Increasing global ocean oxygenation and the Ordovician Radiation: Insights from Th/U of carbonates from the Ordovician of western Utah

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Abstract

The Cambrian and Ordovician radiations were the most important biodiversification events in the history of animal life, yet they were separated by intervals of recurrent anoxic sedimentation and regional bioturbation extinction events in the Late Cambrian and Early Ordovician. Recent work linked bioturbation extinction events to positive carbon isotopic excursions interpreted to represent enhanced organic matter burial under anoxic conditions. This led to the hypothesis that an increase in oceanic oxygenation following the last of the bioturbation extinctions paved the way for the rapid diversification of the Ordovician Radiation. Here we test the hypothesis of increasing ocean oxygenation using Th/U preserved in carbonate rocks from the Lower-Middle Ordovician succession near Ibex, Utah, USA. The global seawater uranium inventory is expected to vary inversely with the amount of deep-water anoxic deposition due to uranium sequestration in black shales. Therefore in shallow water carbonates higher Th/U ratios may reflect increased global ocean anoxia. Our data show that the highest Th/U values are coincident with the heaviest carbon isotopic values reported from the base of this succession, which is latest Tremadocian in age. Th/U then decreases and remains low through the Floian up through the contact with the Kanosh Formation, a shale-dominated unit with interspersed limestone units. The geochemistry of the carbonates within the Kanosh Formation likely represents local rather than global conditions in the marine environment. We interpret the overall decrease in Th/U ratios throughout the Tremadocian to Floian interval to represent an increase in global seawater uranium concentration. These data are consistent with the hypothesis that an increase in ocean oxygenation occurred prior to the major pulses of diversification associated with the Ordovician Radiation.

1. Introduction

The start of the Phanerozoic was characterized by two major biodiversification events. Although the fossil records of most animal phyla were established by the end of the Cambrian Radiation, it was during the Ordovician that radiation at the family, genus, and species levels

led to the levels of diversity characteristic of the remainder of the Paleozoic (e.g., Droser and Finnegan, 2003; Harper, 2006; Servais et al., 2009). In particular, this event ushered in the change in dominance from the Cambrian Evolutionary Fauna to the Paleozoic Evolutionary Fauna, which dominated marine paleocommunities until the End Permian mass extinction (e.g., Droser and Finnegan, 2003; Harper, 2006; Servais et al., 2009).

Despite the importance of these two biotic events, the geochemistry of early Paleozoic oceanic environments is not fully understood. An increasing number of studies suggest that the early Paleozoic may have been a time of recurrent and widespread anoxia in the oceans (Zhuravlev and Wood, 1996; Hough et al., 2006; Hurtgen et al., 2009; Gill et al., 2011; Thompson and Kah, 2012; Saltzman et al., 2015; Kah et al., 2016; Kidder and Tomescu, 2016). Episodic anoxic events in the oceans may have contributed to multiple regional extinction events during the interval of time between the two radiations. Saltzman et al. (2015) tied bioturbation events to positive carbon isotopic excursions interpreted to have resulted from increased organic matter burial under anoxic conditions. According to this hypothesis, major pulses of diversification associated with the Ordovician Radiation did not begin until after a prolonged period without positive isotopic excursions during the Floian stage of the Ordovician, interpreted to reflect increasing oxygenation of the deep ocean (Saltzman et al., 2015). Here, we present an independent test of the Saltzman et al. (2015) hypothesis using Th/U preserved in shallow water carbonate rocks of the Ordovician succession near Ibex, Utah. Our Th/U results suggest that the Floian was indeed a time of increasing deep ocean oxygenation.

2. Th/U in carbonates as an indicator of global redox conditions

Th/U in siliciclastic rocks has been used with great success as an indicator of local redox conditions (e.g., Wignall and Myers, 1988; Jones and Manning, 1994; Wignall and Twitchett, 1996; Dypvik and Harris, 2001; Bond et al., 2004). Thorium has one redox state (Th^{4+}) and is quickly removed from the water column via adsorption on detrital material, in particular clay minerals, iron, aluminum, and manganese oxides, and organic matter (e.g., Adams and Weaver, 1958; Kelepertsis, 1981; Roy-Barman et al., 2009; Kritsanuwanat et al., 2015). In contrast, uranium has two redox states: highly soluble U^{6+} , which forms uranyl carbonate complexes, and insoluble U^{4+} , which forms uranous fluoride complexes that are commonly associated with organic-rich sediments (Adams and Weaver, 1958; Wignall and Twitchett, 1996; Brennecke et al., 2011; Romaniello et al., 2013; Andersen et al., 2014). As such, sediments deposited under reducing conditions tend to be enriched in uranium without a concomitant increase in the flux of thorium, leading to decreased Th/U ratios (e.g., Wignall and Myers, 1988; Wignall and Twitchett, 1996).

Brennecka et al. (2011) used Th/U in carbonate rocks as an indicator of global redox. They argued that the incorporation of uranium into marine carbonate sediments is a function of the availability of uranium in seawater (Brennecka et al., 2011). During times of increased anoxic deposition, the uranium concentration in seawater decreases as uranium is sequestered in organic-rich black shales. Thus, sediments deposited in oxygenated shallow-water carbonate environments should show an increase in Th/U as the amount of anoxic sedimentation in the oceans increases (Brennecka et al., 2011). Indeed, Brennecka et al. (2011) reported such an increase across the End Permian mass extinction, which they interpreted to represent enhanced anoxic deposition following the mass extinction. Because the $\delta^{13}\text{C}$ of seawater is also tied to the burial of organic matter, Th/U should generally track $\delta^{13}\text{C}$ such that an increase in anoxic sedimentation would lead to increases in both Th/U and $\delta^{13}\text{C}$ in carbonate rocks. This was not the case with the End Permian mass extinction, however, which is characterized by a negative carbon isotopic anomaly, most likely due to an influx of light carbon to the oceans (e.g., Knoll et al., 1996; Payne and Kump, 2007; Retallack and Jahren, 2008).

The processes by which uranium becomes incorporated into carbonate minerals are not yet fully understood (e.g., Shen and Dunbar, 1995; Kelly et al., 2003; Romaniello et al., 2013). However, the rationale for the use of Th/U in carbonates as a global redox indicator is supported by studies of recent biogenic carbonates in the Bahamas that show abundances and isotopic compositions of uranium and thorium that reflect those of seawater (Robinson et al., 2004; Romaniello et al., 2013). Romaniello et al. (2013) demonstrated that bulk carbonate sediments show enrichment in uranium concentration and isotopic composition relative to that of biogenic phases. They suggested that this enrichment is due to authigenic deposition of uranium when it diffuses into the sediment and becomes insoluble in reducing pore waters (Romaniello et al., 2013). This is of particular concern in shallow water, seagrass-rich carbonate sediments such as those found in the Bahamas today, which can have high sediment organic matter content (Romaniello et al., 2013). Studies of ancient carbonate rocks indicate that up to 20% of the uranium in a rock may come from the insoluble fraction (Adams and Weaver, 1958). Because of the high solubility of uranium under oxidizing conditions, it is unlikely that such enrichments would be due to uranium associated with detrital materials as they enter a basin, but rather are better explained by authigenic enrichment onto clay minerals and organic matter in reducing pore waters.

Because thorium reflects detrital input, abundances of thorium can be used to control for sedimentation rate when interpreting abundances of uranium in ancient carbonate rocks. This is particularly true in isolated platform environments like the Bahamas where the only terrigenous input is wind-blown dust. Under such scenarios, the concentration of thorium should either be considerably less or of a similar magnitude to that of uranium (e.g., Robinson et al., 2004), and changes in Th/U should reflect changes in the concentration of dissolved

uranium in seawater (e.g., Brennecke et al., 2011). However, in mixed carbonate-siliciclastic depositional settings, increased detrital input may lead to concentrations of thorium that greatly exceed that of uranium. In such scenarios, very high Th/U most likely reflects proximity to the source of terrigenous material (Baranov, 1956).

The elemental abundance data reported here are from a mixed carbonate-siliciclastic succession representing over 11 million years of nearly continuous deposition from the late Tremadocian into the early Darriwilian (Edwards and Saltzman, 2014). Previous studies of Th/U in siliciclastic rocks have typically relied on field-portable gamma ray spectrometers, which measure gamma rays resulting from the decay of Th and U in all mineral phases (e.g., Wignall and Myers, 1988; Wignall and Twitchett, 1996; Bond et al., 2004). Our approach was to target shallow-marine carbonate rocks, identify and microsample the best-preserved matrix material in thin section, and measure elemental abundances using solution ICP-MS. This allowed us to better constrain the potential sources of thorium and uranium and to characterize the diagenetic history of the samples.

3. Geologic background

3.1. Depositional setting

Samples were collected from the Pogonip Group near Ibex, Utah (Fig. 1), from the C, G, H, J, K, and Camp sections of Hintze (1951) (see Supplementary Fig. 1 for detailed locality information). The studied material includes samples from the uppermost part of the House Limestone, the Fillmore Formation, the Wah Wah Limestone, the Juab Limestone, the Kanosh Formation, and the Lehman Formation (Fig. 2a). The biostratigraphy of the Ordovician succession at Ibex was thoroughly discussed in Edwards and Saltzman (2014) and references therein.

The Ordovician succession at Ibex was deposited on a mixed carbonate-siliciclastic ramp near the equator (e.g., Ross et al., 1989; Edwards and Saltzman, 2014). The lower third of the studied succession is comprised of the lower half of the Fillmore Formation, which includes approximately 300 meters of recurring intraformational conglomerate limestones separated by silty limestone and poorly exposed siltstone (Fig. 2a). The abundance of intraformational conglomerate suggests a prolonged period of relative sea level stasis during which the basin was periodically influenced by storm deposition (Dattilo, 1993). The lower 120 meters of the Fillmore Formation contain multiple units with microbialite mounds consisting of various stromatolite and thrombolite morphologies (Fig. 2a) (Hintze and Davis, 2003; Miller et al., 2012).

The middle part of the succession (the upper Fillmore Formation, Wah Wah Limestone, and Juab Limestone) is characterized by fossiliferous, ledge-forming limestones separated by

139 poorly-exposed silty limestones. Another major mound-bearing interval begins at
140 approximately 450 meters (Fig. 2a). Microbialite features are much more difficult to distinguish
141 in the muddy matrix of these mounds, which are characterized by having abundant sponges
142 and receptaculitids.

143 The upper part of the studied succession consists of the shale-dominated Kanosh
144 Formation and the higher-energy, sandy carbonates and dolostones of the Lehman Formation.
145 The Kanosh Formation is mostly poorly-exposed shale with abundant, thin, and fossiliferous
146 limestone beds (e.g., Wilson et al., 1992; Marenco et al., 2013), many of which exhibit extensive
147 secondary phosphatization (Supplementary Figs. 2, 3). The paleoenvironmental interpretation
148 of the Kanosh Formation has been the subject of some debate. Based partly on observations
149 from more distal equivalents of the Kanosh Formation, Ross et al. (1989) interpreted the
150 Kanosh Formation to represent a poorly-oxygenated “black shale facies”. However, Wilson et al.
151 (1992) argued that in the Ibex area, the Kanosh Formation was deposited under well-
152 oxygenated, normal marine conditions based on the occurrence of echinoderm and bryozoan
153 holdfasts attached to hardgrounds throughout the formation. Marenco et al. (2013) argued
154 that low organic carbon and sulfide abundances in the carbonates of the Kanosh Formation
155 near Ibex support the interpretation of Wilson et al. (1992). The Lehman Formation is overlain
156 by the Eureka Quartzite, which represents a major break in carbonate deposition in this area.

157 *3.2. Carbon isotope stratigraphy*

158 A high-resolution $\delta^{13}\text{C}$ profile for the Ordovician of the Ibex area was generated by
159 Edwards and Saltzman (2014) and is reproduced here in Figure 2b. The heaviest isotopic values
160 (between 0 and +2‰) occur near the base of the studied succession, which includes the last of
161 the Early Ordovician biotic extinction events (Saltzman et al., 2015). The majority of the
162 succession is characterized by $\delta^{13}\text{C}$ values between -2 and 0‰. The isotopic profile from the
163 top of the Juab Limestone through the base of the Lehman Formation is considerably depleted
164 in the Ibex area (values are between -2 and -4‰) compared to correlative strata of the Shingle
165 Pass area (Nevada), Argentina, and Newfoundland (Buggisch et al., 2003; Thompson and Kah,
166 2012; Edwards and Saltzman, 2014). Edwards and Saltzman (2014) interpreted this interval of
167 low $\delta^{13}\text{C}$ to be anomalous, possibly due to basin restriction during the deposition of the Kanosh
168 Formation. In this work we will refer to this interval of depleted $\delta^{13}\text{C}$ as the Kanosh Carbon
169 Isotopic Anomaly and will treat geochemical data from that interval separately from the rest of
170 the succession.

4. Materials and methods

4.1. Sample selection

All samples were cleared of visible secondary phases using a water-cooled rock saw. Samples then underwent petrographic analysis for the identification of the least-altered carbonate matrix. All samples exhibited some degree of recrystallization, with most matrix material consisting of microspar after micrite. Thin section billets were then micro-drilled under a binocular microscope using a Carpenter Systems Microsampler.

4.2. Elemental analysis

Approximately 1 mg of microsampled powder was dissolved in 1 ml of 0.32 M trace metal grade nitric acid. Within a period of about one hour, samples were centrifuged to pelletize insoluble material. An aliquot of 0.5 ml was then diluted to 10 ml with 0.32 M trace metal grade nitric acid for analysis in an Agilent 7500 series quadrupole ICP-MS. Our dissolution method was designed to minimize leaching of the non-carbonate fraction. A set of bulk powders was dissolved using our nitric acid method and the method of Brennecke et al. (2011), using an initial dissolution in 1 M hydrochloric acid followed by reconstitution in 3 M nitric acid. Results from these two methods were very similar, but when different, our method resulted in lower Th/U values, suggesting that the nitric acid method might result in less leaching of the non-carbonate fraction (Supplementary Fig. 4). ICP-MS runs were calibrated with Agilent standards and were corrected offline for drift and procedural blanks.

Starting sample and insoluble masses were measured using a microbalance with 1 microgram precision in order to determine elemental abundances in the starting sample (reported as ppm or ppb in Supplementary Tables 1 and 2). However, because of the uncertainty with the tiny mass measurements for insolubles, we report and interpret all elemental abundance data as ratios relative to measured calcium and magnesium ($X/(Ca+Mg)$), which normalizes elemental data to the amount of carbonate sample dissolved. Because these normalized ratios result in very small numbers, we multiply the ratios by some multiple of ten: 10^6 for Th, U, and Cd; 10^5 for Ba; 10^3 for (Na+Al), Mn, and Sr; 100 for Fe. These multipliers are implied when we refer to normalized abundances below.

Replicate microsamples were analyzed in order to quantify procedural uncertainty. Relative standard deviations of these replicates averaged 25% for normalized Th, 16% for normalized U, 22% for Th/U, 16% for normalized (Na+Al), 10% for normalized Fe, 12% for normalized Ba, 35% for normalized Cd, 4% for normalized Mn, 1% for normalized Sr, and 4% for Sr/Mn.

4.3. $\delta^{34}S_{CAS}$, total sulfur, total organic carbon

Sulfur isotopic compositions of carbonate-associated sulfate (CAS) were determined for samples from the Juab Limestone and Lehman Formation according to the methods reported in Marenco et al. (2013). Total sulfur and total organic carbon abundances were determined for samples from the House Formation, Fillmore Formation, Wah Wah Limestone, Juab Limestone, and Lehman Formation according to the methods reported in Marenco et al. (2013). Recent work has demonstrated large within-sample variability in $\delta^{34}S$ of CAS (Present et al., 2015). For this reason, we only interpret trends in averages instead of sample to sample variability.

5. Results

Because of the variety of carbonate lithologies sampled, the elemental results exhibit significant fluctuations. We will only interpret trends in the five-point moving averages for normalized elemental abundances in order to investigate long-term environmental changes. Results that were considerably higher or lower than both immediately adjacent samples were excluded from the moving averages and Figure 2, but are reported in Supplementary Tables 1 and 2. Two normalized U results, one normalized Ba result, one normalized Cd result, and four normalized Fe results were excluded in this fashion (Tables 1 and 2).

Not counting the Kanosh Carbon Isotopic Anomaly, the highest Th/U values occur at the bottom of the succession, with average values between 2 and 4 (Fig. 2C). Starting at approximately 130 m, Th/U averages between 1 and 2 until it starts to increase near the base of the Kanosh Carbon Isotopic Anomaly (Fig. 2C). Th/U returns to values between 1 and 2 at approximately 790 m. Normalized Th concentrations average between 0 and 4 for the first one hundred meters of section but then exhibit average values between 0 and 2 until they start to increase near the base of the Kanosh Carbon Isotopic Anomaly (Fig. 2C). Normalized U concentrations average between 0.5 and 1 until approximately 430 m, where they increase to values between 1 and 1.5 (Fig. 2D).

The increase in Th/U associated with the Kanosh Carbon Isotopic Anomaly is coincident with an increase in normalized Th to average values between 2 and 7 (Fig. 2C). Although normalized uranium values remain higher during the lower part of the Kanosh Carbon Isotopic Anomaly, the five-point moving average is lowered by an interval of sustained low normalized U values ranging from 0.5 to 1 between 725 m and 789 m, which we will refer to as the Kanosh Uranium Anomaly (Fig. 2D).

Normalized concentrations of sodium and aluminum are assumed to reflect the leaching of elements from aluminosilicates during the sample dissolution process. Normalized (Na+Al) averages between 0 and 3 for most of the first 340 meters after which it increases to average values between 3 and 4 (Fig. 2E). Normalized (Na+Al) increases to values exceeding 5 near the

base of the Kanosh Carbon Isotopic Anomaly (Fig. 2E). Supplementary Figure 5 displays crossplots between normalized (Na+Al) and Sr, Mn, Cd, Ba, U, and Th. There is much variability in the crossplots, but Ba and Th show much stronger positive covariance with (Na+Al) than do Sr, Mn, Cd, and U.

For most of the succession, normalized barium averages remain below 0.5 (Fig. 2F). Normalized barium averages increase to values above 0.5 near the base of the Kanosh Carbon Isotopic Anomaly, and then again to values approaching 1 near the start of the Kanosh Uranium Anomaly (Fig. 2F). Similarly, normalized cadmium averages are below 0.5 for most of the succession but increase to values higher than 0.5 near the base of the Kanosh Carbon Isotopic Anomaly (Fig. 2G). The cadmium lower detection limit for our analysis is 20 ppb in the starting rock sample. The average cadmium concentration in the entire succession is 73 ppb. The samples that make up the normalized cadmium increase within the Kanosh Carbon Isotopic Anomaly contain an average of 365 ppb cadmium, which is well above the average for the succession.

Normalized iron averages remain between 1 and 2 until the base of the Kanosh Carbon Isotopic Anomaly, where they increase to values between 2 and 3 (Fig. 2H). Normalized Mn averages are below 1 for most of the succession but show a well-constrained increase to values exceeding 7 beginning near the base of the Kanosh Carbon Isotopic Anomaly (Fig. 2I). Sr/Mn values average above 1 for the first 450 meters, but then decrease to values between 0.5 and 1 until the base of the Kanosh Carbon Isotopic Anomaly, where they drop below 0.5 (Fig. 2J). Normalized strontium values remain remarkably constant throughout the succession but exhibit a slight increase during the Kanosh Carbon Isotopic Anomaly (Fig. 2J).

Figure 2K presents new $\delta^{34}\text{S}_{\text{CAS}}$ data from the Juab Limestone and Lehman Formations plotted with the data reported in Marenco et al. (2013) from the Ibex area and data from Newfoundland (Thompson and Kah, 2012). The three-point moving average lines through the Ibex and Newfoundland data show considerable overlap except near the Kanosh Uranium Anomaly, where the Ibex $\delta^{34}\text{S}_{\text{CAS}}$ data exhibits significant depletion compared to the Newfoundland data (Fig. 2K). Throughout the succession, total organic carbon content largely remains well below 1 weight percent and total sulfur remains below 0.04 weight percent (Supplementary Table 3).

6. Discussion

6.1. Increasing seawater uranium availability

Throughout most of the succession, lower Th/U seems to reflect an overall increase in normalized uranium concentrations of about 50 to 100% relative to the base of the succession.

There are a number of reasons why we believe this represents an increase in the availability of uranium in seawater.

First, organic carbon abundances are uniformly low. If organic carbon were to positively correlate with uranium, a likely explanation would be that localized water or sediment column redox fluctuations led to increased uranium accumulation (Romaniello et al., 2013). It is probable that some organic matter has been removed via burial processes, but this should more strongly affect the lower part of the succession, which has been more deeply buried. Rather, this is the part of the succession with the lowest normalized uranium. Similarly, Ba and Cd are commonly associated with high organic matter accumulation (e.g., Bishop, 1988; Janssen et al., 2014), yet these elements show no correlation with increased uranium content in this succession.

Second, increases in normalized uranium are independent of increases in normalized (Na+Al). It is possible that the increase in uranium could be explained by increased input of uranium-bearing terrigenous material. However, the major increase in uranium at about 430 meters occurs without any change in (Na+Al). Similarly, the major increase in (Na+Al) at the start of the Kanosh Carbon Isotopic Anomaly occurs without any change in normalized uranium. Thorium, on the other hand, shows a much stronger correlation with (Na+Al). Indeed, normalized thorium values increase dramatically with (Na+Al) at the start of the Kanosh Carbon Isotopic Anomaly. Furthermore, normalized uranium is low during the Kanosh Uranium Anomaly when indicators of terrigenous input are high (see *The anomalous Kanosh Formation: local overprint on global signals* below).

Third, the increase in normalized uranium occurs across multiple repeated facies. If increased uranium were controlled by a facies-specific factor, such as sea level, sediment composition, or substrate consistency, then one would expect normalized uranium to exhibit an oscillating pattern, with high and low values tied to specific facies. Rather, our results indicate an increase that continues across multiple facies. Much of the sample to sample variation is likely caused by facies changes, but the overall increase in average values is most likely not facies-controlled.

6.2. The anomalous Kanosh Formation: local overprint on global signals

The Kanosh Carbon Isotopic Anomaly is strongly coincident with an influx of terrigenous material, as indicated by increases in Th, (Na+Al), Ba, Fe, and Mn. Of these, elevated manganese shows the best correlation with the entire Kanosh Carbon Isotopic Anomaly. Low Sr/Mn values can be used to assess the degree of diagenesis in carbonate rocks (e.g., Montanez et al., 1996), but diagenetic alteration should lead to an increase in manganese and a loss of strontium, if Sr/Mn reflects diagenesis of carbonate mineralogy. Rather, results from the Kanosh Carbon Isotopic Anomaly show a slight increase in strontium associated with a much

larger increase in manganese. It is more likely that the increase in manganese abundance represents an influx of terrigenous Mn-bearing minerals that were leached during the sample dissolution process.

Elevated barium and cadmium concentrations are commonly associated with nutrient-rich, high-productivity regions in the modern ocean (e.g., Bishop, 1988; Lea and Spero, 1994; Janssen et al., 2014). In the Kanosh Carbon Isotopic Anomaly, barium is correlated with (Na+Al), which suggests that much of this barium is associated with terrigenous material. However, the correlation between cadmium and (Na+Al) is much weaker, indicating that the elevated cadmium may reflect increased nutrient levels in the basin. We propose that the Kanosh Carbon Isotopic Anomaly represents a switch to a highly productive basin, likely fed by nutrients from terrigenous runoff. The highly phosphatized nature of the Kanosh Formation carbonates supports this interpretation, given the strong association between phosphate and cadmium in highly productive regions of the modern ocean (e.g., Martin et al., 1976; Boyle, 1986; van Green and Husby, 1996; Janssen et al., 2014). An alternative hypothesis is that prolonged oxic to suboxic conditions in the basin resulted in higher P retention in sediments (Algeo and Ingall, 2007). Studies of modern environments have shown that when bottom waters are anoxic, decomposition of organic matter within the sediment column ultimately leads to the release of P to the overlying water column (e.g., Ingall et al., 2005; Algeo and Ingall, 2007). In oxic bottom waters, however, the diffusion of oxygen into the sediments ultimately allows for authigenesis of phosphorous-bearing minerals within the sediments, thus leading to increased phosphorous retention (e.g., Froelich et al., 1988; Algeo and Ingall, 2007). It is likely that increased nutrient input and organic matter production worked in tandem with increased bottom-water oxygenation and sediment phosphorous retention, resulting in the phosphatization seen in the Kanosh Formation.

An influx of terrigenous material could also have been associated with ^{13}C -depleted soil-derived carbon. If this were the case, then carbonate sediments should record a proximal to distal gradient in $\delta^{13}\text{C}$, which reflects the mixing of oceanic and terrigenous carbon. Such a gradient is suggested by the relative depletion in $\delta^{13}\text{C}$ from the Ibex area compared to that of the more distal Shingle Pass section during the Kanosh Carbon Isotopic Anomaly (Edwards and Saltzman, 2014). Similarly, increased continental runoff could have been associated with ^{34}S -depleted sulfate from the weathering of soils and shales. Such an influx of light sulfur could account for the depleted $\delta^{34}\text{S}_{\text{CAS}}$ values from the Ibex area during the Kanosh Carbon Isotopic and Uranium Anomalies relative to those from Newfoundland.

Increased organic matter production may have overwhelmed oxygen in the more distal parts of the basin. Although the rocks of the Kanosh Formation in the Ibex area were likely deposited under oxygenated conditions (Wilson et al., 1992; Marengo et al., 2013), black shales

have been reported from more distal equivalents of the Kanosh Formation (Ross et al., 1989). It is possible that black shale sedimentation in more distal parts of the basin drew down uranium concentrations, leading to increased uranium content in the black shale sediments but decreased abundances in more proximal rocks. When combined, the $\delta^{13}\text{C}$, $\delta^{34}\text{S}_{\text{CAS}}$, and normalized uranium data suggest local overprints on global signals.

6.3. Increasing oceanic oxygen and the Ordovician Radiation

To our knowledge, this study represents the first attempt to utilize Th/U in carbonates from a mixed carbonate-siliciclastic succession using solution ICP-MS. Similar studies of correlative successions, such as those in Newfoundland and Argentina, would shed light on whether or not our results reflect global changes in seawater uranium concentrations.

If our interpretations are correct, then the decrease in Th/U from the Tremadocian through the Floian likely reflects a decrease in the amount of anoxic deposition in the Ordovician oceans, as suggested by the global $\delta^{13}\text{C}$ data (Saltzman et al., 2015). Oxygen isotopic compositions of tropical conodont phosphate suggest that the Early Ordovician was characterized by a cooling trend in seawater temperatures to modern day tropical temperatures by the Darriwilian, when the major pulses of diversification of the Ordovician Radiation took place (Fig. 3; Trotter et al., 2008). Such a cooling trend should have resulted in increased solubility of oxygen in seawater, and may also have strengthened ocean ventilation by overturning with an increased equator-to-pole thermal gradient. Rather than acting directly to catalyze biodiversity pulses, increasing oxygen may have contributed to the Ordovician Radiation by ending bioturbation events, which tended to suppress diversification between the Cambrian and Ordovician Radiations (Saltzman et al., 2015). It should also be noted that the biggest increase in uranium abundance in this succession is coincident with a local increase in the role of metazoans in reef-building. It is unclear at this point if this ecological shift is truly related to increasing oxygen because such a transition occurred earlier in other parts of the world (e.g., Adachi et al., 2013; Choh et al., 2013). Although many factors contributed to the Ordovician Radiation (Servais et al., 2009), it is likely that increasing oxygenation of the oceans or the cessation of major anoxic or euxinic episodes played an important role. The majority of the diversification associated with the Ordovician Radiation occurred later in the Darriwilian (above the studied succession), but diversity began to increase within some groups (e.g., brachiopods, trilobites, and echinoderms) during the Floian (Fig. 3) after oxygen began to increase on a global scale.

7. Conclusions

Th/U analysis of carbonate rocks from the Lower-Middle Ordovician succession near Ibex, Utah suggests a global increase in oceanic oxygen which began shortly after the last

biomere extinction event during the late Tremadocian. The Kanosh Carbon Isotopic Anomaly represents localized effects superimposed on this global oxygen increase. The increase in oxygen likely prevented further biomere extinction events that could have hindered the Ordovician Radiation.

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References

- Adachi, N., Liu, J., Ezaki, Y., 2013. Early Ordovician reefs in south China (Chenjahe section, Hubei Province); deciphering the early evolution of skeletal-dominated reefs. *Facies* 59, 451-466.
- Adams, J.A.S., Weaver, C.E., 1958. Thorium-to-uranium ratios as indicators of sedimentary processes; example of concept of geochemical facies. *Bulletin of the American Association of Petroleum Geologists* 42, 387-430.
- Adrain, J.M., Edgecombe, G.D., Fortey, R.A., Hammer, O., Laurie, J.R., McCormick, T., Owen, A.W., Waisfeld, B.G., Webby, B.D., Westrop, S.R., Zhou, Z.-y., 2004. Trilobites, in: Webby, B.D., Paris, F., Droser, M.L., Percival, I.G. (Eds.), *The Great Ordovician Biodiversity Event*. Columbia University Press, New York, NY, pp. 231-254.
- Algeo, T.J., Ingall, E., 2007. Sedimentary C_{org} :P ratios, paleocean ventilation, and Phanerozoic atmospheric pO_2 . *Palaeogeography, Palaeoclimatology, Palaeoecology* 256, 130-155.
- Andersen, M.B., Romaniello, S., Vance, D., Little, S.H., Herdman, R., Lyons, T.W., 2014. A modern framework for the interpretation of $^{238}U/^{235}U$ in studies of ancient ocean redox. *Earth and Planetary Science Letters* 400, 184-194.
- Baranov, V.I., Ronov, A.B., Kunashova, K.G., 1956. Geochemistry of dispersed thorium and uranium in clays and carbonate rocks of the Russian platform. *Geochemistry (USSR)* 3, 227-235.
- Bishop, J.K.B., 1988. The barite-opal-organic carbon association in oceanic particulate matter. *Nature (London)* 332, 341-343.
- Blakey, R.C., 2011. Middle Ordovician North American Paleogeographic Map. <http://www2.nau.edu/rcb7/namO470.jpg>.
- Bond, D., Wignall, P.B., Racki, G., 2004. Extent and duration of marine anoxia during the Frasnian–Famennian (Late Devonian) mass extinction in Poland, Germany, Austria and France. *Geol. Mag.* 141, 173-193.
- Boyle, E.A., 1986. Paired carbon isotope and cadmium data from benthic foraminifera; implications for changes in oceanic phosphorus, oceanic circulation, and atmospheric carbon dioxide. *Geochimica et Cosmochimica Acta* 50, 265-276.
- Brennecke, G.A., Herrmann, A.D., Algeo, T.J., Anbar, A.D., 2011. Rapid expansion of oceanic anoxia immediately before the end-Permian mass extinction. *Proceedings of the National Academy of Sciences* 108, 17631-17634.

421 Buggisch, W., Keller, M., Lehnert, O., 2003. Carbon isotope record of Late Cambrian to Early Ordovician
 422 carbonates of the Argentine Precordillera. *Palaeogeography, Palaeoclimatology, Palaeoecology* 195,
 423 357-373.
 424 Choh, S.-J., Hong, J., Sun, N., Kwon, S.-W., Park, T.-Y., Woo, J., Kwon, Y.K., Lee, D.-C., Lee, D.-J., 2013.
 425 Early Ordovician reefs from the Taebaek Group, Korea; constituents, types, and geological implications.
 426 *Geosciences Journal (Seoul)* 17, 139-149.
 427 Dattilo, B.F., 1993. The Lower Ordovician Fillmore Formation of western Utah; storm-dominated
 428 sedimentation on a passive margin. *Geology Studies* 39, 71-100.
 429 Droser, M.L., Finnegan, S., 2003. The Ordovician Radiation: A follow-up to the Cambrian Explosion?
 430 *Integrative and Comparative Biology* 43, 178-184.
 431 Dypvik, H., Harris, N.B., 2001. Geochemical facies analysis of fine-grained siliciclastics using Th/U, Zr/Rb
 432 and (Zr+Rb)/Sr ratios. *Chemical Geology* 181, 131-146.
 433 Edwards, C.T., Saltzman, M.R., 2014. Carbon isotope ($\delta^{13}\text{C}_{\text{carb}}$) stratigraphy of the Lower–Middle
 434 Ordovician (Tremadocian–Darriwilian) in the Great Basin, western United States: Implications for global
 435 correlation. *Palaeogeography, Palaeoclimatology, Palaeoecology* 399, 1-20.
 436 Froelich, P.N., Arthur, M.A., Burnett, W.C., Deakin, M., Hensley, V., Jahnke, R., Kaul, L., Kim, K.H., Roe, K.,
 437 Soutar, A., Vathakanon, C., 1988. Early diagenesis of organic matter in Peru continental margin
 438 sediments; phosphorite precipitation. *Marine Geology* 80, 309-343.
 439 Gill, B.C., Lyons, T.W., Young, S.A., Kump, L.R., Knoll, A.H., Saltzman, M.R., 2011. Geochemical evidence
 440 for widespread euxinia in the Later Cambrian ocean. *Nature* 469, 80-83.
 441 Harper, D.A.T., 2006. The Ordovician biodiversification: Setting an agenda for marine life.
 442 *Palaeogeography, Palaeoclimatology, Palaeoecology* 232, 148-166.
 443 Harper, D.A.T., Cocks, L.R.M., Popov, L.E., Sheehan, P.M., Bassett, M.G., Copper, P., Holmer, L.E., Jin, J.,
 444 Rong, J., 2004. Brachiopods, in: Webby, B.D., Paris, F., Droser, M.L., Percival, I.G. (Eds.), *The Great*
 445 *Ordovician Biodiversification Event*. Columbia University Press, New York, NY, pp. 157-178.
 446 Hintze, L.F., 1951. Lower Ordovician detailed stratigraphic sections for western Utah. *Bulletin - Utah*
 447 *Geological and Mineralogical Survey*, 100.
 448 Hintze, L.F., Davis, F.D., 2003. *Geology of Millard County, Utah*. *Bulletin Utah Geological Survey* 133.
 449 Hough, M.L., Shields, G.A., Evins, L.Z., Strauss, H., Henderson, R.A., Mackenzie, S., 2006. A major sulphur
 450 isotope event at c. 510 Ma: a possible anoxia-extinction-volcanism connection during the Early-Middle
 451 Cambrian transition? *Terra Nova* 18, 257-263.
 452 Hurtgen, M.T., Pruss, S.B., Knoll, A.H., 2009. Evaluating the relationship between the carbon and sulfur
 453 cycles in the later Cambrian ocean: An example from the Port au Port Group, western Newfoundland,
 454 Canada. *Earth and Planetary Science Letters* 281, 288-297.
 455 Ingall, E., Kolowith, L., Lyons, T., Hurtgen, M., 2005. Sediment carbon, nitrogen and phosphorus cycling
 456 in an anoxic fjord, Effingham Inlet, British Columbia. *American Journal of Science* 305, 240-258.
 457 Janssen, D.J., Conway, T.M., John, S.G., Christian, J.R., Kramer, D.I., Pedersen, T.F., Cullen, J.T., 2014.
 458 Undocumented water column sink for cadmium in open ocean oxygen-deficient zones. *Proceedings of*
 459 *the National Academy of Sciences* 111, 6888-6893.
 460 Jones, B., Manning, D.A.C., 1994. Comparison of geochemical indices used for the interpretation of
 461 palaeoredox conditions in ancient mudstones. *Chemical Geology* 111, 111-129.
 462 Kah, L.C., Thompson, C.K., Henderson, M.A., Zhan, R., 2016. Behavior of marine sulfur in the Ordovician.
 463 *Palaeogeography, Palaeoclimatology, Palaeoecology*, this issue.
 464 Kelepertsis, A.E., 1981. The geochemistry of uranium and thorium in some Lower Carboniferous
 465 sedimentary rocks (Great Britain). *Chemical Geology* 34, 275-288.
 466 Kelly, S.D., Newville, M.G., Cheng, L., Kemner, K.M., Sutton, S.R., Fenter, P., Sturchio, N.C., Spötl, C., 2003.
 467 Uranyl Incorporation in Natural Calcite. *Environmental Science & Technology* 37, 1284-1287.

468 Kidder, D.L., Tomescu, I., 2016. Biogenic chert and the Ordovician silica cycle. *Palaeogeography*,
 469 *Palaeoclimatology*, *Palaeoecology*, this issue.
 470 Knoll, A.H., Bambach, R.K., Canfield, D.E., Grotzinger, J.P., 1996. Comparative Earth history and Late
 471 Permian mass extinction. *Science* 273, 452-457.
 472 Kritsanawanuwat, R., Sahoo, S.K., Fukushi, M., Chanyotha, S., 2015. Distribution of rare earth elements,
 473 thorium and uranium in Gulf of Thailand's sediments. *Environmental Earth Sciences* 73, 3361-3374.
 474 Lea, D.W., Spero, H.J., 1994. Assessing the reliability of paleochemical tracers; barium uptake in the
 475 shells of planktonic foraminifera. *Paleoceanography* 9, 445-452.
 476 Marengo, P.J., Marengo, K.N., Lubitz, R.L., Niu, D., 2013. Contrasting long-term global and short-term
 477 local redox proxies during the Great Ordovician Biodiversification Event: A case study from Fossil
 478 Mountain, Utah, USA. *Palaeogeography*, *Palaeoclimatology*, *Palaeoecology* 377, 45-51.
 479 Martin, J.H., Bruland, K.W., Broekow, W.W., 1976. Cadmium transport in the California Current, in:
 480 Windom, H.L., Duce, R.A. (Eds.), *Marine Pollutant Transfer*. Heath, Lexington, Mass., pp. 159-184.
 481 Miller, J.F., Evans, K.R., Dattilo, B.F., 2012. The great American carbonate bank in the miogeocline of
 482 western central Utah; tectonic influences on sedimentation. *AAPG Memoir* 98, 769-854.
 483 Montanez, I.P., Banner, J.L., Osleger, D.A., Borg, L.E., Bosserman, P.J., 1996. Integrated Sr isotope
 484 variations and sea-level history of Middle to Upper Cambrian platform carbonates; implications for the
 485 evolution of Cambrian seawater $^{87}\text{Sr}/^{86}\text{Sr}$. *Geology* 24, 917-920.
 486 Payne, J.L., Kump, L.R., 2007. Evidence for recurrent Early Triassic massive volcanism from quantitative
 487 interpretation of carbon isotope fluctuations. *Earth and Planetary Science Letters* 256, 264-277.
 488 Present, T.M., Paris, G., Burke, A., Fischer, W.W., Adkins, J.F., 2015. Large Carbonate Associated Sulfate
 489 isotopic variability between brachiopods, micrite, and other sedimentary components in Late Ordovician
 490 strata. *Earth and Planetary Science Letters* 432, 187-198.
 491 Retallack, Gregory A. J., Jahren, A. H., 2008. Methane release from igneous intrusion of coal during Late
 492 Permian extinction events. *The Journal of Geology* 116, 1-20.
 493 Robinson, L.F., Belshaw, N.S., Henderson, G.M., 2004. U and Th concentrations and isotope ratios in
 494 modern carbonates and waters from the Bahamas. *Geochimica et Cosmochimica Acta* 68, 1777-1789.
 495 Romaniello, S.J., Herrmann, A.D., Anbar, A.D., 2013. Uranium concentrations and $^{238}\text{U}/^{235}\text{U}$ isotope ratios
 496 in modern carbonates from the Bahamas; assessing a novel paleoredox proxy. *Chemical Geology* 362,
 497 305-316.
 498 Ross, R.J., Jr., James, N.P., Hintze, L.F., Poole, F.G., 1989. Architecture and evolution of a Whiterockian
 499 (early Middle Ordovician) carbonate platform, basin ranges of Western U.S.A. *Special Publication Society*
 500 *of Economic Paleontologists and Mineralogists* 44, 167-185.
 501 Roy-Barman, M., Lemaitre, C., Ayrault, S., Jeandel, C., Souhaut, M., Miquel, J.C., 2009. The influence of
 502 particle composition on thorium scavenging in the Mediterranean Sea. *Earth and Planetary Science*
 503 *Letters* 286, 526-534.
 504 Saltzman, M.R., Edwards, C.T., Adrain, J.M., Westrop, S.R., 2015. Persistent oceanic anoxia and elevated
 505 extinction rates separate the Cambrian and Ordovician radiations. *Geology* 43, 807-810.
 506 Servais, T., Harper, D.A.T., Li, J., Munnecke, A., Owen, A.W., Sheehan, P.M., 2009. Understanding the
 507 Great Ordovician Biodiversification Event (GOBE); influences of paleogeography, paleoclimate, or
 508 paleoecology? *GSA Today* 19, 4-10.
 509 Shen, G.T., Dunbar, R.B., 1995. Environmental controls on uranium in reef corals. *Geochimica et*
 510 *Cosmochimica Acta* 59, 2009-2024.
 511 Sprinkle, J., Guensburg, T.E., 2004. Crinozoan, blastozoan, echinozoan, asterozoan, and homalozoan
 512 echinoderms, in: Webby, B.D., Paris, F., Droser, M.L., Percival, I.G. (Eds.), *The Great Ordovician*
 513 *Biodiversification Event*. Columbia University Press, New York, NY, pp. 266-280.

514 Thompson, C.K., Kah, L.C., 2012. Sulfur isotope evidence for widespread euxinia and a fluctuating
515 oxycline in Early to Middle Ordovician greenhouse oceans. *Palaeogeography, Palaeoclimatology,*
516 *Palaeoecology* 313–314, 189-214.

517 Trotter, J.A., Williams, I.S., Barnes, C.R., Lécuyer, C., Nicoll, R.S., 2008. Did cooling oceans trigger
518 Ordovician biodiversification? Evidence from conodont thermometry. *Science* 321, 550-554.

519 van Green, A., Husby, D.M., 1996. Cadmium in the California current system; tracer of past and present
520 upwelling. *Journal of Geophysical Research* 101, 3489-3507.

521 Walker, J.D., Geissman, J.W., Bowring, S.A., Babcock, L.E., 2012. *Geologic Time Scale v. 4.0.* Geological
522 Society of America.

523 Wignall, P.B., Myers, K.J., 1988. Interpreting benthic oxygen levels in mudrocks; a new approach.
524 *Geology* 16, 452-455.

525 Wignall, P.B., Twitchett, R.J., 1996. Oceanic anoxia and the end Permian mass extinction. *Science* 272,
526 1155-1158.

527 Wilson, M.A., Palmer, T.J., Guensburg, T.E., Finton, C.D., Kaufman, L.E., 1992. The development of an
528 Early Ordovician hardground community in response to rapid sea-floor calcite precipitation. *Lethaia* 25,
529 19-34.

530 Zhuravlev, A.Y., Wood, R.A., 1996. Anoxia as the cause of the mid-Early Cambrian (Botomian) extinction
531 event. *Geology* 24, 311-314.

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Figure and Table Captions

Fig. 1. Paleogeographic reconstruction of Laurentia during the Middle Ordovician showing the approximate location of the Ibex succession. Lines of latitude are approximate. Detailed locality information can be found in Hintze (1951) and in Supplementary Fig. 1. Modified from Marenco et al. (2013) after Blakey (2011).

Fig. 2. A) Stratigraphic column and generalized composite lithologic column for the Ordovician succession near Ibex, Utah. Multiple patterns within a given box indicate interbedded lithologies, as opposed to precise locations of beds. Dates for stage boundaries are from Walker et al. (2012). B) $\delta^{13}\text{C}$ data from Edwards and Saltzman (2014) that were measured from carbonate rocks from the same localities as this study. Solid line is a three-point moving average. Red shading highlights the Kanosh Carbon Isotopic Anomaly. C-J) Normalized elemental abundances and ratios. Dark lines are five-point moving averages through the data, which include a four-point average, three-point average, and two-point average for the stratigraphically highest five data points in each plot. Red lines are five-point moving averages through Th/U and Sr/Mn. Gray shading connects zero to the five-point moving average lines. Red shading highlights increased or decreased elemental abundances associated with the Kanosh Carbon Isotopic Anomaly. K) $\delta^{34}\text{S}_{\text{CAS}}$ data from the Ibex area (solid grey and black dots) and Newfoundland (open grey squares). Ibex data is from this study (black dots) and from Marenco et al. (2013) (grey dots). Newfoundland data is from Thompson and Kah (2012). Data are correlated according to the biostratigraphy discussed in Marenco et al. (2013). Solid line and dashed line are three-point moving averages through the Ibex data and Newfoundland data, respectively. Red shading highlights intervals where $\delta^{34}\text{S}_{\text{CAS}}$ from Ibex is depleted relative to correlative data from Newfoundland.

Fig. 3. Summary figure comparing Th/U results to global $\delta^{13}\text{C}$, paleotemperature, and diversity. Trem. refers to “Tremadocian”. A) Five-point moving average line through Th/U results from the Ibex area. Dashed line represents inferred global values during the anomalous Kanosh interval. LBE refers to “last biomere extinction” here and in B. B) Simplified trace through the global compilation of $\delta^{13}\text{C}$ data of Saltzman et al. (2015). C) Simplified trace through the paleotemperature reconstruction of Trotter et al. (2008). D) Genus level diversity for trilobites and brachiopods and species level diversity for echinoderms. Trilobite data is from Adrain et al. (2004), brachiopod data is from Harper et al. (2004), and echinoderm data is from Sprinkle and Guensburg (2004).

Figure 1

Figure 2

Figure 3