al., 2016). The new <sup>40</sup>Ar/<sup>39</sup>Ar age for Bentonite B at Nipple Creek 377 378 (NC-B) is also equivalent within uncertainty to the youngest zircon U-Pb data of the bentonite (Barker et al., 2011; Meyers et al., 2012b), indicating that these two radioisotopic chronometers 379 380 are synchronized. The new age of Bentonite D from Nipple Creek (NC-D) overlaps within total temporal uncertainty of the <sup>40</sup>Ar/<sup>39</sup>Ar age of Meyers et al. (2012b), but does not overlap with the 381 other new age for Bentonite D at Lohali Point, Arizona (90-O-34) (Table 2). Its mean <sup>40</sup>Ar/<sup>39</sup>Ar 382 age is 230 kyr younger than the mean age from Meyers et al. (2012b) and 357 kyr younger than 383 the ash at Lohali Point (Fig. 7). Thus, the NC-D date represents an outlier and we exclude it from 384 calculations of the age of the CTB. 385

When anchored to the short eccentricity traced floating astronomical time scale for the Portland Core (Meyers et al., 2001), the new  ${}^{40}$ Ar/ ${}^{39}$ Ar dates for bentonites B (NC-B), C (NC-C, K-07-01C), and D (90-O-34-D) produce numerical age estimates for the Cenomanian-Turonian boundary (Table 2, Table DR1 in Data Repository). The 2 $\sigma$  uncertainties on individual CTB age estimates derive from the full radioisotopic, stage boundary placement (±25 kyr), and astrochronologic (±25 kyr) sources of uncertainty combined in quadrature (*sensu* Sageman et al., 2014b). The weighted mean age and 2 $\sigma$  uncertainty for the CTB from all four anchoring scenarios

for new dates is 94.05 $\pm$ 0.08 Ma. If we include all recent <sup>40</sup>Ar/<sup>39</sup>Ar dates for these bentonites and 393 U-Pb dates that do not exhibit evidence for inheritance (Barker et al., 2011; Meyers et al., 2012b; 394 Eldrett et al., 2015; Jicha et al., 2016), the weighted mean CTB age is 93.95±0.05 Ma. The CTB 395 age estimate from the four new <sup>40</sup>Ar/<sup>39</sup>Ar dates of this study is within uncertainty of recent 396 radioisotopically calibrated ages reported for the boundary (Barker et al., 2011; Meyers et al., 397 398 2012b; Eldrett et al., 2015). However, the weighted mean age options proposed for the CTB from the new bentonite dates and from the compilation of new and recent dates (Fig. 7) are nominally 399 older than the Meyers et al. (2012) age used for the CTB in the Geologic Time Scale (GTS) 2012 400 (Ogg and Hinnov, 2012) by 150 kyr and 50 kyr, respectively. 401

Although the new radioisotopically anchored and astronomically tuned age estimate for the 402 CTB from southern Utah is consistent with existing geochronologic records, the onset age for 403 OAE2 differs with the record from Texas. The U-Pb anchored astronomical time scale from the 404 Iona-1 Core in the Eagle Ford of Texas places the age of the base of OAE2 ~300 kyr older (94.8-405 406 94.9 Ma) (Eldrett et al., 2015; Eldrett et al., 2017) than the records of the central WIB (94.55±0.16) Ma) (this study) and the Yezo Group, Japan (Du Vivier et al., 2015b). Several studies spanning a 407 wide range of ages demonstrate that the astronomical calibration of the FCs standard at 28.201 Ma 408 (Kuiper et al., 2008) yields <sup>40</sup>Ar/<sup>39</sup>Ar dates that are indistinguishable from, or slightly younger 409 than, CA-ID-TIMS (chemical abrasion-isotope dilution thermal ionization mass spectrometry) U-410 Pb dates from zircons in the same, or correlative, rocks (e.g., Meyers et al., 2012b; Rivera et al., 411 2014; Sageman et al., 2014b; Singer et al., 2014; Andersen et al., 2017). This is true unless the U-412 Pb zircon dates show clear patterns of inheritance (e.g., Wotzlaw et al., 2013) as is the case for 8 413 of the 10 ash beds for which Eldrett et al. (2015) report U-Pb dates. It is thus unlikely that the 414 disagreement between our new date for the onset of OAE2 from the central WIB and the U-Pb age 415

reported by Eldrett et al. (2015) in the Iona-1 Core reflect miscalibration of the <sup>40</sup>Ar/<sup>39</sup>Ar 416 chronometer. Rather, we suspect that pre-eruptive zircon crystallization or inheritance biases most 417 of the U-Pb dates from the Eagle Ford to older ages, as several ash beds appear anomalously old 418 and do not obey stratigraphic superposition (Eldrett et al., 2015). Meyers et al. (2012b) also 419 previously noted inherited zircons based on U-Pb dating of several bentonites in the central WIB. 420 421 Alternatively, this offset between the proposed initiation ages for OAE2 may result from the use of the O1 cycle for tuning the age-depth model in the Eagle Ford, as discussed above. 422

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### **Eustatic Lowstand Preceding OAE2**

Spatial variability in the development of hiatuses locally in the WIB underscores an 425 undulating nature to bathymetry of the epeiric seaway, even within the same structural zones of 426 the basin, such as the "axial basin." Modern shallow marine foreland basins, such as the Persian 427 Gulf Basin, exhibit analogous local variation in bathymetry linked to long-lived geologic structures 428 (Kassler, 1973). Similarly, we posit that some deformation of the Rock Canyon Anticline could 429 have occurred during the Cretaceous and contributed to local shoaling, exposing the bathymetric 430 high to wave base mixing and winnowing during sea level lowstands. 431

The basal OAE2 hiatus at the GSSP locality and Portland Core occurs within the uppermost 432 ammonite Metoicoceras mosbyense Biozone, and has previously been interpreted to represent a 433 minor lowstand in the WIB (Sageman, 1985; Arthur and Sageman, 2005; Gale et al., 2008). Along 434 the western margin of the basin in southern Utah, the shoreline progrades ~150 km east ("S1" 435 genetic sequence in Fig. 2) and a regression incises ~10 m of strata below the OAE2 CIE at some 436 sites (Uličný, 1999; Laurin et al., 2019). Therefore, the basal OAE2 hiatus at the Pueblo GSSP 437

locality and Portland Core may represent Late Cenomanian winnowing of a bathymetric high 438 during a minor lowstand in the basin. Similarly, intervals of the middle Hartland Shale contain 439 thin beds of winnowed skeletal limestones that correlate shoreward to a clastic wedge, suggesting 440 another lowstand (Sageman, 1985, 1996). Bone beds, such as the one reported from the basal 441 OAE2 hiatal surface at the Pueblo GSSP locality (Eicher and Diner, 1989), commonly correspond 442 443 to transgressive surfaces in sequence stratigraphic models of epeiric seaways (Brett, 1995). Thus, the thin bone bed at the GSSP locality could instead represent a condensed bed that correlates to 444 sediment starvation during the transgression overlying genetic sequence S1 of Utah (equivalent to 445 Unit 6B of Uličný, 1999). Regardless of whether the hiatus corresponds directly to winnowing 446 during relative sea level fall or condensation from the immediately subsequent transgression, the 447 pre-OAE2 hiatus and shoreline trajectories in the WIB are reasonably interpretable as associated 448 with a lowstand sequence boundary. 449

Moreover, a compilation of global relative sea level records, constrained by ammonite 450 biostratigraphy and/or  $\delta^{13}$ C chemostratigraphy, reveals coeval sequence boundaries and lowstands 451 underlying OAE2 at many localities, including: the English Chalk (Gale et al., 1993), the Paris 452 Basin (Robaszynski et al., 1998), Germany (Voigt et al., 2006; Richardt et al., 2013), Czech 453 454 Republic (Uličný et al., 1997), Peru (Navarro-Ramirez et al., 2016), Mexico (Elrick et al., 2009), southern New Mexico (Mack et al., 2016), the northern Gulf of Mexico (Lowery et al., 2017), 455 Jordan (Wendler et al., 2014), Lebanon (Grosheny et al., 2017), Israel (Buchbinder et al., 2000), 456 Egypt (Nagm et al., 2014), and Morocco (Kuhnt et al., 2009). Consistency among these global 457 Upper Cretaceous relative sea level records ties the hiatus in the uppermost Hartland Shale in the 458 WIB to an apparent eustatic lowstand preceding the onset of OAE2, coeval with or just preceding 459 a major pulse of LIP volcanism (Fig. 8). The link between LIP initiation and eustatic lowstand is 460

461 consistent with original hypotheses of volcano-tectono-eustatic feedbacks at the onset of OAE2,
462 followed by eustatic transgression with expanded shelfal area and organic carbon deposition
463 (Arthur et al., 1987). However, eccentricity pacing of relative sea level through the event along the
464 western margin of the seaway indicates at least a partial background control from climatic
465 processes as well (Jones et al., 2019; Laurin et al., 2019).

466

### 467 Refined Timing of LIP Volcanism and the OAE2 Carbon Cycle Perturbation

468 The apparently conformable Osi chemostratigraphy from the Angus Core, with its highresolution astronomical and radioisotopic time scale, provides a refined timeline of LIP volcanic 469 470 activity in relation to the carbon cycle perturbation at the onset of OAE2 (Figs. 5, 8). Globally, all Osi records of OAE2, including from the WIB, exhibit a geologically rapid increase in the flux of 471 hydrothermal/volcanic osmium to the marine realm (Turgeon and Creaser, 2008; Du Vivier et al., 472 2014; Du Vivier et al., 2015b; Schröder-Adams et al., 2019; Sullivan et al., in press). In the case 473 of the astronomically tuned record from the Angus Core, the precipitous unradiogenic Osi 474 excursion occurs abruptly in less than 20 kiloyears beginning 60 kiloyears before the CIE, with a 475 subtle decrease in Osi preceding the main Osi excursion, 80-100 kiloyears before the CIE (Figs. 2, 476 5, 8). Assuming that a massive increase in the hydrothermal/mantle C flux coincided with this 477 rapid hydrothermal Os pulse (e.g., Kuroda et al., 2007), carbon release to the ocean-atmosphere 478 479 system on this time scale would have occurred rapidly enough to potentially alter marine carbonate chemistry (Du Vivier et al., 2015a) (Fig. 8). 480

The positive carbon isotope excursion marking the onset of OAE2 occurred only after a significant temporal lag following the abrupt onset of LIP volcanism, on the order of 10s of

kiloyears. This study quantifies that lag at  $59\pm10$  kiloyears using the astronomical time scale for 483 the Angus Core (see Results, Figs. 4-5, 8), a similar, though slightly longer duration than previous 484 estimates (Turgeon and Creaser, 2008; Du Vivier et al., 2015a). Fundamentally, this lag represents 485 the time between (1) the onset of massive submarine LIP volcanism, CO<sub>2</sub> degassing, and delivery 486 of reduced metals to the marine realm; and (2) the carbon cycle perturbation of OAE2 recorded in 487  $\delta^{13}$ C records, which ultimately reflects the spread in areal extent of anoxic and sulfidic marine 488 bottom waters and burial/preservation of organic carbon (Scholle and Arthur, 1980; Owens et al., 489 490 2013).

The duration of the lag exceeds interpreted oceanic mixing time scales by an order of 491 magnitude and, therefore, cannot solely represent the time needed to circulate water masses rich 492 with biolimiting nutrients derived from submarine volcanic or continentally weathered sources, 493 even in a sluggish mid-Cretaceous ocean (e.g., Turgeon and Creaser, 2008). It is possible that 494 osmium cycle proxies (i.e., Os<sub>i</sub>) are more sensitive to submarine LIP volcanism than carbon cycle 495 496 proxies, and we have overestimated the pace of LIP CO<sub>2</sub> outgassing; tens of kiloyears could have been needed to accumulate CO<sub>2</sub> in the atmosphere. However, OAE2 preserves one of the longest-497 lived and most abruptly initiated unradiogenic Osi excursions known from the Phanerozoic, 498 499 suggesting a rapidly initiated and long-lived episode of prolific volcanism.

Alternatively, circulation of the marine dissolved oxygen reservoir typically provides a buffer against the prolonged expansion of anoxic bottom waters and organic carbon burial exhibited during OAEs. The inertia between volcanic CO<sub>2</sub> input and widespread anoxia/carbon burial likely represents the globally-averaged drawdown of this substantial marine oxygen reservoir during OAE2. Accordingly, the presented duration of the Os-C lag is equivalent to the duration of a gradual drawdown of redox sensitive trace metals and bottom water oxygen levels at Demerara Rise (tropical Atlantic) which precedes OAE2 (Hetzel et al., 2009; Ostrander et al., 2017). The subsequent global-net enhanced burial and accumulation of organic carbon only drove the OAE2 CIE following this 10's of kyr deoxygenation process (Fig. 8). This implies that the preservation of organic carbon due to anoxic/euxinic bottom and pore waters, mediated by organic matter sulfurization (Raven et al., 2018), was a key paleoceanographic feedback that ultimately triggered the OAE2 CIE (Mort et al., 2007), perhaps more so than the initial increases in marine primary productivity.

### 513 Multiple Volcanic Pulses

In addition to a volcanic pulse preceding OAE2, <sup>192</sup>Os concentrations increase in the 514 interval underlying Bentonite A, consistent with a second episode of submarine volcanism (Table 515 1; Figs. 3-4). In this interval within the upper half of the Os<sub>i</sub> excursion in the WIB, already 516 unradiogenic Os<sub>i</sub> values at each site decrease further, subtly but consistently, and by more than 517 analytical uncertainty. Values of Osi decrease in the SH#1, Angus, and Portland cores respectively 518 by 0.066, 0.026, and 0.053 below Bentonite A (Table 1; Figs. 3-5). Thus, the WIB osmium 519 chemostratigraphy indicates that the LIP emanated at least two pulses of volcanic activity that 520 punctuated an elevated background rate of volcanism spanning the onset and the early interval of 521 OAE2 (Fig. 8). Similar scenarios of multiple pulses of volcanism (Sullivan et al., in press) and 522 anoxia (Jenkyns et al., 2017; Clarkson et al., 2018) during the event have been reported, hinting 523 at links between the intensity of volcanism and marine deoxygenation, although correlations 524 appear to exhibit offsets in the precise timing of these processes. 525

526

## 527 Re-Os Geochemical Dynamics in an Epeiric Seaway

The proximal-distal transect of the mid-latitudes of the WIB constrains spatial variability 528 of Osi chemostratigraphic records in a shallow continental seaway through a period of massive 529 volcanism and eustatic transgression. Osmium chemostratigraphy of both Quaternary and 530 Cenomanian-Turonian records exhibit a degree of spatial variability in Osi composition among 531 oceanic basins, highlighting the sensitivity of a given locality's record to water mass heterogeneity 532 533 and the proximity of weathered sources of osmium (Du Vivier et al., 2014; Du Vivier et al., 2015b; Rooney et al., 2016). Despite fluctuating sea level in the WIS and likely some degree of basin 534 restriction, the unradiogenic Osi excursion and enrichment in <sup>192</sup>Os at the onset of OAE2 is robustly 535 preserved in each of the three sites transecting the depositional settings in the basin, heralding a 536 pulse of LIP volcanism (Fig. 5). 537

Values of Os<sub>i</sub> are equivalent across the basin during the syn- and post-OAE2 intervals, 538 including at the most proximal locality - SH#1 (Fig. 6). However, Osi values in the SH#1 Core are 539 highly radiogenic prior to OAE2 compared to sites in the axial basin, at a time when the shoreline 540 of the western margin of the seaway was closer to the site (~35 km, cf. Laurin and Sageman, 2007). 541 The radiogenic values in this interval reflect the proximity of continentally weathered Os sources 542 in the Sevier Belt. It appears that when the shoreline was within 10's of kilometers of the site, the 543 544 Osi proxy was sensitive to runoff from the Sevier Belt, whereas when the shoreline was more than  $\sim 100$  km away, the proxy tracked values of Os<sub>i</sub> that characterize the broader seaway and pelagic 545 marine records. Nonetheless, the pre-OAE2 interval at SH#1 exhibits a shift to unradiogenic values 546 below the major Os<sub>i</sub> excursion (Fig. 3), similar to records globally (Du Vivier et al., 2014; Du 547 Vivier et al., 2015b). These findings indicate that the proxy remains sensitive to major changes in 548 the global fluxes of the marine Os cycle in proximal marine settings during LIP episodes, despite 549 offsets in the absolute values of Osi trends. 550

551

#### 552 CONCLUSION

553 Our new chemostratigraphic compilation from the Angus and SH#1 cores spans the onset 554 of OAE2 in the WIB. The proximal-distal transect defines spatial variability and local controls on 555 the Re-Os proxy for volcanism in a semi-restricted epeiric seaway. Observations support prolific 556 LIP volcanic activity in the Late Cenomanian, most likely in the Caribbean and Arctic regions. 557 Notably, the characteristic unradiogenic Os<sub>i</sub> chemostratigraphic marker of volcanism preceding 558 OAE2 extends to SH#1, the most proximal setting studied in the WIB.

New <sup>40</sup>Ar/<sup>39</sup>Ar dates for traceable bentonites in the WIB, combined with recently published 559 560 radioisotopic analyses, yield an astronomically calibrated age for the Cenomanian-Turonian stage boundary of  $93.95\pm0.05$  (2 $\sigma$ ) Ma, which is consistent with other recent age estimates but slightly 561 older than the GTS 2012 age. The integrated radioisotope geochronology, astrochronology, 562 chemostratigraphy, and biostratigraphy from the WIB provide a high-resolution age model 563 refining the chronology of triggers and paleoenvironmental feedbacks for OAE2. Most notably, a 564 59±10 kyr lag between intensification of LIP volcanism and widespread, globally-averaged 565 organic carbon burial is quantified at the onset of OAE2. This lag during the initial phase of 566 volcanism suggests net-deoxygenation of the global ocean over tens of kiloyears, past a threshold 567 for widespread organic C preservation, was a critical process in the ultimate initiation of OAE2. 568 Further, the rapid onset of LIP volcanism preceding OAE2 is consistent with a scenario of 569 increased  $pCO_2$ , altered marine carbonate chemistry, and decreased aragonite/calcite saturation 570 levels in the global ocean (Du Vivier et al., 2015a). Additionally, a second pulse of LIP volcanism 571 572  $\sim$ 100 kyr after the onset of the CIE is consistent with earlier investigations.

The refined chronostratigraphic framework is also used to assess stratigraphic 573 conformability and correlation of reference sites for the CTB in the WIB. The duration of a hiatus 574 in the crucial onset interval of OAE2 at Pueblo, CO (Base Turonian GSSP) and the Portland Core 575 is equivalent to the geologically brief temporal lag between volcanism and carbon cycle 576 perturbation. This hiatus is associated with a minor eustatic lowstand and subsequent transgression 577 578 preceding OAE2, recorded in many shallow marine settings globally, which is potentially linked to tectonic or climatic feedbacks from the coeval initiation of LIP volcanism. Based on Osi 579 chemostratigraphic correlation, minor  $\delta^{13}$ C excursions underlying the main OAE2 CIE in the Eagle 580 Ford of Texas appear to correspond to the "A" segment of the  $\delta^{13}$ C record in the central WIB. 581 Additionally, residual offsets in recent time scales for OAE2 may originate in part from biases in 582 radioisotope geochronology, such as zircon inheritance, and/or differences in astrochronologic 583 tuning methodologies and chemostratigraphic definitions of the event. 584

585

#### 586 ACKNOWLEDGEMENTS

We thank: Antonia Hofmann, Geoff Nowell, and Chris Ottley for assistance with Re-Os 587 geochemical analyses; Steve Meyers for providing the ATS for the Portland Core; Bryan Wathen 588 for mineral separation; Rosie Oakes, R. Mark Leckie, Julio Sepulveda, Tim Bralower, Scott 589 Karduck, and Amanda Parker for assistance logging and sampling the SH#1 Core; R. Mark Leckie, 590 591 Jiří Laurin, and David Uličný for insightful discussions on the stratigraphy of the Kaiparowits Plateau; Brad Cramer and an anonymous referee for constructive reviews improving the quality of 592 the manuscript; the USGS for drilling the SH#1 Core; and Encana for donating the Angus Core to 593 594 Northwestern University. This article represents a portion of the doctoral research of MMJ at Northwestern University. BBS acknowledges funding from NSF Earth-Life Transitions grant 595

- 596 #1338312 and thanks the U.S. BLM for sample collection permit 9560 (UT-030). DS
- 597 acknowledges funding from the TOTAL Endowment Fund and the Dida Scholarship.

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#### **1053** Figure Captions

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Figure 1. Early Turonian map of North American Western Interior Basin marking primary
localities of cores investigated or discussed in this study (adapted from Roberts and Kirschbaum,
1995; Ma et al., 2014). AZ-Arizona, USA; CO-Colorado, USA; GSSP-global boundary stratotype

1057 section and point; NC-Nipple Creek outcrop; SH#1 – Smoky Hollow #1 Core.

Figure 2. Lithostratigraphy and ammonite biostratigraphy of the Cenomanian-Turonian boundary
interval in the Western Interior Basin from central Colorado to southern Utah (modified from
Tibert et al., 2003). Regional bentonites of Elder (1988) and Leithold (1994). Shoreline trajectory
of genetic sequences scaled versus age (modified from Laurin et al., 2019). Ls.-limestone; OAE2Oceanic Anoxic Event 2; Ss-sandstone; GSSP-global boundary stratotype section and point; SH#1
– Smoky Hollow #1 Core.

**Figure 3.** Chemostratigraphy of the Angus Core. From left to right: wt.% carbonate content and wt.% total organic carbon (TOC) (open circles = new data in Data Repository, black/blue circles from Joo and Sageman, 2014), bulk organic carbon isotopic ratios  $\delta^{13}C_{org}$  (Joo and Sageman, 2014), initial osmium isotope ratios Os<sub>i</sub>, rhenium concentrations (green circles), 192-osmium concentrations (orange squares) (Table 1). Mbr.-member; OAE2-Oceanic Anoxic Event 2.

**Figure 4.** Chemostratigraphy of the Smoky Hollow (SH#1) Core in southern Utah. From left to right: wt.% carbonate content, wt.% total organic carbon (TOC), and bulk organic carbon isotope ratios ( $\delta^{13}C_{org}$ ) from Jones et al. (2019);  ${}^{40}Ar/{}^{39}Ar$  bentonite ages, initial osmium isotope ratios (Osi), rhenium concentrations (green circles), and 192-osmium concentrations (orange squares) from this study.  ${}^{40}Ar/{}^{39}Ar$  bentonite dates correlated from the nearby Nipple Creek outcrop section. Stratigraphic column, correlated ammonite biostratigraphy, bentonite stratigraphy, and 1075 Cenomanian-Turonian boundary placement updated (see Fig. DR3 in Data Repository) from Jones
1076 et al. (2019). See text for discussion. Lithology legend in Fig. 5. Fm.-formation; fs-flooding
1077 surface; OAE2-Oceanic Anoxic Event 2; VPDB-Vienna Pee Dee belemnite; P.f.1078 *Pseudaspidoceras flexuosum.*

Figure 5. Initial osmium isotope records of the Western Interior Basin. Stratigraphic columns for 1079 the SH#1 Core (updated from Jones et al., 2019), Angus Core (this study), Portland Core near 1080 1081 GSSP (Meyers et al., 2012b), and Iona-1 Core from the Maverick Basin, Texas (redrafted from 1082 Eldrett et al., 2015) (L-R). Bentonite labels A-D in red for central WIB sites; these bentonites may 1083 be present in the Iona-1 Core of Texas, however, they were originally reported to pinch out in New Mexico before reaching Texas (Elder, 1988), complicating exact bentonite correlations to the Iona-1084 1085 1 Core. Bandpass filters for the SH#1 (Jones et al., 2019), Angus (Ma et al., 2014), Portland 1086 (Meyers et al., 2012b), and Iona-1 cores (Eldrett et al., 2015). Quantified durations of Portland Core/GSSP hiatuses from Meyers and Sageman (2004) and this study (see Results). Carbon 1087 isotope ( $\delta^{13}C_{org}$ ) chemostratigraphy in black for the SH#1 (Jones et al., 2019), Angus (Joo and 1088 1089 Sageman, 2014), Portland (Sageman et al., 2006; Du Vivier et al., 2014), and Iona-1 cores (Eldrett et al., 2015) define the OAE2 excursion (dark grey shading=short, end of plateau definition; light 1090 grey and dark grey shading=long definition). Initial osmium isotope ratios (Osi) (open circles/red 1091 1092 line) preserve unradiogenic (hydrothermal/LIP) excursion underlying OAE2 for SH#1 and Angus cores (this study), Portland Core (Du Vivier et al., 2014), and Iona-1 Core (Sullivan et al., in press). 1093 Fm.-formation; OAE2-Oceanic Anoxic Event 2. 1094

1095 **Figure 6.** Timeseries of  $\delta^{13}$ Corg and Re-Os geochemical records from the SH#1 (light red), Angus 1096 (blue), and Portland (black) cores through OAE2. Break in Portland Core timeseries during lag

1097 (grey) signifies hiatus. From left to right, figure plots bulk carbon isotope ratios ( $\delta^{13}C_{org}$ ), initial

osmium isotope composition (Osi), osmium-192 concentration, and rhenium concentration.
Timeseries for Angus Core from astrochronology (Ma et al., 2014), Portland Core from
astrochronology (Meyers et al., 2001) and linear interpolation of ammonite biozones below hiatus
(this study), and SH#1 Core from astrochronology (Jones et al., 2019) and linear interpolation of
sedimentation rates below OAE2 CIE. See text for methods and discussion. OAE2-Oceanic
Anoxic Event 2.

Figure 7. Left - Plot of all recent <sup>40</sup>Ar/<sup>39</sup>Ar (circles) and CA-ID-TIMS U-Pb (squares) ages for the 1104 B, C, and D bentonites in the Western Interior Basin. Right - recent age estimates for the 1105 1106 Cenomanian-Turonian boundary (CTB), including the GTS2012 age from Meyers et al. (2012b). Filled circles represent data from this study. All data are shown with  $2\sigma$  full external uncertainties. 1107 Note that U-Pb dates of Meyers et al. (2012b) from Lohali Point, Arizona for bentonites C and D 1108 are not plotted due to the presence of inherited zircons, similar to trends exhibited in several plotted 1109 U-Pb ages for Bentonite B. The Eldrett et al. (2015) youngest zircon date for bentonite "B4" is 1110 1111 from a horizon that is 0.5-1.0 short eccentricity cycle below where they place Bentonite B and thus is not considered further when discussing age calculations (see Eldrett et al., 2015 supplement for 1112 details). The age from "Bighorn River (n=6)" corresponds to the age derived from all six zircons 1113 1114 analyzed from the bentonite sample, whereas "Bighorn River (n=3)" corresponds to the youngest three zircon ages from the horizon (Barker et al., 2011). Several samples possessing inherited 1115 zircons or considered outliers (diamonds) are not included in the calculation of the weighted mean 1116 age of the Cenomanian-Turonian boundary for this study (grey shading and dashed line). See text, 1117 Table 2, and Table DR1 in Data Repository for determination of the CTB age. 1118

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**Figure 8.** Refined conceptual timeline of OAE2. From left to right – sea level history during OAE2 (Jones et al., 2019) and isotopic records of osmium (this study), calcium (Du Vivier et al., 2015a), thallium (Ostrander et al., 2017), and carbon (Joo and Sageman, 2014) as proxies for LIP volcanic activity, carbonate chemistry, marine deoxygenation, and carbon cycle response of organic carbon burial, respectively. Dashed line in  $\delta^{44}$ Ca profile reflects missing time in Portland Core. Data from other sites and within and outside WIB confirm coincident timing of  $\delta^{44}$ Ca and Os<sub>i</sub> excursions. See text for discussion.

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## **1128 TABLE CAPTIONS**

1129 Table 1. RHENIUM-OSMIUM GEOCHEMISTRY OF THE ANGUS AND SH#1 CORES1130 THROUGH OCEANIC ANOXIC EVENT 2.

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1132 TABLE 2. SUMMARY OF <sup>40</sup>AR/<sup>39</sup>AR AGE DATA FOR BENTONITES B, C, AND D AT
1133 NIPPLE CREEK (NC) OUTCROP, UTAH, USA; LOHALI POINT, ARIZONA, USA; AND
1134 PUEBLO, COLORADO, USA.

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1136 <sup>1</sup>GSA Data Repository item 20<mark>XXxxx</mark>, (1) Complete Ar geochronology data, bentonite correlations and collection in Kaiparowits Plateau, Cenomanian-Turonian boundary age 1137 1138 calculations, core photos and description of hiatuses, and Angus Core depth scale alignment correction; (2) available 1139 Time scale tables for cores, is online at www.geosociety.org/pubs/ft20xx.htm, or on request from editing@geosociety.org. 1140

















TABLE 1. RHENIUM-OSMIUM GEOCHEMISTRY OF THE ANGUS A	AND SH#1 CORES THROUGH OCEANIC ANOXIC
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Angus Core Samples	Depth (m)	Re (ppb)	±	Os (ppt)	±	<sup>192</sup> Os (ppt)	±	<sup>187</sup> Re/ <sup>188</sup> Os	±	<sup>187/188</sup> Os	±
KU/5U-1_AA/454-2.5CM	22/1.95	6.15	0.02	/1.8	0.4	25.3	0.2	483.7	3.3	1.444	0.012
KU/45-1_AA/460 <sup>+</sup> 1/cm	22/3.98	6.62	0.02	133.3	0.6	49.0	0.2	269.0	1.5	1.076	0.007
KU/5U-2_AA/46/ <sup>*</sup> +5.5Cm	2276.00	8.54	0.02	161.0	U./	60.9	0.3	279.0	1./	0.827	0.006
KU/5U-3_AA/4/1-10.5cm	2277.06	3.55	0.01	453.4	1.4	184.8	1.0	38.3	0.2	0.227	0.002
KU/45-2_AA/4/4 <sup>-</sup> -9cm	2277.99	37.88	0.09	1422.6	4.2	567.0	2.2	132.9	0.6	0.402	0.002
KU/45-3_AA/4//`+3cm	22/9.22	10.66	0.03	/08.1	2.3	285.9	1.5	/4.2	0.4	0.300	0.002
KU75U-4_AA7478°-7Cm	2279.42	/1.09	0.18	2338.2	6.5	931.4	3.4	151.8	U./	0.407	0.002
KU75U-5_AA7478°+9cm	2279.58	64.41	0.16	2951.0	٨./	1183.9	4.3	108.2	0.5	0.350	0.002
KU745-4_AA7479 <sup>-</sup> +2cm	22/9.82	42.64	0.11	2241.1	6.2	902.2	3.b	94.0	0.4	0.323	0.002
KU/5U-6_AA/4/9 <sup>-</sup> +18cm	2279.98	89.31	0.22	1644.6	5.3	632.6	2.2	280.9	1.2	0.689	0.003
KU745-5_AA7480 <sup>-</sup> +9.5cm	2280.20	47.78	0.12	282.9	1.5	89.7	0.4	1059.1	5.2	2.439	0.014
KU/5U-/_AA/481 <sup>-</sup> -1.5Cm	2280.39	45.86	0.12	278.4	1.5	87.9	0.4	1038.2	5.1	2.489	0.014
KU/45-6_AA/481 <sup>-</sup> +16CM	2280.57	47.57	0.12	279.8	1.5	87.7	0.4	1079.5	5.3	2.562	0.015
KU75U-8_AA7483 <sup>-</sup> -8.5Cm	2280.93	56.60	0.14	274.9	1.6	82.0	0.3	13/3.0	6.6	3.071	0.017
KU/43-/_AA/489 +14.3011	2202.99	29.12	0.Uð	102.2	T.U	53.5	U.3	994.4	5.1	2.310	0.014
SH#1 Core Samples	Depth (m)	Re (ppb)	±	Os (ppt)	±	<sup>192</sup> Os (ppt)	±	<sup>187</sup> Re/ <sup>188</sup> Os	±	<sup>187/188</sup> Os	±
RO/51-1_SH#1-94.66m	94.66	4.03	0.01	50.7	0.3	1/./	0.1	451.3	2.9	1.504	0.012
KU/51-2_SH#1-106.2/M	106.27	5.86	0.02	61.4	0.3	21.6	0.1	540.2	3.3	1.4/1	0.011
KU/51-3_SH#1-113.58m	113.58	2.96	0.01	/9.9	0.5	30.5	0.3	193.1	1.8	U./68	0.010
KU/51-4_SH#1-116.58m	116.58	3.95	0.01	96.2	0.4	37.4	0.2	209.9	1.3	0.600	0.005
KU/51-5_SH#1-11/.58M	117.58	7.64	0.02	126.5	0.5	48.0	U.3	312.8	۵.۲	0.701	0.005
KU/51-6_SH#1-118.08m	118.08	2.35	0.01	148.7	0.7	59.8	0.5	/8.U	0.7	0.330	0.004
KU/51-/_SH#1-118.58m	118.58	1./6	0.01	36.2	0.2	14.1	0.1	248.9	2.5	0.593	0.008
KO121-8_SH#1-119.08m	119.08	2.41	0.01	165.5	0.8	66.9	0.6	/1.8	0.7	0.291	0.004
КО/41-6_SH1: 119.53m	119.53	1.27	0.01	333.2	3.2	136.2	2.8	18.5	0.4	0.204	0.006
KO/41-/_SH1:119./9m	119.79	2.72	0.01	206.6	1.1	83.9	0.9	64.6	0.7	0.255	0.004
KU751-9_SH#1-120.03m	120.03	6.60	0.02	143.1	0.6	55.7	0.3	235.8	1.4	0.591	0.004
K0103-1_2H1-32:1	120.29	13.80	0.04	282.4	1.2	203.9	U.b	251.1	1.5	0.603	0.005
KO103-2_SH1-35:10	121.03	1.52	0.02	404.8	1.4	162.3	0.9	92.2	0.6	0.355	0.003
KO103-3_2H1-32:15	121.78	1.34	0.01	50.0	0.4	19.8	U.3	134.7	2.0	0.470	0.009
KO141-8_SH1: 122.02m	122.02	10.79	0.03	201.6	0.8	/8.2	0.4	2/4.2	1./	0.615	0.005
KO741-9_SH1: 122.29m	122.29	7.68	0.02	1/5.4	0.7	69.1	0.4	221.2	1.4	0.497	0.004
RO741-10_SH1: 122.53m	122.53	1.30	0.01	38.0	0.4	13.3	0.2	193.9	2.9	1.488	0.029
RO703-4_SH1-36:1	122.78	2.91	0.01	29.9	0.3	9.7	0.1	599.3	6.1	2.275	0.030
RO751-10_SH#1-123.21m	123.21	1.32	0.01	18.2	0.2	6.0	0.1	438.9	5.4	2.137	0.030
RO703-5_SH1-36:3	123.98	0.81	0.01	26.0	0.3	8.9	0.2	181.7	4.1	1.710	0.050

#### Notes:

<sup>a</sup>Initial osmium isotope ratios (Osi) are calculated using an age of 94.4 Ma

<sup>b</sup>T=0 for the floating time scale is placed at the base of the carbon isotope excursion of Oceanic Anoxic Event 2

EVEN	1 2 IN I	ERVAL	
rho	Os; <sup>a</sup>	±	Floating <sup>b</sup> time (kyr)
0.673	0.683	0.017	4/5
0.605	0.652	0.009	320
0.633	0.388	0.009	186
0.612	0.16/	0.002	113
0.590	0.193	0.003	61
0.627	0.184	0.003	-12
0.581	0.168	0.003	-25
0.578	0.180	0.003	-35
0.594	0.175	0.002	-51
0.574	0.247	0.005	-59
0.627	0.//2	0.022	-/1
0.624	0.855	0.022	-81
0.628	0.863	0.023	-91
0.625	0.910	0.027	-108
סכס.ט	0.755	0.022	-233
rho	Os; <sup>a</sup>	±	Floating <sup>b</sup> time (kyr)
0.653	0.794	0.016	849
0.654	0.620	0.017	532
0.666	0.464	0.012	302
0.623	0.270	0.007	169
0.639	0.209	U.UU8	132
0.654	0.207	0.005	115
0.651	0.201	0.012	98
0.654	0.178	0.005	79
0.683	0.175	0.006	63
0.663	0.154	0.005	53
0.633	0.220	0.007	44
U.626	0.207	0.007	34
0.612	0.210	0.004	/
U.665	U.258	0.012	-20
0.634	0.183	0.007	-36
0.615	0.149	0.006	-48
0.670	1.183	0.034	-59
0.703	1.331	0.039	-70
0.707	1.446	0.039	-90
0.670	1.424	0.057	-124

		_ 40					
TABLE 2.	SUMMARY O	F AR/	AR DATA AN	D CENOMANIAN	I-TURÓNIAN	BOUNDARY	AGE

						Weighted mean	
Sample	Locality	Latitude	Longitude	Ν	MSWD	Age (Ma) $\pm 2\sigma^{a}$	$\pm 2\sigma^{b}$
Single sani	dine incremental heating						
NC-D	Nipple Creek outcrop, UT	37.123	-111.672	10/11	1.40	93.443 ± 0.090	± 0.166
NC-C	Nipple Creek outcrop, UT	37.122	-111.673	8/12	0.35	94.011 ± 0.060	± 0.152
NC-B	Nipple Creek outcrop, UT	37.121	-111.672	10/11	1.20	94.082 ± 0.057	± 0.152
Single sanidine fusions							
K-07-01-C	Pueblo, CO, USA	38.28	-104.74	20/20	1.12	94.022 ± 0.147	± 0.204
90-0-34	Lohali Point, AZ, USA	36.185	-109.884	24/27	1.15	93.799 ± 0.065	± 0.154

#### Notes:

Ages calculated relative to 28.201 Ma Fish Canyon sanidine (Kuiper et al. 2008) using decay constants of Min et al. (2000)

<sup>a</sup> Age uncertainty includes analytical uncertainty + J uncertainty.

<sup>b</sup> Total age uncertainty includes decay constrant, standard age, J, and analytical uncertainties.

<sup>c</sup> CTB age calculated by anchoring Portland Core astronomical timescale to ash date

<sup>d</sup> CTB age uncertainty includes radioisotopic, stage boundary placement, and astrochronological time scale uncertainties combined in quadrature.

For single crystal incremental heating experiments, N = number of plateau ages/number of experiments For single crystal fusion data, N = number of dates included in weighted mean/number of fusions

Ages for the Cenomanian-Turonian Boundary are calculated by anchoring the floating astronomical

time scale of the SH#1 Core to the new <sup>40</sup>Ar/<sup>39</sup>Ar ages (see text for discussion).

CTB age (Ma) <sup>c</sup> $\pm 2\sigma^{d}$					
n/a	n/a				
94.129	± 0.156				
93.914	± 0.156				
94.140	± 0.207				
94.065	± 0.158				