Lithium-isotope evidence for enhanced silicate weathering during OAE 1a

(Early Aptian Selli event)

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Abstract

An abrupt rise in temperature, forced by a massive input of CO_2 into the atmosphere, is commonly invoked as the main trigger for Oceanic Anoxic Events (OAEs). Global warming initiated a cascade of palaeoenvironmental perturbations starting with increased continental weathering and an accelerated hydrological cycle that delivered higher loads of nutrients to coastal areas, stimulating biological productivity. The end-result was widespread anoxia and deposition of black shales: the hallmarks of OAEs. In order to assess the role of weathering as both an OAE initiator and terminator (via CO_2 sequestration) during the Early Aptian OAE 1a (Selli Event, ~120 Ma) the isotopic ratio of lithium isotopes was analysed in three sections of shallow-marine carbonates from the Pacific and Tethyan realm and one basinal pelagic section from the Tethyan domain. Because the isotopic composition of lithium in seawater is largely controlled by continental silicate weathering and high- and low-temperature alteration of basaltic material, a shift to lighter δ^7Li values is expected to characterize OAEs. The studied sections illustrate this phenomenon: δ^7Li values decrease to a minimum coincident with the negative carbon-isotope excursion that effectively records the onset of OAE 1a. A second negative δ^7Li excursion occurs coeval with the minimum in strontium isotopes after the event. The striking similarity to the strontium-isotope record argues for a common driver. The formation and destruction (weathering) of an oceanic LIP could account for the parallel trend in both isotope systems. The double-spike in lithium isotopes is probably related to a change in weathering congruencies. Such a chemostratigraphy is consistent with the hypothesis that an increase in silicate weathering, in conjunction with organic-carbon burial, led to drawdown of atmospheric CO_2 during the early Aptian OAE 1a.

Keywords: OAE 1a, Selli Event, Li isotopes, silicate weathering

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1. Introduction

The history of global climate can be divided into intervals of low-CO_2 icehouse periods and high-CO_2 greenhouse periods that are punctuated by short term hyperthermals (Berner & Kothavala, 2001; Came et al., 2007; Fischer, 1982; Föllmi, 2012; Hay & Floegel, 2012; Jenkyns, 2003; Pagani et al., 2014; Veizer et al., 2000; Zeebe, 2012). In particular, short-term phenomena (< 1 Myr) such as Oceanic Anoxic Events (OAEs) are marked by strong environmental changes, thought to have been triggered by the rapid injection of huge amounts of CO_2 into the ocean-atmosphere system from volcanic sources (Jenkyns, 2010, 2003; Larson, 1991; Larson & Erba, 1999; Weissert & Erba, 2004; Weissert et al., 1998). The increase of atmospheric pCO_2 at the onset of OAEs would have initiated a cascade of palaeoenvironmental perturbations starting with rapid global warming, possibly causing dissociation of gas hydrates as a climatic amplifier, as well as promoting increased weathering and enhanced nutrient runoff into the oceans that resulted in enhanced marine productivity and organic-carbon flux to the seafloor. These palaeoenvironmental changes culminated in widespread oxygen depletion and globally distributed deposition of black shales, which are characteristic features of OAEs (Jenkyns, 2003; Schlanger & Jenkyns, 1976). Since a large part of the CO_2 injected into the atmosphere would have been ultimately absorbed by seawater to cause a fall in pH, ocean acidification is commonly envisaged as a twin evil of global warming and seawater anoxia, all initially triggered by a large increase in atmospheric pCO_2 (Erba, 2004; Erba et al., 2010; Hönisch et al., 2012; Jenkyns, 2010; Kump et al., 2009; Wissler et al., 2003; Zeebe, 2012).

The Cretaceous, characterized by overall high temperatures and pCO_2, was marked repeatedly by OAEs, two of which are of particular significance: OAE 1a (early

Aptian) and OAE 2 (Cenomanian–Turonian boundary). The early Aptian OAE 1a or Selli event (~120 Ma) has been much studied in terms of carbon-, calcium-, osmium- and strontium-isotope stratigraphy: Blättler et $al.$ (2011); Bottini et $al.$ (2012); Erba et $al.$ (2010); Jenkyns (1995); Jenkyns et $al.$ (1995); Jones & Jenkyns (2001); Keller et $al.$ (2011); Méhay et $al.$ (2009); Menegatti et $al.$ (1998); Tejada et $al.$ (2009); van Breugel et $al.$ (2007); Wissler et $al.$ (2004). This event is conventionally interpreted as triggered by the massive outgassing of the Ontong Java, Manihiki and Hikurangi submarine large igneous province (LIP; Larson & Erba, 1999; Méhay et $al.$, 2009; Tarduno et $al.$, 1991 Tejada et $al.$, 2009), which introduced large quantities of isotopically light carbon into the atmosphere-ocean system, producing a stepwise decline in $\delta^{13}C$ and lowering the pH of the oceans. Addition of methane-derived carbon from dissociation and oxidation of gas hydrates has also been invoked as an accompanying phenomenon (Beerling et $al.$, 2002; Jahren et $al.$, 2001). Higher atmospheric pCO$_2$ and higher temperatures are indicated from oxygen isotopes on bulk carbonate and TEX$_{86}$ data from organic matter (Ando et $al.$, 2008; Dumitrescu et $al.$, 2006; Schouten et $al.$, 2003). Biomarkers and redox-sensitive trace metals suggest the development of poorly oxygenated to anoxic watermasses and local photic-zone euxinia (Pancost et $al.$, 2004; Westermann et $al.$, 2013). Oxygen-deficiency favoured the burial of huge amounts of organic matter in the sedimentary record as globally distributed marine black shales, which ultimately caused the drawdown of atmospheric CO_2. However, enhanced silicate weathering is an additional mechanism for drawing down this greenhouse gas (Berner et $al.$, 1983; Dessert et $al.$, 2003; Raymo et $al.$, 1988; Urey, 1952) and thereby helping to terminate the event.

The role of silicate weathering in sequestering at least 1/3 of the total volume of CO_2 injected into the atmosphere at the onset of an OAE has been recently demonstrated for the Cenomanian–Turonian event using lithium isotopes in carbonate sequences

from northern (UK) and southern (Italy) Europe (Pogge von Strandmann *et al*., 2013). For OAE 1a, a pulse of silicate weathering at the beginning of the event is supported by the presence of a well-defined radiogenic 'spike' in osmium isotopes from two sections in Italy and, more ambiguously, one from the central Pacific (Bottini *et al*., 2012; Tejada *et al*., 2009). Enhanced weathering rates have been also proposed on the basis of a negative shift in $\delta^{44/42}$Ca (Blättler *et al*., 2011), although calcium isotopes can potentially be affected by ocean acidification, temperature changes and/or calcification rate (Fantle & Tipper, 2014). This continental weathering pulse is not unequivocally captured by the marine strontium-isotope curve, although some relatively radiogenic values do overlap with the OAE 1a record (Jones & Jenkyns, 2001). Essentially, however, the weathering pulse was probably too short or too small to offset the overwhelming contribution of non-radiogenic strontium delivered by enhanced hydrothermal/magmatic activity associated with construction (Bralower *et al*., 1997; Jones & Jenkyns, 2001) and/or destruction of the LIP (Allègre *et al*., 2010; Pogge von Strandmann *et al*., 2013). In a more qualitative way, sedimentological studies also suggest enhanced weathering at the onset of OAE 1a: Stein *et al*. (2012), for instance, proposed at least a local increase in continental chemical weathering on the basis of a rise in the relative abundance of the clay mineral kaolinite in south-east France. Furthermore, Weissert (1990) and Wortmann *et al*. (2004) reported a sudden influx of siliciclastic, commonly quartz-rich, material in the North Atlantic, Neo- and Tethyan realm and mature glauconite-bearing quartz sandstones in the Tethys, suggestive of a change to more humid and warmer conditions.

In this study, Li-isotope ratios of marine carbonates are determined in two shallow-water carbonate-platform successions and one adjacent basinal section from southern Italy as well as one carbonate-platform section through a north Pacific guyot. These new data, together with published strontium-, calcium- and osmium-

isotope ratios, are used in order to constrain the importance of silicate weathering and atmospheric CO_2 consumption during OAE 1a.

2. Weathering and the Li-isotope composition of the oceans

In nature, lithium is composed of two stable isotopes – [6]Li and [7]Li – and is predominantly found in silicate minerals (Kisakürek *et al.*, 2005; Millot *et al.*, 2010). In modern oceans, Li has a residence time of about 1 Myr and the principal input fluxes are continental weathering and hydrothermal activity, which are roughly equivalent (Hathorne & James, 2006; Misra & Froelich, 2012). The main sinks are secondary mineral formation during alteration of the oceanic crust and the incorporation of Li into marine sediments (Chan & Edmond, 1988; Chan *et al., 2006; 1992*; Hathorne & James, 2006*;* Stoffyn-Egli & MacKenzie, 1984). The isotopic ratio of Li in modern oceans is ~31‰ (Tomascak *et al.*, 1999). The continental crust has an average lithium-isotope composition of 0 $\pm$ 3‰ (Teng *et al.*, 2004), whereas mid-ocean-ridge basalts usually have isotopic values of 3–5‰ (Elliott *et al.*, 2006; Tomascak *et al.*, 2008, 1999). The difference of the isotopic ratio between the ocean water and continental and marine silicates is a function of high- and low-temperature alteration of these minerals. During the weathering processes, clay minerals are formed that preferentially incorporate the light [6]Li, leaving an isotopically heavy solution behind (e.g. Dellinger *et al.*, 2015; Huh *et al.*, 2001, 1998; Kisakürek *et al.*, 2005; Pogge von Strandmann *et al.*, 2010, 2006; Vigier *et al.*, 2009). As a result, the riverine lithium isotopic ratio carries the combined signal of secondary mineral formation, which contributes solutions with relatively high δ^7Li and low [Li] (incongruent weathering), and primary silicate dissolution, which contributes solutions with a relatively low δ^7Li and high [Li] (congruent weathering, where river δ^7Li equals rock δ^7Li). Hence, the δ^7Li of rivers is controlled by the ratio of primary mineral dissolution to secondary

mineral formation, which can be defined as the weathering congruency or intensity (Dellinger *et al.*, 2015; Kisakürek *et al.*, 2005; Liu *et al.*, 2015; Misra & Froelich, 2012; Pogge von Strandmann *et al.*, 2013, 2010). The global mean riverine δ^7Li today is about 23‰ (Huh *et al.*, 1998) with values extending between 1.2 and 43% (Dellinger *et al.*, 2015; Huh *et al.*, 2001; Kisakurek *et al*, 2005; Lemarchand *et al.*, 2010; Liu *et al.*, 2015; Pogge von Strandmann & Henderson, 2015; Pogge von Strandmann *et al.*, 2010, 2006; Vigier *et al.*, 2009).

Therefore, changes in weathering rates and congruency can be investigated by determining riverine [Li] and δ^7Li. However, while, theoretically, [Li] and δ^7Li in rivers should have linked behaviour (i.e. enhanced secondary mineral formation should decrease [Li] and increase δ^7Li), during fluvial transport Li may also be desorbed/dissolved from previously formed secondary minerals. In this study we consider riverine [Li] and its isotopic ratio as independent parameters: an approach that is in agreement with studies on modern river catchments (Bouchez *et al.*, 2013; Dellinger *et al.*, 2015; Huh *et al.*, 1998; Li & West 2014, supplementary material; Liu *et al.*, 2015; Millot *et al.*, 2010; Pogge von Strandmann & Henderson, 2015; Wanner *et al.*, 2014) that do not show any, or at least a non-linear, relationship between [Li] and δ^7Li. This independence of riverine [Li] and its isotopic ratio is probably caused by the varied combination of processes acting on the course of the river in different parts of the catchment, where different weathering regimes prevail.

Marine carbonates represent a minimal sink for Li compared to silicates. Li concentrations in carbonates are strongly temperature-dependent and can therefore not be used as a proxy for weathering rates (Marriott *et al.*, 2004a, 2004b). However, the incorporation of lithium has a constant isotopic fractionation factor of about 3–5‰ for inorganically precipitated and most biogenically secreted calcite, and around 11‰ for aragonite (Marriott et al., 2004). Fractionation values reported of 9‰ in calcite

(whichever Marriott this is) are likely due to impure carbonate mineralogy (Henderson, pers. comm.). The incorporation into carbonates has a negligible effect of temperature, salinity and Li/Ca values (Hathorne & James, 2006; Marriott *et al*., 2004a, b; Misra & Froelich, 2012, 2009; Rollion-Bard *et al*., 2009). Planktonic foraminifera show a slightly more variable offset and a species-specific fractionation related to the biomineralization process (Hall *et al*., 2005; Hathorne and James, 2006). However, this offset does not exceed 0–4‰ and its effects are suggested to be minimal when analysing bulk carbonates. Whereas a recent work proposes a change in fractionation for a certain foraminiferal genus with varying concentrations of dissolved inorganic carbon (Vigier *et al*., 2015), deep- and shallow-water corals seem not to be affected by variations in pH or pCO_2 values (Rollion-Bard *et al*., 2009). Additionally, according to Misra & Froelich (2012) and Pogge von Strandmann *et al*. (2013), foraminifera and bulk carbonates as old as 70 and 94 Ma are reliable archives for seawater δ^7Li. As a consequence, lithium-isotope ratios in bulk marine carbonates can be used as a proxy for assessing the role of enhanced weathering as both initiator of past OAEs, *via* intensified nutrient runoff fuelling primary productivity in coastal areas, and terminator of OAEs *via* CO_2 sequestration.

3. Study Sites

Three shallow-water carbonate-platform sections (i.e. Resolution Guyot, Monte Raggeto and Santa Maria 4 core), as well as one basinal pelagic section (Coppitella) recording the Early Aptian OAE 1a have been analysed for δ^7Li (Fig. 1). The benefit of analysing sections with deposits that have been accumulated in different oceans and in various water depths is the ability potentially to recognize a global signal. Resolution Guyot, located in the north Pacific Ocean, is a flat-topped seamount built of Hauterivian–Albian poorly cemented platform carbonates overlain by pelagic

calcareous oozes (Jenkyns, 1995). The Aptian interval is characterized by bioclastic limestones with debris of caprinid rudists, cyclically arranged packstone-wackestones, cyanobacterial laminites and oolitic grainstones (Jenkyns & Wilson, 1999). The other three sections, Monte Raggeto, Santa Maria 4 core and Coppitella, are situated in southern Italy (part of the Apennines) and were formerly positioned in the central Tethyan realm. The Monte Raggeto section is representative of the inner part of the Apennine Carbonate Platform and is mainly composed of well-cemented ostracodal mudstones, peloidal and algal-foraminiferal wackestone-packstones and subordinate requienid-ostreid floatstones (Amodio et al., 2003; D'Argenio et al., 2004; Di Lucia et al., 2012; Wissler et al., 2004). The sediments of the Santa Maria 4 core were deposited in the inner part of the Apulian Carbonate Platform and are characterized principally by well-cemented cyanobacterial laminites, ostracodal mudstones, foraminiferal-algal wackestone-packstones and orbitolinid-sponge packstones to floatstones, (Amodio et al., 2013, 2003; D'Argenio et al., 2011). The Coppitella section is representative of the proximal part of the Ionian Basin, facing the Apulian Platform to the east, and is constituted by well-lithified pelagic limestones and marls containing planktonic foraminifera, coccoliths and radiolaria locally reconstituted as chert nodules (Luciani et al., 2001). This sequence probably also contains some platform-derived fine-grained carbonates (peri-platform ooze of Schlager & James, 1978). Notably, the guyot carbonates are the most poorly lithified of all four sections (porosity ~40% in some samples) and their carbon- and strontium-isotope characteristics match those of coeval unaltered skeletal calcitic material (Jenkyns & Wilson, 1999). Additionally, the carbonates have been accumulated in the middle of the palaeo-Pacific Ocean, manifestly excluding any basinal restriction. Therefore, we consider Resolution Guyot as the most promising section for yielding a pristine Li-isotope signal reflecting changes in palaeo-seawater conditions.

For pinpointing the Early Aptian OAE 1a and correlating the sections, prior published

studies of these sections have been taken into account (Fig. 2). For Resolution Guyot the record of OAE 1a has been identified by Jenkyns (1995) on the basis of carbon-isotope stratigraphy. The Coppitella section has been analysed by Luciani *et al*. (2001) for bio- and carbon-isotope stratigraphy identifying the record of OAE 1a. Wissler *et al.* (2004) and Di Lucia *et al.* (2012) studied the Monte Raggeto section and identified the typical carbon-isotope signature of OAE 1a. This interpretation is supported by magneto-, sequence and cyclostratigraphic investigations (Amodio *et al*., 2013, 2003; D'Argenio *et al*., 2011, 2004; Wissler *et al*., 2004). The Santa Maria 4 core has not been studied previously for carbon isotopes. However, a correlation with the Monte Raggeto section on the basis of cyclo- and sequence stratigraphy was possible, thereby pinpointing the stratigraphic signature of OAE 1a (Amodio *et al*., 2013, 2003; D'Argenio *et al*., 2011).

Correlation of the sections was obtained using carbon-isotope stratigraphy and the previously defined position of the OAE 1a record. The carbon-isotope curve of Resolution Guyot, with suggested stratigraphy based partly on strontium isotopes, has been taken from Jenkyns & Wilson (1999) with data from Jenkyns (1995) and Jenkyns *et al*. (1995); the Monte Raggeto carbon-isotope curve is taken from Di Lucia *et al*. (2012); and the carbon-isotope and biostratigraphy of the Coppitella section is from Luciani *et al*. (2001). The Santa Maria 4 core has been specifically analysed for carbon-isotope ratios in this study, although the record is not unequivocal. The nomenclature of the δ^{13}C intervals of the carbon-isotope excursion associated with the Selli event is taken from Bralower *et al*. (1999) and Menegatti *et al*. (1998).

4. Methods & Experimental set-up

Sample preparation and geochemical analyses were carried out in the Department of

Earth Sciences at the University of Oxford. For Li-isotope analyses, 0.2 gramms of bulk carbonates have been used and the method described in detail in Pogge von Strandmann *et al.* (2013) was followed. The accuracy of the measurements and external reproducibility was determined by measuring seawater and obtaining a value of 31.4 ± 0.6‰ (2sd, n = 5). This isotopic ratio agrees with that of the long-term 3-year uncertainty value of seawater recorded at Oxford of 31.3 ± 0.6‰ (n = 45).

The newly produced lithium-isotope data have been used together with previously published analyses to build a series of dynamic box models of the seawater Li, Ca, Sr and Os cycles across the Selli event in order to explore the causes of isotopic variations. Calcium and strontium isotopes, both measured in Resolution Guyot, are taken from Blättler *et al.* (2011) and Jenkyns *et al.* (1995), respectively. Osmium-isotope data, measured on the Cismon section in northern Italy, are taken from Bottini *et al.* (2012).

The box models were built from the simple mass-balance equation, which is shown here for lithium.

$$\frac{dN_{Li}}{dt} = F_r + F_h - F_{sed} \qquad (Eq\ 1)$$

where N_{Li} represents the seawater reservoir of Li, and F_x the input and output fluxes (r = river; h = hydrothermal; sed = uptake into marine sediments + alteration of the oceanic crust). The isotopic balance equation can then be defined as:

$$N_{Li}\frac{dR_{SW}}{dt} = F_r(R_r - R_{SW}) + F_h(R_h - R_{SW}) - F_{sed}(R_{sed} - R_{SW}) \qquad (Eq\ 2)$$

where R_x is the isotopic ratio of the different fluxes. R_{sink} is defined by $\Delta_{sink} = R_{sink} - R_{SW}$ with $\Delta^7 Li_{sink} = 15 - 16‰$ (Chan *et al.*, 1993; Huh *et al.*, 1998; Misra & Froelich, 2012). The calculation of the sink of Li is based on the assumption that partitioning of Li into sinks has a constant partition coefficient k: $F_{out} = k \times N \qquad (Eq\ 3)$.

The other elements were calculated similarly (Pogge von Strandmann et al., 2013). Diagenetic fluxes and aeolian dust were taken into account as additional sources for Sr and Os, respectively. Cosmic dust as another source for Os was not included into the model because it is believed that it will not dissolve in seawater and consequently, it is unlikely to have an effect on this short time period. However, low- and high-temperature hydrothermal activity was differentiated in the Os model. Although Sr and Os isotopes do not fractionate during the uptake into marine sediments, Li and Ca isotopes do, which was accounted for in the model. Li, Ca and Sr isotopes were modelled in 10 kyr steps, whereas 5 kyr steps were taken for Os due to its short residence time. The initial hydrothermal flux was estimated to be proportional to the spreading rate as determined by the Geocarb II model (Berner, 1994). It has been assumed that the elemental concentrations are in the same proportion as today. Pre-excursion conditions were estimated to be in steady state, where riverine fluxes and isotopic ratios were calculated to match pre-excursion values. It is important to note that model solutions are non-unique but are chosen to be as conservative as possible, i.e. as close to modern values as possible. As a result, our values represent minimum estimates of changes.

5. Results

The most prominent feature of the lithium-isotope curve in the studied sections is a pronounced negative shift of about 4.5–11‰ from pre-OAE 1a values, reaching a minimum at a level close to the base of the C3 interval (Fig. 3). The Coppitella section which, based on carbon-isotope stratigraphy, starts just below the onset of OAE 1a, does not show a negative shift but shows low δ^7Li at its base that could correspond to the minimum recorded in the other sections. Following this minimum, all four sections record a recovery to slightly more positive δ^7Li values during the C4–

C5 interval. Subsequently, at the end of the C8 interval, although not as evident in every section, δ^7Li values decrease gently to a second minimum and eventually recover to values similar to the pre-event state (Fig. 3). In the Coppitella section, a second negative shift is visible. However, this negative shift starts earlier (within the C7-C8 interval) and no data are available above the C8 interval.

6. Discussion

6.1 Potential causes of the negative Li-isotope excursions

Before interpreting the pronounced negative excursion in the δ^7Li curve at the onset of OAE 1a as a primary seawater signal, several competing alternatives must be evaluated.

Could relatively light δ^7Li be produced by leaching of silicates or organic matter during sample preparation? Leaching experiments and mass-balance calculations (Pogge von Strandmann *et al*., 2013) indicate that Al/Ca values in carbonates have to be higher than 0.8 mmol/mol before silicate leaching has a sizeable effect (> 0.5‰) on Li isotope values. Al/Ca ratios in our samples are all below 0.5 mmol/mol and also Mg/Ca and Mn/Ca ratios do not show any specifically high values. Organic material is more resistant to leaching in diluted HCl than silicates, and in any case has very low [Li], and thus we are confident that it has not been leached. Additionally, shallow-water platform carbonates usually contain only a very limited amount of organic material due to the depositional environment being commonly turbulent and highly oxygenated. Therefore, we can exclude leaching of silicates and organic matter as a significant driver for the negative excursion in the Li-isotope curve.

Lithium isotopes fractionate differently during precipitation of $CaCO_3$ polymorphs,

with the result that δ^7Li is about 8‰ lighter in aragonite than in calcite (Marriott *et al*., 2004b), two polymorphs of calcium carbonate that can be precipitated or secreted from seawater. If this isotopic difference were retained after inversion of aragonite to low-Mg calcite, a negative shift of δ^7Li in platform carbonates could have been caused by a relative increase in aragonite abundance. Addressing this possibility would entail knowledge of the original composition and relative abundance of these two minerals in the sections. However, no clear relation between facies of the analysed platform carbonates, their Sr/Ca ratio and their δ^7Li was observed; and changing ratios of calcite and aragonite should have affected the Sr/Ca ratio, given that strontium is preferentially substituted into aragonite (e.g. Morse & Mackenzie, 1990; Tucker & Wright, 1990). Moreover, unless a high-frequency global control on original mineralogy is accepted, it is very difficult to explain coeval δ^7Li excursions in different platforms in different palaeoceanographic settings. The latter argument can also be used to dismiss the hypothesis that the negative excursions are a diagenetic artefact because the studied successions experienced very different post-depositional and burial/uplift histories. Furthermore, Resolution Guyot has been largely unaffected by diagenetic processes, because the section has never been uplifted and deformed, unlike the units within the Apennine mountain belt that must have been affected by processes involving fluid transfer during lithification. In addition, the pelagic Coppitella section is dominantly composed of the essentially monomineralic calcitic remains of nannofossils and planktonic foraminifera (Luciani *et al*., 2001).

6.2 Constraints from multi-isotope excursions

Because all other possible explanations for the negative excursion in δ^7Li at the onset of OAE 1a can be discarded, this signal must record changes in the isotopic

ratio of lithium in the oceans. However, shallow-water carbonate platforms, accumulating sediment near mean sea level, suffer from numerous hiatuses, which can be either related to times of non-deposition or erosion of formerly deposited sediments. Since three of the four sections analysed in this study are composed of such shoal-water carbonates (Resolution Guyot, Santa Maria 4 core and Monte Raggeto), chemostratigraphic profiles will not necessarily match perfectly.

As discussed earlier, relatively light seawater Li-isotope values may be driven either by a sudden (with respect to the residence time of Li) intensification in hydrothermal activity or by a sudden increase in weathering rates (flux) and/or more congruent weathering. Recently, it has been proposed that changes in Cenozoic seawater δ^7Li may have been affected by changes in the seawater Li sinks (Li & West, 2014). However, while a change in clay mineralogy may be relevant as a control on δ^7Li over long time scales, such as the Cenozoic Era, it is unlikely to have played a role in the significantly more rapid changes discussed here: the negative δ^7Li excursions occurred within some hundred thousands of years. In order to constrain the driver for the negative δ^7Li excursion, we combine the Li-isotope data in a simple dynamic box model with Sr-, Os- and Ca-isotope data, measured in the studied sections or in other sections that can be precisely correlated by carbon-isotope stratigraphy. The chosen isotope systems are controlled by different factors. Li isotopes can be used as a proxy for silicate-weathering congruency, although weathering of basaltic (oceanic) or granitic (continental) crust cannot be differentiated due to their similar isotopic values (Teng *et al*., 2004). Ca isotopes may hold information about weathering of both continental crust and carbonates (Blättler *et al*., 2011). Strontium isotopes and, similarly, osmium isotopes are mainly influenced by the competing effects of continental silicate weathering, driving the isotopic ratios to more radiogenic values, and oceanic hydrothermal activity, basalt and/or carbonate weathering, which drive the Sr- and Os- isotope ratios to more unradiogenic values

(Allègre *et al*., 2010; Palmer & Edmond, 1989 for Sr; Peucker-Ehrenbrink & Ravizza, 2000 for Os). Thus, strontium and osmium isotopes are strongly dependent on the lithology that has been weathered, while such is not the case with lithium isotopes. For modelling and further discussion, Li-isotope data solely from Resolution Guyot will be used, which we expect to provide the most pristine record. In figure 4, a comparison of the isotopic trends of Li, Os, Ca and Sr through the OAE 1a interval is presented. Ca isotopes, measured on Resolution Guyot, show a negative excursion of about 0.1–0.2‰ spanning the whole event and reaching a minimum at the end of the C8 interval, which has been interpreted as the response to a 3-fold increase in continental weathering rates in relation to the OAE (Blättler *et al*., 2011). Sr isotopes, also measured in Resolution Guyot (Jenkyns *et al.*, 1995), display a gradual shift to more unradiogenic values before they start to recover in the beginning of the C9 interval. According to Jones & Jenkyns (2001), this negative excursion in strontium isotopes can be interpreted as the result of increased ocean-ridge hydrothermal activity. Os isotopes, studied by Bottini *et al*. (2012) and Tejada *et al*. (2009) in the Cismon core and Gorgo a Cerbara section, respectively, show a drop to more unradiogenic values just before the onset of OAE 1a, interrupted by a short radiogenic 'spike' right at the beginning of the event. Osmium-isotope values start to increase in the middle of the C5 interval. Unfortunately, no data for osmium isotopes for the upper part of the event are available. Both research groups interpreted the osmium-isotope data as being the response of enhanced oceanic hydrothermal activity relative to weathering rates of continental crust, interrupted by a pulse of increased continental weathering rates at the onset of OAE 1a.

6.3 Dynamic modelling of the isotope excursions

By applying a dynamic (non-steady state) box model to Li isotopes and taking the

boundary conditions from the other proxies, an attempt is made herewith to disentangle the effects of the different processes and especially to assess the role of silicate weathering in sequestering atmospheric CO_2 as one of the processes driving the system to recover from the OAE. The dynamic box model was established by using the formulae described above, taking into account input and output fluxes and seawater concentration. For the duration of the strontium-isotope excursion, the age assignments used follow Bralower *et al*. (1997), who reported minimum values after 6 Myr and fully recovered values after 11 Myr. According to Jones & Jenkyns (2001), the strontium-isotope curve reached its minimum after 8 Myr and recovered fully after about 14.5 Myr. Both estimates of the duration are comparable and result in rather small differences in the durations of the fluxes, since both estimates are far longer than the residence time of lithium in the oceans. For the duration of the single intervals related to OAE 1a, the time scale of Malinverno *et al*. (2010) has been used.

Strontium isotopes are highly sensitive to hydrothermal activity, and thus are used in order to constrain the hydrothermal input. The isotopic data suggest an increase of at least ~17% in hydrothermal activity for 6 Myr, after which the Sr-isotope curve reached its minimum (end of C8 interval). This estimate is in agreement with the conclusions of Jones & Jenkyns (2001), who suggested an increased hydrothermal flux of 7–35% during the Aptian. Such an increase in hydrothermal activity would cause a negative shift in lithium isotopes of about 0.8‰ (Fig. 5a), which is much less than the first negative swing of about 4.5–11‰. Consequently, other mechanisms, such as congruent silicate weathering and/or enhanced weathering rates, likely helped to decrease lithium-isotope values. Assuming a constant weathering congruency (no change in riverine δ^7Li), and increased hydrothermal activity of 17%, the first negative shift in the lithium-isotope curve would need at least a 40x increase in silicate weathering rates for 200 ka, after which Li-isotope values would experience a minimum (Fig. 5b). With this duration of perturbed silicate weathering, seawater

δ^7Li could recover within 500 ka, which is the duration of the first Li-isotope excursion, following the age model of Malinverno *et al.* (2010). For this relatively short time of recovery, the residence time of lithium in the oceans during the Aptian is estimated to be about one-third of today's – about 300 kyr (similar to assumptions for OAE2 – Pogge von Strandmann *et al.*, 2013; compare Fig. 6b). However, the recovery phase of δ^7Li involves seawater values of about 41‰ (equivalent to values of ~37‰ in carbonates), which are not recorded in the sections. Li/Ca ratios, even though temperature- and salinity-dependent (Marriott *et al.*, 2004a, 2004b), show no obvious positive relationship with δ^7Li, which otherwise might indicate a large increase in continental weathering rates. Additionally, the respective trend of the other proxies would not be consistent with such a geochemical model: Sr and Os isotopes would show a radiogenic excursion to values of 0.709 for ^{87}Sr/^{86}Sr and 0.693 for ^{187}Os/^{186}Os, albeit highly dependent on the nature of the weathered material, whereas $\delta^{44/42}$Ca would decrease by about 0.9‰. We conclude, therefore, that a 40-fold increase in weathering rates of the continental crust is incompatible with the observed features.

A low riverine δ^7Li of 2‰, compared to a mean present-day value of 23‰, would reflect the average composition of continental crust driven by congruent weathering: this figure, together with increased hydrothermal activity of 17%, would cause a negative shift in the marine Li-isotope ratio of around 3‰, assuming constant weathering rates (Fig. 5c). The resulting shift in δ^7Li is less than what is observed in the studied sections and involves an unlikely scenario, where almost no formation of clay minerals occurs in global rivers, which normally cause a shift to heavier riverine Li isotope values relative to the bedrock composition. While similar riverine values have been reported from the modern Amazon (Dellinger et al., 2015), this is due to leaching of secondary clays, and therefore associated Li fluxes are very low, and are unlikely to have had significant influence on global seawater. Therefore, a

combination of increased hydrothermal activity, or at least some process involving basalt-seawater interaction, weathering rates, and more congruent weathering seems to have been a likely trigger for the negative shifts in lithium isotopes. In fact, the first negative shift of 4.5–11‰, as observed in the studied sections, can be produced by an increase in hydrothermal activity/basalt-seawater interaction of 17%, a 2.5-fold increase in riverine Li flux (driven by an enhanced silicate weathering rate) and a decrease in riverine δ^7Li to about 12‰, as illustrated in figure 5d (driven by more congruent silicate weathering), which might be triggered by a change in weathering regime (Dellinger et $al.$, 2015) due to higher pCO$_2$ values. These values therefore represent a minimum estimate of a change in weathering regime. The 2.5x increase in weathering rates has been chosen because this value is supported by Ca- and Sr-isotope systems.

However, modelling both observed negative δ^7Li excursions, with the second minimum in the C8 interval as being the result of another weathering pulse, which might have been hidden in the strontium-isotope record due to a predominant input by hydrothermal activity or by weathering of marine basalts, is incompatible with a single negative shift in calcium isotopes. Although Ca isotopes represent a very complex isotope system with many parameters influencing the isotopic ratio (Fantle & Tipper, 2014), Ca and Li isotopes seem to be coupled at least in modern glaciated river catchments in Iceland (Hindshaw et $al.$, 2013). This dissociation between the calcium- and lithium-isotope systems during the Aptian OAE 1a may be an artefact caused by different residence times. However, calcium isotopes suggest an increase in weathering rates for 6 Myr, after which the Ca- and the synchronous Sr-isotope record start to recover. Assuming a constant lithium flux recording constantly increased weathering rates, as suggested by Ca isotopes, implies that the weathering congruency would have to have varied. Allowing a lithium flux dissociated from its isotopic composition, as observed in several modern river catchments (e.g.

Dellinger *et al.*, 2015; Huh *et al.*, 1998; Millot *et al.*, 2010), and suggested for some case histories from the geological record (Li & West, 2014; Wanner *et al.*, 2014), makes it possible to model the observed features, whereas changing the residence times of Os, Sr and Ca do not change the main signal (Fig. 6). We predict, furthermore, that the Os-isotope record after OAE 1a, for which no data are currently available, will remain at low values until Sr-isotope values recover. This prediction is made on the basis of our dynamic box model and is in agreement with the low Sr-isotope values, caused by enhanced hydrothermal/magmatic activity and/or weathering of mafic rocks, both mechanisms that will introduce relatively low Os-isotopes values.

6.4 Causes of the observed excursions

In order to assess the trigger mechanism for a change in weathering congruency and the remarkably low values of the Os-isotope record throughout the event, which cannot be explained by hydrothermal activity alone, it might be helpful to constrain first the type of rock that has been weathered. The striking similarity between the strontium- and lithium-isotope curve argues for a common driver. Importantly, Allègre *et al.* (2010) suggested a major role for weathering of oceanic island arcs in contributing about 60% of the modern mantle-derived Sr-isotope flux to the oceans. Consequently, our estimated hydrothermal flux is most likely a combination of hydrothermal activity and weathering of mantle-derived rocks related to the formation of the Ontong Java-Manihiki-Hikurangi oceanic Plateau (Taylor, 2006). Therefore, the hydrothermal fluxes that have been estimated in previous works (e.g. Jones & Jenkyns, 2001 for the Aptian) most likely represent overestimates. The impact of weathering the continental crust is illustrated by the record of a single abrupt shift to more radiogenic values identified in the Os-isotope record at the beginning of OAE

1a (Bottini *et al.*, 2012; Tejada *et al.*, 2009). Hereafter, although Ca- and Li-isotopes indicate increased weathering rates and more congruent weathering, osmium- and strontium-isotope system record an overwhelming input of mantle-derived isotopes. The overall geochemistry could thus be explained by the alteration of the LIP and its mainly submarine, but partly subaerially erupted fresh and easily weatherable basaltic material (Thordarson, 2004), introducing unradiogenic strontium and osmium isotopes to the ocean and, contemporaneously light lithium isotopes. Weathering congruency might have changed in correspondence to the availability of fresh mafic material, while weathering rates remained consistently high. This process can also be contrasted to the likely Cretaceous background weathering regime that existed prior to OAE 1a: peneplained continents, thick soils and little chemical weathering due to a lack of freshly exposed silicate material. The recovery phases in δ^7Li between and after the negative spikes might be best explained by a changing weathering regime, as clays increasingly precipitate, responding to prolonged periods of riverine oversaturation (e.g. Pogge von Strandmann & Henderson, 2015). In our dynamic box model we used a partition coefficient for the Li sink, which is responsive to the seawater concentration, in order to illustrate this phenomenon.

Smaller variations in Li-isotope values during the event likely indicate variations in weathering rates and congruencies that might relate to changes in pCO$_2$, temperature and the hydrological cycle. For instance, with rising atmospheric pCO$_2$, temperature would have increased, as would dissolution of exposed lithological material, leading to a low riverine δ^7Li until secondary minerals could have formed and weathering became more incongruent, resulting in a higher riverine δ^7Li. During the Aptian OAE 1a, Heimhofer *et al*. (2004) suggested that atmospheric pCO$_2$ fluctuations were less than 10–15%, as interpreted from organic and inorganic carbon-isotope geochemistry and palynological analysis of climate-sensitive flora. However, much larger swings in atmospheric CO$_2$ are implied by carbon-isotope data

from pedogenic carbonates in China (Li *et al.*, 2014). Furthermore, Erba *et al.* (2010) suggested 5 major CO_2 pulses and one methane pulse on the basis of nannofossil assemblages and dwarfism at the onset of OAE 1a, possibly resulting in a doubling of atmospheric pCO_2 (Méhay *et al.*, 2010). Temperature reconstructions based on the organic geochemical proxy TEX_{86} show ranges from 30 to 36°C in tropical sea-surface waters (Dumitrescu *et al.*, 2006) and 26 to 29°C in the higher latitudinal Southern Ocean (Jenkyns *et al.*, 2012). Dumitrescu *et al.* (2006) identified 2 prominent cooling episodes of about 4°C, which could be related to the massive burial of organic carbon as well as weathering of silicate rocks. Alternatively, weathering and destabilisation of previously altered secondary minerals due to an accelerated hydrological cycle introducing light δ^7Li might have caused smaller variations in the Li-isotope record, as suggested by Wanner *et al.* (2014) to explain early Cenozoic δ^7Li.

While the general isotopic trend seems to be consistent in all four sections, with some minor differences that could be due to small gaps in the carbonate-platform sections or slight discrepancies in the age models, absolute δ^7Li values differ dramatically from one section to the other (Fig. 7). Significantly, there is a relatively consistent offset of several ‰ between the sections. The highest δ^7Li values are recorded in Resolution Guyot; the lowest are recorded in the Monte Raggeto section and in the Santa Maria 4 core. The Li-isotope curves of the two Tethyan carbonate platforms are shifted by about 4–6‰ to lower values with respect to data from Resolution Guyot. The values recorded in the Coppitella section are intermediate, being lighter than those from Resolution Guyot by about 2‰ for the first part of the curve (from C3 to the base of C7) before dropping to distinctly lower values in the C7 interval. Consequently, sections closest to the continent, namely the Santa Maria 4 core and the Monte Raggeto section, show lower absolute Li-isotope values. Nevertheless, there is no evidence for an adjacent river carrying lighter Li isotopes in

the suspended material from basaltic and/or continental terrain (Pogge von Strandmann *et al*., 2010). Local effects like upwelling/downwelling and/or submarine groundwater discharge, which have been proposed as influences on Ca isotopes (Holmden *et al*., 2012), might have affected the local Li-isotope record. However, modern oceans are considered to be isotopically homogenous with respect to lithium (Chan & Edmond, 1988; Stoffyn-Egli & MacKenzie, 1984). Although the residence time of Li in the oceans might have changed through time, as proposed by Pogge von Strandmann *et al*. (2013), there is no clear evidence of a Cretaceous Li residence time shorter than the ocean mixing time that could have led to isotopic differences in watermasses. Furthermore, data from Cretaceous pelagic sediments (nannofossil-foraminiferal chalks) from northern Europe and a platform-carbonate succession from the Tethys suggest a homogenous ocean with respect to Li isotopes during OAE 2 (Pogge von Strandmann *et al*., 2013), although that study also showed some small differences between sections. Therefore, local watermass properties seem an unlikely explanation for the differences in absolute values unless the sites in question were close to proximal sources of lithium. Based on studies of unaltered belemnite rostra, Ullmann *et al*. (2013) suggested a Late Jurassic (~155–148 Ma) Li isotope composition of skeletal calcite of about 27 $\pm$ 1‰, which corresponds closely to the absolute δ^7Li values from Resolution Guyot: a largely unaltered shallow-water section that has not undergone large-scale lithification. Therefore, it seems that at least the Li-isotope record of the other sections have been shifted due to diagenetic overprints and/or original differences in the relative abundance of aragonite *vs* calcite and/or vital effects (although the latter has not been observed in modern calcifying organisms, aside from some foraminifera species (Hathorne & James, 2006)). Another possibility would be an irregular oceanic circulation that might have caused an isotopically inhomogeneous ocean during OAE 1a. Possibly some partial restriction of the watermasses represented by the Tethyan sections might also have

influenced absolute values. However, these biases were manifestly not strong enough to eliminate the original marine signal, but rather acted to move the curves as a whole to more negative values.

6.5 Global-scale implications

A negative shift of marine Li-isotope ratio driven by congruent weathering has also been reported for the Cretaceous–Tertiary (K–T) boundary level (Misra & Froelich, 2012) and for OAE 2 (Pogge von Strandmann *et al.*, 2013). The magnitude of the δ^7Li negative excursion during the K–T boundary event is the same as the first negative excursion during OAE 1a (5‰) but the drop in lithium isotopes of the latter is estimated to occur in half the time (500 kyr for K–T boundary event; 200 kyr for the first negative excursion during OAE 1a). The OAE 2 lithium-isotope excursion lasted about the same length of time but is about 2–3x larger than the first OAE 1a excursion. OAE 1a is so far the only event showing a second decreasing trend in Li isotope values shortly after the event, suggesting decoupled behaviour of the lithium flux and isotopic composition.

By far the largest part of the Ontong Java-Manihiki-Hikurangi Plateau was emplaced approximately 120 Ma ago (Taylor, 2006). On the basis of indirect evidence, a first eruption phase attributed to the emplacement of the LIP, and identified on the basis of osmium-isotope ratios, started around 200 kyr before OAE 1a (Bottini *et al.*, 2012). Suggested consequential environmental changes would have been a rise in atmospheric pCO$_2$, causing increased weathering rates and a shift to more congruent weathering, recorded by calcium and lithium isotopes. However, the amount of fresh basalt was apparently still limited enough to allow the signature of continental crust weathering to be registered in the osmium-isotope curve as a radiogenic 'spike' just at the onset of OAE 1a. Progressively, with increased eruption of basalt, the osmium

and strontium isotopes record the overwhelming input of mafic rock weathering and hydrothermal activity. Calcium and lithium isotopes would not have been affected by this change in mineralogy. Additionally, the δ^7Li signature is the same in hydrothermally altered and pristine basalts (Verney-Carron *et al*., 2015). However, weathering apparently started to become more incongruent, probably in correspondence to an increase in clay-mineral formation, due to longer water-rock interaction times, and the development of relatively more and wider floodplains (Pogge von Strandmann & Henderson, 2015). Thus, an apparent recovery phase of the lithium-isotope curve can be observed in the C5–C6 interval, while calcium-isotope values remain low, indicating continuously high weathering rates. Enhanced hydrothermal input had less control on δ^7Li than on ^{87}Sr/^{86}Sr (Fig. 5a, Pogge von Strandmann *et al.*, 2013) and therefore did not conflict with the evidence of a recovery phase in the lithium-isotope record. Possibly, with an increase in eruption activity, fresh basaltic material was continuously brought to the surface of the plateau, changing weathering patterns again to more congruent weathering and causing the second drop in lithium isotopes (end of C8 interval). After about 6 Myr, weathering rates and hydrothermal activity apparently started to decrease, whereas clay-mineral formation started to increase, allowing all isotopic systems to recover. Mafic silicates, such as basalts, are more easily weathered than other silicate rocks, and act as a major atmospheric CO_2 sink (Amiotte Suchet & Probst, 1993; Dessert *et al*., 2003). Therefore, as with OAE 2, during OAE 1a weathering of continental crust and, more importantly, basaltic material, probably related to growth and decay of the largest oceanic LIP on Earth (Taylor, 2006), were potent mechanisms for the sequestration of atmospheric CO_2 together with burial of organic matter (Pogge von Strandmann *et al*., 2013).

7. Conclusions

In this study, three Aptian shallow-water carbonate and one basinal pelagic section have been studied for Li isotopes. In all 4 sections, a negative shift in Li isotopes can be observed starting prior to OAE 1a and a second negative excursion in δ^7Li after the event. Simple dynamic box modelling suggests that the first negative shift was probably caused by a coeval increase in basalt-seawater interaction, weathering rates and weathering congruency. A 2.5x increase in weathering rates and a shift to congruent weathering (riverine δ^7Li of about ~12‰, which equals a shift of about 11‰ towards lighter values from the present-day value) is proposed for the first negative excursion. However, dissociation of the lithium flux (weathering rates) and its isotopic composition (weathering congruency) is suggested with coeval constantly increased weathering rates. Moreover, it is suggested that weathering primarily affected mafic silicates derived from the Ontong Java-Manihiki-Hikurangi LIP, causing consequent drawdown of CO_2. The hydrothermal flux calculated in previous studies is most likely overestimated since the unradiogenic input of strontium and osmium into the oceans due to weathering of mafic material was not considered. This work adds new evidence of the importance of silicate weathering, as well as organic-matter burial, in sequestering atmospheric CO_2 during Oceanic Anoxic Events.

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Figure Captions

Figure 1 Location map of the four sections analysed for lithium isotopes (indicated by black dots): 1 – Resolution Guyot; 2 – Santa Maria 4 core; 3 – Coppitella; 4 – Monte Raggeto. The orange stars illustrate the position of the Cismon core (5) and the Gorgo a Cerbara section (6). Resolution Guyot is located in the Pacific Ocean; the other sections in the former central Tethyan domain. The sediments of the Monte Raggeto section constituted part of the Apennine Carbonate Platform; the carbonates of the Santa Maria 4 core were deposited in the Apulian Carbonate Platform and the deposits of the Coppitella section in the adjacent deep-water pelagic basin. Reconstruction based on the palaeocontinental maps of Smith *et al*. (1981).

Figure 2 Correlation of the sections analysed by carbon-isotope stratigraphy pinpointing the Early Aptian OAE 1a (grey band) as identified by previous studies. Carbon isotopes from the Santa Maria 4 core were measured in this study; the interval of OAE 1a was located by Amodio *et al*. (2013, 2003) and D'Argenio *et al*. (2011) on the basis of cyclo- and sequence stratigraphy. The carbon-isotope data from Monte Raggeto is taken from Di Lucia *et al*. (2012) and the stratigraphic position of the OAE 1a record follows Amodio *et al*. (2013, 2003), D'Argenio *et al.* (2011,

2004), Di Lucia *et al*. (2012) and Wissler *et al*. (2004), based on carbon-isotope, sequence, magneto- and cyclostratigraphic investigations. Carbon isotopes of the Coppitella section are taken from Luciani *et al*. (2001), who identified the record of OAE 1a by integrated bio- and carbon-isotope stratigraphy. The carbon-isotope curve from Resolution Guyot and the exact position of the record of OAE 1a is taken from Jenkyns (1995).

Figure 3 Carbon- and lithium-isotope stratigraphy of the sections studied. Carbon-isotope data are partially taken from previously published studies, as indicated in figure 2 and in the text. In all four sections, a negative shift in lithium-isotope values can be observed right before the onset of OAE 1a. A second negative shift is observable higher in the stratigraphy, albeit not clearly in every section. Both negative shifts are indicated by green arrows. The 2σ error bar gives the external reproducibility.

Figure 4 Correlation of Li isotopes with other proxies for increased (continental) weathering: Li isotopes (green points; this study), Sr isotopes (blue triangles; Jenkyns *et al.*, 1995) and Ca isotopes (red squares; Blättler *et al*., 2011) from Resolution Guyot compared with the Os-isotope record from the Cismon core (violet diamonds; Bottini *et al*., 2012). Li-, Sr- and Ca-isotope values start to decrease at about the same interval before the beginning of OAE 1a. Ca and Li isotopes reach a minimum right at the onset of the event with a coeval spike to more radiogenic values in Os isotopes, reflecting transiently enhanced continental weathering. Grey bar indicates the record of OAE 1a.

Figure 5 Dynamic box model results for the first negative lithium-isotope excursion. The age model for OAE 1a is based on Malinverno *et al.* (2010) and the duration of the strontium-isotope curve is based on Bralower *et al.* (1997). a – A 1.17x increase in hydrothermal activity as suggested by strontium isotopes (see discussion) is not enough to create a 4.5–11‰ shift in lithium isotopes. b – In order to create a 4.5–11‰ shift in δ^7Li with a combined increase of hydrothermal activity (1.17x) and constant weathering congruency, weathering rates would have to increase by a factor of 40 (solid line), which seems unrealistic. For comparison, an increase in weathering rates of 3x (dashed line) and 10x (dotted line), both together with a 1.17x increase in hydrothermal activity is illustrated. c – An increase in hydrothermal activity (1.17x) and constant weathering rates coupled with more congruent weathering, corresponding to riverine δ^7Li of 2‰ (solid line; dotted line: 5‰; dashed line: 10‰), would be responsible for a 3‰ negative shift in lithium isotopes. d – A coupled increase in hydrothermal activity (1.17x) together with enhanced weathering rates (2.5x) and congruent weathering (riverine δ^7Li ~10‰) can account for the observed shift in lithium isotopes.

Figure 6 Dynamic box model results for both negative lithium-isotope excursions. Increased hydrothermal activity of 1.17x and enhanced weathering rates by 2.5x for 6 Myr. The solid lines mark the responses of the different isotope systems utilizing the modern residence times, whereas the dotted lines represent a 0.3x modern residence time and the dashed lines a 3x modern residence time. a – Osmium isotopes show low values as reported by Tejada *et al.* (2009) and Bottini *et al.* (2012), assuming weathering of mafic unradiogenic material during OAE 1a. There are no data for the time period after the event. However, we predict that Os-isotope values stay low until the Sr-isotope record has recovered. b – Lithium isotopes show

the observed trend with decoupled weathering congruency and weathering rates. The observed pattern can be produced by an increase in weathering congruency for 200 kyr with δ^7Li values of 12‰. Subsequently, weathering became more incongruent with δ^7Li values of 18‰, which are still lower than the pre-event values. After about 4.62 Myr weathering congruency increases again with δ^7Li values of about 10‰. c – Strontium isotopes show the observed trend with riverine values down to 0.7084 reflecting enhanced weathering rates of mafic unradiogenic material. d – $\delta^{44/40}$Ca trend modelled with a lower riverine $\delta^{44/40}$Ca of 0.3‰. The modelled trend is in agreement with the calcium-isotope data reported by Blättler *et al*. (2011) as $\delta^{44/42}$Ca.

Figure 7 Li-isotope curves plotted against time (time model after Malinverno *et al*., 2010). At the onset of OAE 1a, a negative shift in lithium isotope values can be observed. Note the differences in absolute values between the sections. See discussion for explanation.