Ca and Mg isotope constraints on the origin of Earth’s deepest \(\delta^{13}C\) excursion

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Abstract

Understanding the extreme carbon isotope excursions found in carbonate rocks of the Ediacaran Period (635–541 Ma), where \(\delta^{13}C\) of marine carbonates (\(\delta^{13}C_{\text{carb}}\)) reach their minimum (\(-12\%_{\text{oo}}\)) for Earth history, is one of the most vexing problems in Precambrian geology. Known colloquially as the ‘Shuram’ excursion, the event has been interpreted by many as a product of a profoundly different Ediacaran carbon cycle. More recently, diagenetic processes have been invoked, with the very negative \(\delta^{13}C\) values of Ediacaran carbonates explained via meteoric alteration, late-stage burial diagenesis or growth of authigenic carbonates in the sediment column, thus challenging models which rely upon a dramatically changing redox state of the Ediacaran oceans. Here we present 257 \(\delta^{44/40}Ca\) and 131 \(\delta^{26}Mg\) measurements, along with [Mg], [Mn] and [Sr] data, from carbonates of the Ediacaran-aged Wonoka Formation (Fm.) of South Australia to bring new isotope systems to bear on understanding the ‘Shuram’ excursion. Data from four measured sections spanning the basin reveal stratigraphically coherent trends, with variability of \(\sim 1.5\%_{\text{oo}}\) in \(\delta^{26}Mg\) and \(\sim 1.2\%_{\text{oo}}\) in \(\delta^{44/40}Ca\). This Ca isotope variability dwarfs the 0.2–0.3\%\(_{\text{oo}}\) change seen coeval with the Permian–Triassic mass extinction, the largest recorded in the rock record, and is on par with putative changes in the \(\delta^{44/40}Ca\) value of seawater seen over the Phanerzoic Eon. Changes in both isotopic systems are too large to explain with changes in the isotopic composition of Ca and Mg in global seawater given modern budgets and residence times, and thus must be products of alternative processes. Relationships between \(\delta^{44/40}Ca\) and [Sr] and \(\delta^{26}Mg\) and [Mg] are consistent with mineralogical control (e.g., aragonite vs. calcite, limestone vs. dolostone) on calcium and magnesium isotope variability. The most pristine samples in the Wonoka dataset, preserving Sr concentrations (in the 1000s of ppm range) and \(\delta^{44/40}Ca\) values inherited from an originally aragonitic polymorph, have \(\delta^{13}C_{\text{carb}}\) of \(-8\%_{\text{oo}}\) to \(-7\%_{\text{oo}}\), thereby providing strong geochemical evidence that extremely negative \(\delta^{13}C_{\text{carb}}\) values are primary products of the Ediacaran surface environment.

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1. INTRODUCTION

1.1. Ediacaran Earth history

The Ediacaran Period (635–541 Ma; Knoll et al., 2006) hosts several unique, unprecedented events in the history of Earth’s surface environment. Its beginning at \(\sim 635\) Ma (Condon et al., 2005; Hoffmann et al., 2004; Calver et al., 2013) is marked by the termination of the end-Cryogenian ice age, a glacial epoch global in scope and a potential instance of a ‘snowball Earth’ climate state (Hoffman et al., 1998; Hoffman and Schrag, 2002). In the biotic system, macroscopic, decimeter-scale fossils of debated phylogenetic affinity (variously described as animals, giant protists, macro-algae and lichen, and known informally as the ‘Ediacaran Biota’) first appear in the rock record, known from at least 40 localities (Fedonkin et al., 1998).
While the Ediacaran may not host the origin of animal life, with sponges potentially appearing in the Cryogenian (850–635 Ma; Wallace and Woon, 2008; Love et al., 2009; Sperling et al., 2010; Maloof et al., 2010b) or even Tonian (1000–850 Ma; Neuweiler et al., 2009; Brain et al., 2012), large, complex fossil forms do not become widespread globally until 579 Ma (Bowring et al., 2003).

Broadly coeval with these biological first appearances, extremely negative δ13C values in marine carbonates (δ13C_carb) are recorded in Ediacaran basins around the world (Fig. 1A). Carbon isotopic values drop from +3‰ down to −12‰, making it the most negative δ13C_carb excursion in Earth history. This excursion is known most famously from Oman (Burns and Matter, 1993; Fike et al., 2006; Le Guerroué et al., 2006a), South Australia (Calver, 2000; Husson et al., 2012, 2015), south China (McFadden et al., 2008), and southwestern USA (Corsetti et al., 2003; Kaufman et al., 2007; Bergmann et al., 2011; Verdel et al., 2011), but also from southern Siberia (Pokrovskii et al., 2006; Melezhik et al., 2009), Scotland (Prave et al., 2009), Namibia (Saylor et al., 1998; Workman et al., 2002), northwestern Canada (Macdonald et al., 2013), northwestern Mexico (Loyd et al., 2012) and perhaps Norway (Melezhik et al., 2008). These excursions are strata-bound to the Ediacaran, and thus synchronous at the period level. The events often are referred to informally (and collectively) as the ‘Shuram’ excursion, named after the host formation in Oman, although whether each are of equivalent age at a finer temporal resolution (~1 Myr), and thus truly represent a single excursion, remains to be established independently (Grotzinger et al., 2011). Zircon U–Pb ages from an ash fall in south China strata (Condon et al., 2005) suggest that the excursions are hosted in sediments older than 551.1 ± 0.7 Ma. Maximum ages are much more poorly constrained, with the best estimate being a SHRIMP U–Pb detrital zircon population age of 609 ± 7 Ma from the Khufai Fm., which underlies the Shuram Fm., in Oman (Le Guerroué et al., 2006b). Laurentian chemostratigraphic data and correlation arguments (Prave et al., 2009), however, suggest the excursions are younger than the ~580 Ma Gaskiers glaciation (Bowring et al., 2003).

Fig. 1. Summary figure, adapted from Husson et al. (2015), showing the global and basinal context for the δ44Ca and δ26Mg datasets. (A) ‘Shuram’ excursion δ13C_carb data from Oman (Fike et al., 2006), south China (McFadden et al., 2008), Siberia (Pokrovskii et al., 2006), southwestern USA (Verdel et al., 2011), the Yukon (Macdonald et al., 2013), and South Australia (Husson et al., 2012) plotted by continent and by lithology (limestone vs. dolostone). (B) The width of the bars, color-coded by continent and lithology and labeled with true section thicknesses (in meters), correlates with 1/S, where S is the stretch factor applied to each dataset used to align the different profiles based on their δ13C_carb profile. (C) Simplified geological map, adapted from Raymond et al. (2012) and using the WGS84 datum, of the study area within the Adelaide Rift Complex (ARC). Locations of measured stratigraphic sections are denoted by white symbols, and black outlines highlight the paleocanyon sample sites of Mount Thomas (Fig. 2A) and Saint Ronan (Fig. 2B). (D) Schematic physical stratigraphy, adapted from Giddings et al. (2010), of the lower Wilpena Group, showing the incision of ~1000 m deep paleocanyons, emanating from the upper Wonoka Fm. (Husson et al., 2012, 2015) and cutting down to the Brachina Fm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
The tantalizing, if approximate, concordance between the ‘Shuram’ excursion and the rise of animal life have led many workers to speculate about potential causal connections between the two. For example, Ediacaran δ¹³C profiles have been interpreted as an imprint of transition towards a more oxic Earth surface in which animals with high metabolic demands might be better supported (e.g., Rothman et al., 2003; Fike et al., 2006; McFadden et al., 2008; Bjerrum and Canfield, 2011). Implicit in these models is the assumption that marine stratigraphic records of δ¹³C reflect the evolving δ¹³C of dissolved inorganic carbon (DIC) in contemporaneous global sea water. As the residence time of DIC is long compared to ocean mixing (~10⁴ vs. ~10⁵ years), it is reasonable to expect that secular change in δ¹³C will be recorded in globally disparate marine basins (Kump and Arthur, 1999; Fig. 1A). If the ‘Shuram’ excursion represents a high-fidelity record of carbon cycling, the extreme nature of the event (nadir values of ~12‰; well below the canonical mantle carbon input value of ~5‰; Kump and Arthur, 1999) requires an Ediacaran carbon cycle fundamentally different from the modern. Models focus on large fluxes of remineralized organic carbon, in the form of either methane hydrates (Bjerrum and Canfield, 2011) or a large pool of relictant particulate and dissolved organic carbon (the ‘big DOC’ model; Rothman et al., 2003), to the ocean-atmosphere system. Critically, the most salient data for assessing these styles of models are absolute time constraints, with which the light carbon fluxes, reservoir sizes and oxidant demands needed to drive the excursion could be rigorously described (Bristow and Kennedy, 2008) as well as independently test for synchronicity of the events (Grotzinger et al., 2011). Currently, given the paucity of U–Pb dates, and assuming the ‘Shuram’ excursion records a global event, estimates of duration range widely, from 5 (Bowring et al., 2007) to 50 Myr (Le Guerroué et al., 2006b).

Several models now exist which challenge the primary-DIC interpretation of the ‘Shuram’ excursion, and contend that the extremely negative δ¹³C values observed in Ediacaran successions are diagenetic products. If correct, the implications would be profound not only for our understanding of Ediacaran environmental change and metazoan radiation (e.g., Fike et al., 2006; McFadden et al., 2008), but also for the utility of Shuram-like δ¹³C excursions (and stratigraphic δ¹³C profiles in general) as inter-basin correlation tools (e.g., Halverson et al., 2005; Macdonald et al., 2010; Maloof et al., 2010a; Swanson-Hysell et al., 2010; Rose et al., 2012; see Fig. 1A and B). These explanatory hypotheses include (1) meteoric diagenesis (Knauth and Kennedy, 2009; Swart and Kennedy, 2012), (2) late-stage burial diagenesis (Derry, 2010) and (3) authigenic carbonate models (Schrag et al., 2013). Each proposes a different mechanism for the development of very negative δ¹³C values, although all share the common contention that ‘Shuram’ excursion profiles are the result of post depositional alteration (although in the meteoric and authigenic cases, diagenesis can happen immediately after deposition). Each of these three models thus disconnects Ediacaran δ¹³C records from evolving Ediacaran DIC.

1.2. Testing models in South Australia

Approaches for evaluating the primary versus secondary nature of ‘Shuram’ excursion profiles have most often relied on combining δ¹¹C–δ¹⁸O datasets with field observations and relationships (e.g., Le Guerroué and Cozzi, 2010; Bergmann et al., 2011; Husson et al., 2012, 2015). For example, isotope conglomerate tests from the Ediacaran-aged Wonoka Fm. of South Australia require a syn-depositional age for the extraordinary range of observed δ¹³C values (~12‰ to +5‰; Husson et al., 2012, 2015). In the southern portions of the basin, the Wonoka Fm. is ~700 m of mixed outer shelf limestones and siliciclastics. Moving northward, the basin deepens (Haines, 1990; Husson et al., 2015), and the Wonoka Fm. is host to ~1 km paleocanyons, which are partly filled by tabular-clast carbonate breccias (Figs. 2 and 3). The southern sections record the full 17‰ δ¹³C excursion (~12‰ to +5‰). The redeposited clasts, sourced from eroded southern Wonoka sections, exhibit the same extremely depleted values and range in δ¹³C within single meter-scale deposits (Husson et al., 2012, 2015). The results of these isotope conglomerate tests (Husson et al., 2012, 2015) require that the negative δ¹³C values were acquired in Wonoka Fm. carbonates before those carbonates were brecciated and redeposited in the paleocanyons, and could not be a result of late-stage burial diagenesis (Derry, 2010).

The first-order geological evidence from South Australia similarly does not support the meteoric or authigenic models, in which alteration could theoretically be before canyon-filling and thus not violate the isotope conglomerate tests (Husson et al., 2012, 2015). In classic examples of meteoric diagenesis (Allan and Matthews, 1982; Melim et al., 2001), development of exposure surfaces at the top of carbonate sequences allow for the downward infiltration of altering fluids, especially in cases where local conditions (i.e., relative sea level, recharge rate and the porosity/permeability of the platform sediments) encourage the development of a deep fresh water lens. These fluids are negative relative to seawater in both δ¹³C (a result of soil carbon respiration) and δ¹⁸O (since the fluids are sourced from rainwater). Thus, the δ¹³C profiles of meteorically-altered sequences become more negative stratigraphically upwards, as these exposure horizons are approached (Allan and Matthews, 1982; Melim et al., 2001), as well as exhibit a positive correlation with δ¹⁸O. Covariation between δ¹³C and δ¹⁸O is a feature of many, but not all, ‘Shuram’ excursion successions (Grotzinger et al., 2011). In the Wonoka Fm., the only physical evidence for subaerial exposure is at the top (Haines, 1987; Husson et al., 2012, 2015), where δ¹³C values are at their most positive (+2‰ to +8‰). Furthermore, pervasive, fabric destructive recrystallization, a prominent feature of meteorically altered Plio–Pleistocene platform carbonates of The Bahamas (Melim et al., 2001), is not observed in the Wonoka Fm. (Husson et al., 2012, 2015).

Evidence against the authigenic model as an explanation for the South Australian observations are likewise rooted in facies and textual arguments, as well as in the basin-wide
expression of the 17\textsuperscript{\textdegree}\textsubscript{C} excursion (Husson et al., 2015). Growth of \textdelta^{13}C-depleted carbonates in the sediment pore space is encouraged by anoxic respiration of organic carbon via various respiratory pathways (e.g., sulfate reduction), which produces alkalinity and results in the over-saturation of CaCO\textsubscript{3} in pore fluids (Aller et al., 1996; Higgins et al., 2009). Documented authigenic carbonates have distinctive textures, appearing in the rock record as crystal fans, void-filling cements, and secondary nodules (Grotzinger and James, 2000). While such fabrics occur in some Ediacaran successions which host Shuram-like excursions (Pruss et al., 2008; Macdonald et al., 2013), they are completely absent from the Wonoka Fm. (Haines, 1990; Husson et al., 2012, 2015). Thus, for the authigenic model to satisfy the observations from South Australia, either (a) a locus of authigenic carbonate production must be invoked, producing \textdelta^{13}C-depleted carbonates which are then eroded, transported and deposited as sedimentary beds elsewhere in the basin, or (b) the growth of authigenic carbonate must preserve primary sedimentary structures.

Fig. 2. Geological maps, adapted from (Husson et al., 2015), showing (A) the sinuous, ~1000-m-deep Wonoka paleocanyon at Mount Thomas, with general paleocurrent directions marked from Eickhoff et al. (1988), and (B) the shallower (~100–200 m) cut-fill sequence of Saint Ronan. Map data are displayed as projections onto a Universal Transverse Mercator grid (zone 54S). Red lines indicate the canyon-formation sequence boundary, and yellow units show regions where the canyon-fill is composed predominantly of tabular-clast carbonate breccias, with white symbols indicating outcrop locations sampled in this study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
across the basin, as differences between 0.01–0.02%) and have happened extremely consistently low in total organic carbon abundance (TOC values are process must have affected rocks which are currently very features or syn-depositional, fabric-retentive alteration – the isotope ratios as the relative abundance of 44Ca versus (Grotzinger et al., 2011). To better con-
sclusions with well-preserved sedimentary structures must be 
fundamentally local phenomena, reasons for the ‘Shuram’ 
paleocanyon complexes (Figs. 1C, 2 and 3). We report Ca 
excursion’s global and strata-bound development in succes-
sions – and Kennedy, 2008) – and the observed, puzzling correla-
tions with these datasets cover Shuram-like excursions (n = 12 for South China; 11 for Siberia), and reproduc-
ibility between stratigraphic sections was not tested in these studies.

Calcium in the modern ocean is isotopically homogenous (Zhu and Macdougall, 1998), owing to its long residence time of ~1 Myr (Sarmiento and Gruber, 2006). Ca inputs to the ocean system are mainly from riverine and hydrothermal sources, and the only quantitatively significant output is CaCO3 precipitation and burial (Fantle and Tipper, 2014; Fig. 4A). CaCO3 minerals are fractionated from seawater – 44Ca is preferentially taken up into the solid, leaving seawater enriched in 44Ca – although the degree of this fractionation varies with mineralogy (calcite vs. aragonite; Gussone et al., 2005), temperature (Gussone et al., 2005; Böhm et al., 2006), and precipitation rate (Tang et al., 2008). Modern magnesium isotope systematics share many similarities with calcium. Its long residence time (~10 Myr) leads to isotopic homogeneity in the modern ocean (De Villiers et al., 2005). Carbonate minerals similarly sequester the light isotope of 24Mg over 26Mg, with limestone generally being more fractionated than dolomite, resulting in a seawater δ26Mg heavier than riverine inputs (Tipper et al., 2006; Fig. 4A). In the modern ocean, biogenic calcites show

(2)

$\delta^{26}\text{Mg} = \left( \frac{\text{Mg}_{\text{sample}}}{\text{Mg}_{\text{standard}}} - 1 \right) \times 1000,$

where the standard used is the isotopic composition of modern seawater (Holmden et al., 2012a). We similarly express Mg isotope ratios as the relative abundance of 26Mg versus 24Mg:

$\delta^{26}\text{Mg} = \left( \frac{\text{Mg}_{\text{sample}}}{\text{Mg}_{\text{standard}}} - 1 \right) \times 1000,$

where the standard used is DSM3 (Galy et al., 2003). Previous work on these isotopic systems from strata hosting the ‘Shuram’ excursion include 33 calcium isotope measurements from the Doushantuo Fm. of South China (Sawaki et al., 2014) and 32 magnesium isotope measurements from Siberia (Pokrovsky et al., 2011). Both of these studies focus on the full Ediacaran system (635–541 Ma); thus only a portion of the above datasets cover Shuram-like excursions (n = 12 for South China; 11 for Siberia), and reproducibility between stratigraphic sections was not tested in these studies.

At present, there exists no consensus agreement on a process (or processes) which caused the ‘Shuram’ excursion. Each of the models discussed above has challenges from the geological record to address, from both South Australia and other Ediacaran basins. For primary DIC models, the timescale must be better constrained – the carbon injection and oxidant demands both become unrealistically large if the excursion lasted much longer than ~1 Myr (Bristow and Kennedy, 2008) – and the observed, puzzling correlations between δ13C and δ18O must be addressed. For syn-depositional diagenetic processes, which are fundamentally local phenomena, reasons for the ‘Shuram’ excursion’s global and strata-bound development in successions with well-preserved sedimentary structures must be better elaborated (Grotzinger et al., 2011). To better constrain any explanatory model which meets these demands, we expand upon the chemostratigraphic work of Husson et al. (2012, 2015) with Ca and Mg stable isotope measurements, along with Mg, Mn and Sr abundance data, from four 500–850-m-thick Wonoka Fm. sections and on canyon-fill clasts from the Mount Thomas and Saint Ronan paleocanyon complexes (Figs. 1C, 2 and 3). We report Ca isotope ratios as the relative abundance of 44Ca versus 40Ca using the standard δ notation:

$\delta^{44/40}\text{Ca} = \left( \frac{\text{Ca}_{\text{sample}}}{\text{Ca}_{\text{standard}}} - 1 \right) \times 1000,$

where the standard used is

$\delta^{44/40}\text{Ca} = \left( \frac{\text{Ca}_{\text{sample}}}{\text{Ca}_{\text{standard}}} - 1 \right) \times 1000,$

where the standard used is

$\delta^{26}\text{Mg} = \left( \frac{\text{Mg}_{\text{sample}}}{\text{Mg}_{\text{standard}}} - 1 \right) \times 1000,$

where the standard used is
considerable variability, but in general low-Mg calcite is more negative isotopically than high-Mg calcite, which in turn is more negative than aragonite (Hippler et al., 2009; Ra et al., 2010). One important difference between the Mg and Ca cycles is that Mg has two important sinks – dolomite formation and the formation of Mg-rich clays from the alteration of seafloor basalts (Fig. 4A).

Unlike other isotopic systems which have been used to study the ‘Shuram’ excursion (e.g., $^{87}$Sr/$^{86}$Sr, $^{34}$S of carbonate-associated sulfate, $\delta^{13}$C$_{org}$), calcium and magnesium species are major constituents of carbonate rock (Ca for both limestone and dolomite, Mg for dolomite) and thus are not subject to the same concerns regarding diageneis and isotopic resetting as are trace systems. Additionally, as the residence times for carbon, calcium and magnesium are orders-of-magnitude different from each other ($\sim 10^5$, $\sim 10^6$ and $\sim 10^7$ years, respectively), synchronous changes in each of the isotopic systems are not expected if each of the records represents secular, long-term evolution of seawater composition (Holmden et al., 2012a).

2. GEOLOGICAL SETTING

The Adelaide Rift Complex (ARC; Fig. 1C) was part of a continental margin formed to the present-day east of the Stuart Shelf (Preiss, 2000). The ARC contains very thick Neoproterozoic-to-Cambrian sequences that were folded during the $\sim 500$ Ma Delamerian orogeny (Thomson et al., 1964) and currently are well exposed in the Flinders and Gammon ranges (Fig. 1C). The Wonoka Fm. is part
of the Ediacaran Wilpena Group (Gp.), whose base is the Nuccaleena Fm., the distinctive cap dolostone to the glacial Elatina Fm. of the underlying Umberatana Gp. (Plummer, 1979; Williams, 1979; Rose and Maloof, 2010; Fig. 1D).

The Nuccaleena Fm., based on facies relationships and carbon isotope chemostratigraphy, frequently is correlated to the younger Cryogenian glacial cap units found around the world (Halverson et al., 2005), dated to be ~635 Ma in Namibia (Hoffmann et al., 2004), south China (Condon et al., 2005), and Tasmania (Calver et al., 2013). The Wilpena Gp. consists of two grand shoaling-upward cycles (Preiss, 2000); the first begins with the Nuccaleena Fm. and ends with the shallow marine sandstones of the ABC ranges quartzite (Fig. 1D). The second cycle begins with a flooding surface and deposition of the siltstones of the Bunyeroo Fm., which likely contains the maximum flooding surface of this cycle.

The Wonoka Fm. overlies the Bunyeroo, and varies between 500 and 1500 m in thickness. The Wonoka coarsens and shallows upward into the siliclastic, Ediacara Biota-bearing Pound Subgroup (Fig. 1D). In the southern and central Flinders Ranges (measured sections 2, 4, 6 and 9 on Fig. 1C), the Wonoka begins as a deep-shelf sequence of red siltstones interbedded with thin-bedded (2–5 cm), often fluted turbiditic carbonate beds with abundant climbing-ripples. Carbonate beds become thicker and coarser upward, culminating with the first unequivocally shallow-water carbonates (5–40 m of black, wavy laminated microbialite) ~600 m above the base of the Wonoka. Above these beds, the Wonoka Fm. transitions abruptly into a thick (~30–150 m) package of siliciclastics (unit 10 in the terminology of Haines (1990), who subdivided the Wonoka Fm. into 11 informal lithological units), in which carbonate interbeds are entirely lacking. The uppermost Wonoka Fm. returns to carbonate, with ~5–100 m of dolomitized microbialite, stromatolite-flake grainstones and silty dolostones (unit 11 after Haines, 1990).

In general, the Wonoka Fm. deepens to the north, with sections in the northern Flinders recording outermost-shelf and slope environments. In some northern localities, ~1000-m-deep paleocanyons cut into the underlying Bunyeroo and Brachina formations (e.g., Mount Thomas on Figs. 1C and 2A). The most striking features of the canyon-fill stratigraphy are the meter-to-decameter scale tabular-clast carbonate breccias (Fig. 3B). Importantly, the canyon-fill sequence at Saint Ronan is similarly composed of sub-meter scale tabular-clast carbonate breccias (Fig. 3B). Important suites of paleocanyon-carbonate samples were selected (the resulting vertical resolution for the stratigraphic samples is 10–20 m), and ~5–10 mg of each sample were placed in a 15 milliliter (mL) Falcon centrifuge tube along with 5 mL of a buffered solution of anhydrous acetic acid and ammonium hydroxide (pH of ~5) and allowed to react in a sonicator for 5 h. This style of dissolution is effective in dissolving carbonate phases (both limestone and dolomite), but leaves less soluble sediment components unleached, such as Fe–Mn oxides and clays (Tessier et al., 1979). Thus, the elements liberated during dissolution are assumed to be carbonate-bound. Each solution was then centrifuged at 2500 rpm for ten minutes. The

3. METHODS

3.1. Sample preparation and trace element analysis

For the measured sections of the canyon-shoulder (sections 2, 4, 6 and 9 on Fig. 5), carbonates were sampled at ~2 m resolution for δ13C and δ18O analysis. Mineralogy (limestone vs. dolomite) was determined in the field via the acid test, and clean carbonates with minimal siliciclastic components were targeted. These 884 stratigraphic samples, along with 81 samples from the canyon-fill breccias of the Mount Thomas and Saint Ronan paleocanyons (Fig. 3), were slabbed and polished perpendicular to bedding, and ~20 milligrams (mg) of powder were micro-drilled from individual laminations. The finest grained ground mass was targeted, and any veins or cements of secondary calcite were avoided.

Samples from section 6 were measured at the University of Michigan Stable Isotope Laboratory for δ13C and δ18O. All powders were heated to 200 °C to remove volatile contaminants and water. Samples were then placed in individual borosilicate reaction vessels and reacted at 76 °C with 3 drops of H3PO4 on a Finnigan MAT Kiel I preparation device coupled directly to the inlet of a Finnigan MAT 251 triple collector isotope ratio mass spectrometer. All other samples were measured at Princeton University. All powders were heated to 110 °C to remove volatile contaminants and water in individual borosilicate reaction vials. Powders were reacted at 72 °C with 4–5 drops of H3PO4 on a GasBench II preparation device coupled directly to the inlet of a Thermo DeltaPlus continuous flow isotope ratio mass spectrometer. Precision and accuracy are monitored by running 14 standards for every 72 unknowns. The standard set includes a primary standard (NBS-19) and a secondary, in-house marble standard. δ13C and δ18O were acquired simultaneously on both systems, and isotopic data are reported in the standard delta notation as the δ‰ difference from the VPDB standard (Vienna Pee Dee Belemnite). All samples are measured relative to an internal gas standard, and then converted to the VPDB scale using the known composition of NBS-19 (δ13C = 1.95; δ18O = −2.20) following the data reduction scheme of Paul et al. (2007). Precision is 0.05–0.1‰ (1σ) for δ13C and 0.15–0.2‰ (1σ) for δ18O. These data have already been published in Husson et al. (2015).

For trace element and Ca and Mg isotope analysis, a subset of carbonate samples were selected (the resulting vertical resolution for the stratigraphic samples is 10–20 m), and ~5–10 mg of each sample were placed in a 15 milliliter (mL) Falcon centrifuge tube along with 5 mL of a buffered solution of anhydrous acetic acid and ammonium hydroxide (pH of ~5) and allowed to react in a sonicator for 5 h. This style of dissolution is effective in dissolving carbonate phases (both limestone and dolomite), but leaves less soluble sediment components unleached, such as Fe–Mn oxides and clays (Tessier et al., 1979). Thus, the elements liberated during dissolution are assumed to be carbonate-bound. Each solution was then centrifuged at 2500 rpm for ten minutes. The
upper 4 mL of supernatant, clear of any insoluble residue, was pipetted off into another Falcon tube. Elemental abundances of Mg, Sr, and Mn on samples from measured sections 2 and 9 were determined on a Perkin Elmer Optima 4300 DV inductively-coupled plasma optical-emission spectrophotometer (ICP-OES) at Princeton University. The trace element data for measured sections 4 and 6 and the breccia clasts were determined on a Thermo Scientific Element 2 ICP mass spectrometer (ICP-MS) at Princeton University. These data were published by Husson et al. (2015). Mn and Sr data are presented as weight abundance (ppm) in the original, dissolved carbonate solid, and Mg data is presented as Mg/Ca ratios in mmol/mol (value of 1000 = stoichiometric dolomite).
3.2. Ca and Mg isotope analyses

To develop single-element analytes for Ca and Mg isotopic analysis, samples were processed using a Thermo Dionex 5000+ ion chromatography (IC) system. The automated IC system runs samples through an in-line CS16 cation exchange column which separates various cations and measures peak intensities using changes in conductivity. Collection windows are specified to collect pure Ca or Mg cuts. For Ca separations, samples were diluted to ~20–40 ppm Ca using 0.2% nitric acid (HNO₃) and Mg samples were diluted to ~1.5–4.5 ppm Mg; in both cases, 200 microliters (µL) of solution were run through the column. Collection fractions were dried, treated with concentrated HNO₃, re-dried completely, and re-dissolved in 2% HNO₃ for isotopic analysis.

Ca isotope analysis was performed on a Thermo Neptune Plus inductively-coupled plasma mass spectrometer (ICP-MS) at Princeton University. Analyses were performed at medium-resolution (MR) with an ESI Apex-IR sample introduction and desolvation system. Beam intensities for 43Ca, 44Ca, 43Sr, and 45Ca were measured in cups L2, C, H1 and H2, respectively, with the 43Ca beam measured on the low-mass side shoulder of the peak to avoid interference from ArHH. All samples were diluted to 2 ppm Ca in 2% HNO₃, with sample concentrations matching standard concentrations to within 20%. The resulting 24Mg value of 31 analyses is 4.0 V. Mass 43.5 was measured, which records doubly charged 87Sr, to correct for Sr interferences on the Ca beams.

Each analysis consisted of a single block composed of 80 cycles with an integration time of 2.1 s for each cycle. Where sample size allowed, each sample was measured twice within the same session on the mass spectrometer (over 80% of all samples). Every sample is bracketed by measurements of an in-house Ca standard, which is a single-element high-purity ICP Ca standard (HPS). The standard measurements are used to calculate 44Ca/42Ca, 44Ca/43Ca and 45Ca/42Ca ratios for HPS, which are then used to calculate δ44/42CaHPS, δ44/43CaHPS and δ43/42CaHPS values for the bracketed unknown. Typical within-block uncertainties for 44Ca/42Ca, 45Ca/43Ca and 43Ca/42Ca ratios range between 0.01 and 0.02‰ (1 standard error). For samples, δ44/43CaHPS and δ43/42CaHPS values are converted to the modern seawater reference scale (Holmden et al., 2012a) by using an average of 13 measurements of seawater on the HPS scale (δ44/43CaHPS = 0.54‰ and δ43/42CaHPS = 0.27‰). A plot of δ44/42Ca vs. δ43/42Ca for all samples has a slope of 0.479 ± 0.027 (see Fig. EA1 in the Electronic Annex), which is within uncertainty of the mass-dependent fractionation line between these δ values predicted by theory (0.494; equations 1 and 2 in Holmden et al., 2012b). Values of samples were then converted to δ44/40Ca on the seawater scale according to the equation:

\[
\delta^{44/40}\text{Ca} = 2.05 \times \delta^{44/42}\text{Ca},
\]

where 2.05 is the predicted slope between δ44/42Ca and δ44/40Ca under kinetic isotope fractionation (e.g., Holmden et al., 2012b; Schiller et al., 2012). Accuracy of our measurements is assessed by analysis of the common SRM 915b Ca standard and modern seawater. Both were first passed through the automated column chromatography system, and the mean of 14 analyses of SRM 915b has a seawater offset of −1.21 ± 0.10‰ (Table EA1), indistinguishable from previously published offsets between these two common Ca standards (−1.25‰, Fantle and Tipper, 2014). The external reproducibility of our measurements is defined by full sample replicates (column chemistry followed by mass spectrometry). For Ca isotopes, reproducibility is ~0.09‰ for δ44/42Ca (2σ) and ~0.19‰ (2σ) for δ44/40Ca, based on measurements (n = 62) of an in-house synthetic limestone standard (Ca + minor/trace elements; see Fig. EA1) which underwent the same ion chromatography protocols and sample preparation procedures as samples. At least one, but more typically 3–4, sample of this synthetic limestone standard is measured in each analytical session, comprised of 35–40 unknowns.

Mg isotope analysis was also performed on the Thermo Neptune Plus at Princeton University. Analyses were performed at low-resolution, and beam intensities were measured for 24Mg, 25Mg, and 26Mg on the L3, C, and H3 cups, respectively. All samples were diluted to 150 ppb Mg in 2% HNO₃, with sample concentrations matching standard concentrations to within 20%. The resulting 24Mg beam is typically 4–5 V. Each analysis consists of a single block composed of 22 cycles with an integration time of 8 seconds for each cycle. Every sample is bracketed by two measurements of the DSM3 Mg isotope standard, and every sample was measured twice within the same session on the mass spectrometer, where sample volume allowed. Plots of δ26Mg vs. δ25Mg are made for every machine session to monitor for interferences and provide a quality-control check (see Fig. EA1). To assess accuracy, we analyzed both CAMBRIDGE-1 and seawater, both commonly measured by other labs, as secondary standards. For CAMBRIDGE-1, the mean δ26Mg value of 31 analyses is −2.61 ± 0.11‰ (2σ) and seawater has a mean value of 19 analyses of −0.80 ± 0.11‰ (2σ; Table EA1); both values compare very favorably to previously published numbers (−2.58‰ and −0.82‰ for CAMBRIDGE-1 (Galy et al., 2003) and seawater (Foster et al., 2010) on the DSM3 scale, respectively). Similar to Ca, precision of Mg isotope measurements is assessed also by analysis of an IC-separated, in-house synthetic dolomite standard (Mg/Ca = 1 + minor/trace elements; see Fig. EA1). With 1–2 synthetic dolomites measured in each analytical session (typically comprised of 35–40 unknowns), long-term external reproducibility on δ26Mg is 0.1‰ (2σ; n = 22). Table EA2 in the Electronic Annex is a complete data table, and includes δ13C, δ18O, elemental abundances, δ44/40Ca (relative to modern seawater) and δ26Mg (relative to DSM3). For both
$\delta^{44/40}$Ca and $\delta^{26}$Mg, uncertainties reported are the 2σ values of the replicate analyses made within the same analytical session.

4. RESULTS

4.1. Canyon-shoulder chemostratigraphy

The $\delta^{44/40}$Ca profiles of four measured canyon-shoulder sections, dispersed across the ARC (2, 4, 6 and 9 on Fig. 1C) show a remarkably consistent, stratigraphically coherent trend (Fig. 5). Basal Wonoka carbonates are $-0.8_{\text{oo}}$ to $-0.6_{\text{oo}}$ in $\delta^{44/40}$Ca. In three sections (measured sections 2, 4 and 6 on Fig. 5), $\delta^{44/40}$Ca drops by $\sim 1.2_{\text{oo}}$ to a nadir value of $-1.9$ over 150–200 m of stratigraphy. The one exception is measured section 9; while a drop of $\sim 1.2_{\text{oo}}$ for $\delta^{44/40}$Ca for $\sim 300$ m, and a positive excursion back to basal values (Fig. 6B). $\delta^{44/40}$Mg do not display any clear stratigraphic trend for the basal $\sim 500$ m, and vary between $-3.0_{\text{oo}}$ and $-2.0_{\text{oo}}$ (Fig. 6C). Above 500 m, $\delta^{26}$Mg values rise in sections 4, 6 and 9 from $-2.5_{\text{oo}}$ to $-1.5_{\text{oo}}$, coincident with the transition from limestones (Mg/Ca of $\sim 12.5$) to the dolomitic horizons of the upper-most Wonoka (Fig. 6D). $\delta^{26}$Mg in the upper 200 m are also more tightly clustered than in the basal Wonoka; the standard deviation of $\delta^{26}$Mg in the lower 500 m is 0.32, whereas the standard deviation in the upper 200 m, after stratigraphic detrending with a linear fit, is 0.20 (excluding one outlier from measured section 6 at 620 m).

Coherent stratigraphic patterns also are seen in $\text{[Mn]}$ and $\text{[Sr]}$. Mn levels begin high (5000–6000 ppm), drop to a minimum of 400–1000 ppm over $\sim 250$ m, and rise to basal values over the final $\sim 200$ m (Fig. 6E). The trend in Sr is exactly opposite; values start low at $\sim 150–200$ ppm, rise to a basin maximum of 7000 ppm over $\sim 250$ m, and fall over the final $\sim 200$ m to a minimum of 30–50 ppm in the dolomites of unit 11 (Fig. 6F). Absolute values in Mn are similar section-to-section, whereas for Sr, maxima in measured sections 2, 4, 6 and 9 range between $\sim 700$ and 7000 ppm (although the overall trend in each locality is the same).

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**Fig. 6.** (A) Composite canyon-shoulder lithostratigraphy, labeled with the units of Haines (1988) and color-coded by facies as in Fig. 5. By accounting for the variable thickness of canyon-shoulder sections across the ARC ($\sim 500–850$ m), composite plots of (B) $\delta^{44/40}$Ca, (C) $\delta^{26}$Mg, (D) Mg/Ca ratio (in mmol/mol), (E) Mn abundance (in ppm), (F) Sr abundance (in ppm) and (G) $\delta^{13}$C$_{\text{carb}}$ can be constructed. Data in each subplot is coded by section number with color and shape (Figs. 1C and 5). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Basin-wide trends in $\delta^{44/40} \text{Ca}$, $\delta^{13} \text{C}_{\text{Carb}}$, [Mn] and [Sr] share similar stratigraphic intervals of stasis and change. In each chemostratigraphic dataset, change occurs in the lowermost $\sim$200–250 m and uppermost $\sim$200–250 m; middle Wonoka stratigraphy is characterized by relative stability in isotopic value and trace element abundance (Fig. 6B, E–G). The correlations and anti-correlations between these geochemical datasets are best illustrated in the isotope-isotope and isotope-element cross-plots of Fig. 7. $\delta^{44/40} \text{Ca}$ and $\delta^{13} \text{C}_{\text{Carb}}$ are anti-correlated for $\delta^{13} \text{C}_{\text{Carb}}$ values between $-12^\circ_{\text{oo}}$ and $-7^\circ_{\text{oo}}$; the relationship switches to a positive correlation for $\delta^{13} \text{C}_{\text{Carb}}$ values of $-7^\circ_{\text{oo}}$ to $+5^\circ_{\text{oo}}$ (Fig. 7A). Sr abundances and $\delta^{44/40} \text{Ca}$ values are negatively correlated; the relationship is broadly linear for measured sections 2, 4, and 6, and saturates in section 9, which hosts the highest [Sr] values (Fig. 7B). Unlike [Sr], the correlation between $\delta^{44/40} \text{Ca}$ and Mn abundance is positive (Fig. 7C). Finally, the relationship between $\delta^{44/40} \text{Ca}$ and Mg/Ca is complex. For the lower, falling limb of the $\delta^{44/40} \text{Ca}$ curve.

Fig. 7. Cross-plots of canyon-shoulder $\delta^{44/40} \text{Ca}$ vs. (A) $\delta^{13} \text{C}_{\text{Carb}}$, (B) Sr abundance, (C) Mn abundance and (D) Mg/Ca ratio. The x-axes in subplots C and D are logarithmic. In sub-plots A–C, data points are coded by section (color and shape) and lithology (closed = limestone; open = dolomitic, with the cut-off set to Mg/Ca $> 100$ mmol/mol). In D, points are coded by lithofacies with color and by stratigraphic position with size and shape (i.e., smaller triangles indicate samples from the ‘lower limb’ of the $\delta^{44/40} \text{Ca}$ profile, below $\sim$500 m in Fig. 6B). In each sub-plot, Pearson $r^2$ values between the two plotted variables are listed, color-coded by section. In A, the datasets are sub-divided into ‘anti-correlated’ and ‘positively correlated’ subsets, demarcated by the dashed line and listed with $r^2$ values calculated for each phase. In sub-plots B–D, the $r^2$ values are calculated between $\delta^{44/40} \text{Ca}$ values and log-transformed elemental abundance (Sr, Mn and Mg, respectively). For all correlations, $P$ values are less than 0.005. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
Mg/Ca values remain low (scattering between 10 and 30) and display no correlation with $\delta^{44/40}\text{Ca}$ (‘lower limb’ samples in Fig. 7D). Above 500 m, during the upper, rising limb of the $\delta^{44/40}\text{Ca}$ profile (Fig. 6B), dolomitic-to-pure dolomite horizons become prevalent and $\delta^{44/40}\text{Ca}$ correlates positively with Mg/Ca (‘upper limb’ samples in Fig. 7D).

4.2. Carbonate breccias of Mount Thomas and Saint Ronan paleocanyons

In order to assess the relative timing of the isotopic and trace element relationships observed in the canyon-shoulder (Figs. 5–7), we measured canyon-fill clasts from basal breccia units of Mount Thomas (47 $\delta^{44/40}\text{Ca}$ measurements and 33 $\delta^{33\text{Mg}}$ measurements) and Saint Ronan (24 $\delta^{44/40}\text{Ca}$ measurements) paleocanyons (Figs. 1C, 2 and 3). Carbonates feeding these breccias are sourced from eroded canyon-shoulders (i.e., measured sections 2, 4, 6, and 9 on Fig. 1C), with clasts from single meter-scale breccia units recording the full range of values in $\delta^{13}\text{C}_{\text{Carb}}$ (−12‰ to +5‰) as seen on the intact canyon-shoulder (Husson et al., 2012, 2015; Figs. 5 and 6G). With regards to Ca isotopes, Saint Ronan clasts mostly are similar to the canyon-shoulder data in isotope-isotope and isotope-element cross-plot space (dark green symbols in Fig. 8). Saint

![Fig. 8. Cross-plots of Mount Thomas (Figs. 2A and 3A) and Saint Ronan (Figs. 2B and 3B) canyon-fill clast $\delta^{44/40}\text{Ca}$ vs. (A) $\delta^{13}\text{C}_{\text{Carb}}$, (B) Sr abundance, (C) Mn abundance and (D) Mg/Ca ratio. Canyon-shoulder data is plotted in the background of each sub-plot. Data point symbology and $r^2$ calculation conventions are the same as in Fig. 7, with ‘Mt. Th.’ = Mount Thomas and ‘St. Ro.’ = Saint Ronan (Fig. 2). In A, the Saint Ronan dataset is not split into anti-correlated and positively correlated sub-sets as in Fig. 7A, and the outlier excluded to yield the higher $r^2$ value is labeled with a black arrow. Unless noted, all correlations have $P$ values less than 0.005.](image)


Ronan clasts span the full range in $\delta^{44/40}$Ca values seen in the canyon-shoulder, and display a negative correlation with $\delta^{13}$C$_{\text{carb}}$ (Fig. 8A). Saint Ronan clasts also plot similarly to canyon-shoulder samples in [Sr] and [Mn] space (Fig. 8B and C), although the highest values in [Mn] seen in other Wonoka carbonates are not observed. Finally, there are no dolomites in the Saint Ronan clasts; they in fact have the lowest Mg/Ca values of the full dataset, plotting to the far left in Fig. 8D.

Differences are more readily apparent between the canyon-shoulder and Mount Thomas clast datasets (light purple symbols in Fig. 8). Specifically, the nadir in $\delta^{44/40}$Ca (down to $-1.9\%_\text{o}$) is poorly developed in the Mount Thomas dataset (Fig. 8A). In cross-plot space, there is more scatter in the Mount Thomas clasts compared to the canyon-shoulder data, resulting in generally weaker correlations (Fig. 8A–C). In the case of [Mn], the observed correlation with $\delta^{44/40}$Ca is negative (Fig. 8C), as opposed to the positive relationships seen in the canyon-shoulder and Saint Ronan clasts (Fig. 7C). Dolostones from Mount Thomas breccias have a wider range in $\delta^{44/40}$Ca relative to Mount Thomas clast limestones, whereas the opposite is true in the canyon-shoulder dataset (Fig. 8D). The most obvious dissimilarity, however, between the Mount Thomas and canyon-shoulder datasets is seen in a plot of $\delta^{26}$Mg vs. Mg/Ca (Fig. 9A), where breccia dolomites form a population of distinctly more negative $\delta^{26}$Mg values than the canyon-shoulder dolomites.

### 5. DISCUSSION

#### 5.1. Explaining the canyon-shoulder $\delta^{44/40}$Ca trend

Canyon-shoulder sections of the Wonoka Formation (measured sections 2, 4, 6 and 9 on Fig. 1C) show a stratigraphically-coherent and basin-wide signal in $\delta^{44/40}$Ca (Figs. 5 and 6B). Values drop from $-0.7\%_\text{o}$ to $-1.9\%_\text{o}$ over 100–200 m of basal stratigraphy. The one exception is section 9, which shows the same isotopic drop over $\sim10$ m of vertical distance (Fig. 5). In section 9, a canyon-shoulder section immediately adjacent to the Saint Ronan paleocanyon (Fig. 2B), this step drop in $\delta^{44/40}$Ca occurs across the unit 3/4 contact, which is a proposed sequence boundary (Fig. 5). Both lithologic (Haines, 1987; Husson et al., 2015) and carbon isotopic (Husson et al., 2015) observations suggest that a paleocanyon surface at Saint Ronan emanated from the unit 3/4 contact, with canyon-cutting removing more and more of the basal Wonoka (i.e., unit 3 and lower) carbonates and siltstones as the paleocanyon is approached from the southeast along strike (Fig. 2B). The sudden change in $\delta^{44/40}$Ca supports this model, and suggests that $\sim100$ m of section 9 has been eroded by...
anoxic events 1a and 2 (Fig. 1A) are large compared to excursions observed across the end-Ordovician mass extinction (−0.5–0.6‰; Holmden et al., 2012a), during the Cretaceous Ocean Anoxic events 1a and 2 (−0.4 and 0.2‰, respectively; Blättler et al., 2011) and at the Permian–Triassic boundary (−0.3‰; Payne et al., 2010). The δ⁴⁴/⁴₀Ca changes observed in the Wonoka Fm. are unlikely to represent changes in the δ⁴⁴/⁴₀Ca value of Ediacaran seawater, given constraints from the modern calcium budget. As seawater Ca has one sink (Fig. 4A), mechanisms to change the δ⁴⁴/⁴₀Ca of seawater (δ⁴⁴/⁴₀Ca_sw) include (a) changing the degree of fractionation expressed between seawater and CaCO₃ output (e.g., Sime et al. (2007), Farkas et al. (2007), Fantle (2010), Blättler et al. (2012); Fig. 4B), (b) transient mass flux imbalances, causing [Ca] in seawater to rise or fall (e.g., De La Rocha and DePaolo (2000), Fantle and DePaolo (2005), Payne et al. (2010), Blättler et al. (2011); Fig. 4C), or (c) changing the isotopic composition of the Ca input flux (e.g., Griffith et al., 2008).

To use the first mechanism (a) to explain the 1.2‰ δ⁴⁴/⁴₀Ca downturn in δ⁴⁴/⁴₀Ca seen in the Wonoka Fm. (Figs. 5 and 6B), a step change in the mineralogy of the global CaCO₃ output flux from calcite to aragonite (ɛ⁴⁴/⁴₀ ≈ 0.8‰ and ɛ⁴⁰/⁰ ≈ 1.7‰ where ɛ = δ⁴⁴/⁴₀Ca_sw - δ⁴⁴/⁴₀Ca_CaCO₃; Gussone et al., 2005) would cause a negative excursion of −0.9‰ (Fig. 4B; see also Fantle, 2010). Such a change would be necessary transient, and recover over the time-scale of the Ca residence time (−0.5–1 Myr). As seawater becomes more enriched over its sources of Ca, the now-aragonite CaCO₃ output flux would become more enriched with time as well, stabilizing at a value equal to the input fluxes (−1.1‰; Fig. 4B). To use mass flux imbalances (b) as the mechanism, the global CaCO₃ sink would need to shut down for 1–3 Myr (depending on the concentration of Ca in Ediacaran seawater); this forcing would push δ⁴⁴/⁴₀Ca_sw negatively towards the riverine input value (Fig. 4C). Any carbonate which forms would therefore be δ⁴⁴/⁴₀Ca lighter than carbonates before the sink crashed. Even without considering how the CaCO₃ sink could collapse, it would imply δ⁴⁴/⁴₀Ca values before the basin closed. Experimental work has shown that precipitation rate can control both δ⁴⁴/⁴₀Ca and [Sr] in calcite; increasing precipitation rate by 2 orders of magnitude lowered the δ⁴⁴/⁴₀Ca of the resulting solid by −1.1‰, and increased [Sr] from 400 to 1400 ppm (Tang et al., 2008). The anti-correlation developed by this precipitation rate mechanism is linear, however, and cannot explain the observations from section 9 (Fig. 7B). Alternatively, the sympathetic behavior between [Sr] and δ⁴⁴/⁴₀Ca can be explained with a change in mineralogy. The calcite polymorph is heavier in δ⁴⁴/⁴₀Ca compared to aragonite by −0.9‰ (Fig. 4A). Sr concentrations in modern marine precipitates range between 500–1000 ppm for abiotic calcite (Carpenter and Lohmann, 1992) and 8000–10,000 ppm for aragonitic ooids of The Bahamas and Persian Gulf (Kinsman, 1969). Under this model, the 1.2‰ drop in δ⁴⁴/⁴₀Ca observed in the basal Wonoka canyon-shoulder (Figs. 5 and 6B) is driven mainly by a change from calcite to aragonite (although all Wonoka limestones are now calcite, regardless of their primary polymorph). This model requires that the naturally occurring primary crystals which formed the Wonoka Fm. display a basinwide change in carbonate mineralogy (Gussone et al., 2005), or a local fluid (a seawater–freshwater mixture) that does not reflect seawater δ⁴⁴/⁴₀Ca (Holmden et al., 2012a,b). Two additional lines of evidence support a local process: (1) the covariation between δ⁴⁴/⁴₀Ca and δ¹³C_carb and (2) the covariation between δ⁴⁴/⁴₀Ca and Sr contents. Carbon and calcium have residence times in the modern ocean which differ by an order of magnitude. While models exist which describe sympathetic excursions in both systems (i.e., a massive carbon injection causing negative excursions in the global C and Ca pools; Payne et al., 2010), δ⁴⁴/⁴₀Ca is expected to recover more slowly than δ¹³C_carb. Thus, the observation from the Wonoka Fm. that both δ⁴⁴/⁴₀Ca and δ¹³C_carb appear to return synchronously to pre-exursion values (above 0‰ for carbon and −0.8‰ for calcium; uppermost 200 m in Figs. 5 and 6B) argues for an alternative control on Ca isotope variability.

Wonoka canyon-shoulder carbonates from all four measured sections display clear anti-correlation between δ⁴⁴/⁴₀Ca and [Sr] (Figs. 6B, F and 7B). The relationship is roughly linear in sections 2, 4, and 6, but appears to saturate in section 9 (Fig. 7B). Anti-correlation between [Sr] and δ⁴⁴/⁴₀Ca is observed also in the Saint Ronan breccia clasts (Fig. 3B), thus indicating that this relationship was developed syn-depositionally and is not the product of late-stage diagenesis or alteration. Breccia flows at Saint Ronan range from 0.1 to 0.9 m thick (Husson et al., 2012, 2015), yet show impressive variability in both [Sr] (between 500 and 4000 ppm) and δ⁴⁴/⁴₀Ca (between −0.8‰ and −2.0‰) on measurements of individual clasts (green dots in Fig. 8B). The geochemical variability of clasts from individual flow deposits indicates that the clasts acquired their [Sr] and δ⁴⁴/⁴₀Ca values before being brecciated and redeposited at the bases of the Wonoka paleocanyons.

If the Wonoka Ca isotopic record cannot be easily explained by changes in the global Ca cycle, an alternative is that it reflects an inherently more local process – i.e., a
a calcium isotope offset between calcite and aragonite similar to abiogenic precipitation experiments (Gussone et al., 2005). As the ultimate source of carbonate mud in the Wonoka Fm. remains unknown, assessing whether it represents pure abiogenic precipitation remains a challenge.

In addition, a model that attributes the Ca isotope variability to changes in mineralogy requires that, in intervals that are inferred to be fully or partly aragonitic (based on $\delta^{44/40}Ca$ and [Sr] values), neomorphism to calcite did not reset $\delta^{44/40}Ca$ to heavier values; in other words, these samples were a closed system during recrystallization with respect to Ca, and inherited the more depleted $\delta^{44/40}Ca$ values from the parent aragonite crystal lattice. In most cases (sections 2, 4 and 6 on Fig. 6F), some Sr was lost during this (or some later) transformation; only section 9 preserves potentially aragonitic values of [Sr], and follows a roughly hyperbolic curve in $\delta^{44/40}Ca$-[Sr] cross-plot space predicted by end-member mixing (dashed line in Fig. 7B). This [Sr] loss caused no observable or systematic offset between section 9 and sections 2, 4 and 6 in $\delta^{44/40}Ca$ space (Fig. 6B). Thus, if mineralogy is controlling $\delta^{44/40}Ca$ variability, calcium isotopes are a more faithful recorder of primary mineralogy than trace geochemical systems like [Sr] in the Wonoka Fm.

An important implication of interpreting the negative $\delta^{44/40}Ca$ values as inheritance from an originally aragonite polymorph is that aragonite could not have been a quantitatively important component of the global CaCO$_3$ output, at least from a Ca isotope perspective, during the deposition of the Wonoka Fm. Mass balance at steady state requires the CaCO$_3$ output to match isotopically the riverine source of Ca ($-1.1_{\text{‰}}$). Thus, if the global carbonate sink is aragonite, it will have a Ca isotopic value of $-1.1_{\text{‰}}$ (end of model run on Fig. 4B); to observe the full $\sim-0.9_{\text{‰}}$ isotopic difference between calcite and aragonite in the Wonoka $\delta^{44/40}Ca$ record (Figs. 5 and 6B), the global sink must necessarily be calcitic (Blättler et al., 2012). A quantitatively important, global aragonite sink would predict primary aragonite to have $\delta^{44/40}Ca$ values equal to riverine input ($-1.1_{\text{‰}}$), not $-1.9_{\text{‰}}$ (Fantle and Tipper, 2014). Previous work has suggested that at least the latest Ediacaran was an ‘aragonite-sea’ interval, based upon the preservation style of ooids (Hardie, 1996), presence of MgSO$_4$-rich potash deposits (Hardie, 1990), and high (>2) Mg/Ca ratios inferred from measurements of fluid inclusions in halite (Lowenstein et al., 2001; Horita et al., 2002; Kovalevych et al., 2006). The $\delta^{44/40}Ca$ results from the Wonoka Fm. do not necessarily argue against aragonite being the favored, or even primary, CaCO$_3$ polymorph in the Ediacaran; they only require that CaCO$_3$ that is eventually buried carry a calcitic $\epsilon^{44/40}$ offset from contemporaneous seawater (Fig. 4A and B). As neomorphism from aragonite to calcite crystal lattices can occur very early after deposition in modern settings (Macintyre and Reid, 1995; Furukawa et al., 1997; Reid and Macintyre, 1998; Walter et al., 2007), the Ca system could still be open to seawater, and allow for isotopic re-setting to a smaller, calcitic $\epsilon^{44/40}$ value. As this shift towards heavier values is not observed in the middle portion of the Wonoka canyon-shoulder stratigraphy, closed-system recrystallization is implied, with preservation of primary geochemical signals (i.e., [Sr] and $\delta^{44/40}Ca$).

### 5.2. Constraints from breccia clasts

If the fall in $\delta^{44/40}Ca$ in the basal Wonoka canyon-shoulder is controlled by mineralogy, can the same mechanism be invoked for the rise in $\delta^{44/40}Ca$ in the upper canyon-shoulder (namely, a switch back to calcite above 500 m in Fig. 6B)? The upper limb of the $\delta^{44/40}Ca$ curve differs in several important ways from the basal negative excursion. In each section (Fig. 5), onset of the $\delta^{44/40}Ca$ rise coincides with a facies change, coeval with the first appearance of abundant, thicker-bedded (10–30 cm, as opposed to 2–5 cm beds of the basal carbonate mudstones) grainstones, which are variably affected by a fabric-destructive, syn-depositional diagenetic texture called stylolodontal bedding (Haines, 1988; Husson et al., 2015). The canyon-shoulder becomes more dolomitic above this coarsening horizon, as indicated by rising Mg/Ca values, with the Wonoka fully dolomitized for the final $\sim100$ m (Fig. 6C). These stratigraphic relationships lead to distinctive patterns in $\delta^{44/40}Ca$-Mg/Ca cross-plot space; samples hosting the upper, rising limb of the $\delta^{44/40}Ca$ curve (circles in Fig. 7D) exhibit a positive correlation between $\delta^{44/40}Ca$ and Mg/Ca, and this log-linear array is composed mostly of grainstone samples (green-colored symbols in Fig. 7D). These patterns contrast strongly with lower limb samples (i.e., those samples hosting the downturn in $\delta^{44/40}Ca$; square symbols in Fig. 7D), which are composed of micrite and show the full range of $\delta^{44/40}Ca$ values observed in the Wonoka dataset over a narrow range of Mg/Ca. There are few $\delta^{44/40}Ca$ studies to date on dolomite and dolomitizing processes (Tipper et al., 2008; Jacobson and Holmden, 2008; Komiya et al., 2008; Holmden, 2009; Fantle and Higgins, 2014). Studies of sediment cores and pore-fluids suggest that the equilibrium fractionation factor ($\alpha$) between fluid Ca$^{2+}$ and CaCO$_3$ approaches 1.000 at slow recrystallization rates (Fantle and DePaolo, 2007; Jacobson and Holmden, 2008). If a similar fractionation factor applies to the formation of dolomite and if the system remained open to seawater Ca, dolomitization may push $\delta^{44/40}Ca$ values of CaCO$_3$ heavier, without requiring any isotopic change in the global marine Ca reservoir (Fantle and Higgins, 2014). While instances of dolomitization in the Ordovician Williston Basin have resulted in more negative $\delta^{44/40}Ca$ values, the formation fluid for these dolomites was interpreted as having a $\delta^{44/40}Ca$ value significantly more negative than contemporaneous sea water (Holmden, 2009). An $\alpha$ during dolomitization close to 1.000 may also help explain the large difference between the observed $\delta^{44/40}Ca$ values from the Wonoka canyon-shoulder ($-1.9_{\text{‰}}$ to $-0.7_{\text{‰}}$; Figs. 5 and 6B) and values from putatively correlative, extensively dolomitized Ediacaran strata from South China (Sawaki et al., 2014).
where $\delta^{44/40}\text{Ca}$ values are much heavier and range between $-0.5\%_{\text{oo}}$ and $0\%_{\text{oo}}$.

The stratigraphic evidence therefore suggests that the rise in $\delta^{44/40}\text{Ca}$ in the upper canyon-shoulder is related to dolomitization (Figs. 6B, D and 7D). Constraints on the timing of dolomitization on the canyon-shoulder comes from the geochemistry of the clast populations of Mount Thomas and Saint Ronan paleocanyons (Fig. 3). Dolostones contain 14% of the carbonate clast population of Mount Thomas (Fig. 9B and C), as measured by point count surveys of breccia faces in the field, comparable to the abundance observed in canyon-shoulder sections (as measured by stratigraphic thickness) of 9% (see Husson et al. (2015) for more details). Dolostones of the Mount Thomas breccias, however, cover a much larger $\delta^{13}\text{C_{carb}}$ range ($-10\%_{\text{oo}}$ to $+5\%_{\text{oo}}$) Husson et al. (2015) and Fig. 8A) than dolostones of the canyon-shoulder, which are restricted mostly to values above $0\%_{\text{oo}}$ (Fig. 7A). By contrast, the Saint Ronan breccias contain no dolostone clasts (Fig. 8D). Even though the observed range in $\delta^{13}\text{C_{carb}}$ values of the Saint Ronan can something smaller than Mount Thomas ($-9\%_{\text{oo}}$ to $-3\%_{\text{oo}}$, as opposed to $-12\%_{\text{oo}}$ to $+5\%_{\text{oo}}$), the canyon-shoulder horizons contain dolomitic (Mg/Ca >100) horizons with $\delta^{13}\text{C_{carb}}$ values as low as $-6.3\%_{\text{oo}}$. In other words, based on comparison to intact canyon-shoulder profiles, dolomitic Saint Ronan clasts with $\delta^{13}\text{C_{carb}}$ values above $-6\%_{\text{oo}}$ are expected if dolomitization occurred before brecciation and redeposition in the canyon-fill (Fig. 8A). The Saint Ronan clasts, however, have the lowest Mg/Ca values in the full Wonoka dataset (Fig. 8D). Thus, at least in canyon-shoulder sections feeding the Saint Ronan paleocanyon, dolomitization occurred after the paleocanyon (Fig. 2B) had been cut and filled. By contrast, further north, the relatively small number of dolostones in individual flows ($\sim$14%) suggests that dolomite formation was not in-situ after breccia deposition, but rather occurred in the canyon-shoulder sources feeding the deeper paleocanyon at Mount Thomas before canyon-filling had commenced (Fig. 2A; see caption of Fig. 9B–E). The larger range in Mount Thomas dolomite $\delta^{13}\text{C_{carb}}$ suggests that the now-eroded canyon-shoulder sections, which fed the Mount Thomas paleocanyon, were more pervasively dolomitized (Husson et al., 2015).

Like the observations from the canyon-shoulder, data from the clast populations suggests that dolomite formation, in the case of the Wonoka Fm., shifts $\delta^{44/40}\text{Ca}$ towards heavier values. In $\delta^{44/40}\text{Ca}-\delta^{13}\text{C_{carb}}$ cross-plot space, the undolomitized Saint Ronan clasts (dark green symbols in Fig. 8A) display a single, negatively correlated linear array, as opposed to the canyon-shoulder data that have negatively and positively correlated limbs (the latter of which contains the canyon-shoulder dolomites). Mount Thomas clasts have the same range in $\delta^{13}\text{C_{carb}}$ values ($-12\%_{\text{oo}}$ to $+5\%_{\text{oo}}$) as the intact canyon-shoulder (Fig. 8A; Husson et al., 2012, 2015), suggesting that these breccias sampled complete sections of the canyon-shoulder. In the absence of secondary processes, similar values in $\delta^{44/40}\text{Ca}$ between Mount Thomas clasts and canyon-shoulder samples likewise are expected. Thus, the dearth of very negative $\delta^{44/40}\text{Ca}$ values in the Mount Thomas dataset (4 values out of 47 total are below $-1.5\%_{\text{oo}}$ Fig. 8A) is evidence that the more dolomitic clasts have been pushed towards heavier values; by contrast, 40% of canyon-shoulder $\delta^{44/40}\text{Ca}$ values ($n = 186$) are below $-1.5\%_{\text{oo}}$.

The balance of evidence from the breccia dataset, therefore, suggests that the transformation to dolomite has altered the primary $\delta^{44/40}\text{Ca}$ values of Wonoka carbonates, and is consistent with dolomitization occurring under open system conditions for Ca. Dolomite formation post-dated filling of the Saint Ronan paleocanyon, apparent from the absence of dolomite clasts in the Saint Ronan canyon-fill (Fig. 8D) and the observation that unit 11, the only major dolostone interval in the Wonoka Fm., conformably overlays both canyon-fill and lower canyon-shoulder sections at Saint Ronan (Fig. 2B; Husson et al., 2012, 2015). These upper Wonoka Fm. dolomites are found in the coarsest grained lithofacies of the canyon-shoulder (Figs. 5 and 6A, B, D). The stratigraphic expression of both the Mg/ Ca and $\delta^{44/40}\text{Ca}$ profiles – both increasing towards the top of the canyon-shoulder sections – is suggestive of alteration from above, with downward percolation of dolomitizing fluids perhaps developed in the shallow-water, periodically exposed, lagoonal facies of unit 11 (Haines, 1988; Husson et al., 2012, 2015). Alteration of $\delta^{13}\text{C_{carb}}$, signals in this scenario depends upon the amount of carbon carried by the dolomitizing fluid and its isotopic composition (see below). As this model hinges on post-depositional fluid-rock interactions, the most permeable horizons (a function of grain size, shape and packing, and thus directly related to lithofacies) are most susceptible to alteration, leading to the facies-sorted pattern in both Mg/Ca and $\delta^{44/40}\text{Ca}$ values (Fig. 8D).

5.3. Predicted diagenetic patterns in $\delta^{44/40}\text{Ca}$, $\delta^{26}\text{Mg}$ and $\delta^{13}\text{C}$ in carbonates

If $\delta^{44/40}\text{Ca}$ appears to be variably reset by dolomite formation processes in the upper canyon-shoulder and Mount Thomas clast populations, what are the implications for preserving other isotopic records? Consideration of the Mg isotope dataset further motivates this question. In the upper canyon-shoulder, increasing dolomitization controls $\delta^{26}\text{Mg}$ (Fig. 6C), with the rise of $\sim-1.0\%_{\text{oo}}$ consistent with the difference in $\epsilon$ between limestones and dolostones (Fig. 4A). Thus, canyon-shoulder carbonates broadly fit a single hyperbolic mixing curve in Mg/Ca-$\delta^{26}\text{Mg}$ space (Fig. 9A). Dolomites from the breccia units of Mount Thomas, however, are distinctly more negative ($\mu = -2.5\%_{\text{oo}}, 2\sigma = 0.3$) than the dolomites of the upper canyon-shoulder ($\mu = -1.8\%_{\text{oo}}, 2\sigma = 0.4$; Fig. 9A), implying different formation fluids/processes for the two populations of dolomite, or differential alteration of the $\delta^{26}\text{Mg}$ signal across the basin. The breccia clast population is also different from putatively correlative dolostone samples from Siberia (Pokrovsky et al., 2011), whose values range between $-2.0\%_{\text{oo}}$ and $-1.0\%_{\text{oo}}$ and therefore are similar to
dolostones from the Wonoaka canyon-shoulder (uppermost samples in Fig. 6C). One possible process to explain the more negative $\delta^{26}\text{Mg}$ values of the Mount Thomas dolomite clasts (Fig. 9A) would be a dolomitizing fluid that is depleted relative to seawater – a phenomena that could in theory be due to either the addition of Mg associated with the dissolution of Mg-carbonates or removal of Mg due to the formation of Mg clays (Higgins and Schrag, 2010). The former can be excluded because it would predict very low $\delta^{44}\text{Ca}$ values, as is observed in modern shallow marine carbonates which formed in environments influenced by submarine groundwater discharge (Holmden et al., 2012b); dolomitized clasts, however, are heavy in $\delta^{44}\text{Ca}$ value relative to other Wonoaka carbonates (Fig. 8A).

In order to assess the relative robustness of the $\delta^{44/40}\text{Ca}$, $\delta^{26}\text{Mg}$ and $\delta^{13}\text{C}$ systems to diagenesis, we performed simple calculations of the isotopic effects of fluid-rock interactions (Taylor, 1977; Nabelek, 1987; Banner and Hanson, 1990; Jacobsen and Kaufman, 1999). The models presented in Fig. 10 seek to describe how the isotopic composition of carbonate sediment evolves with progressive (i.e., an increasing water-to-rock (W/R) ratio) alteration by a diagenetic fluid in both closed (i.e., a single batch equilibration at a W/R value) and open (i.e., iterative alteration with passing parcels of fluid) systems. For isotopic tracers of any element, the W/R value at which the system becomes fully reset to a new, altered value depends entirely on the relative concentrations of the element in the fluid and solid. These models describe ‘passive’ isotopic exchange, and do not attempt to model the equilibrium chemistry between altering fluids and mineral phases (Derry, 2010). Thus, if modern seawater is the altering fluid, robustness against resetting proceeds as $\delta^{26}\text{Mg} < \delta^{44/40}\text{Ca} < \delta^{13}\text{C}$ (Fig. 10B–D), given that seawater concentrations progress $[\text{Mg}] > [\text{Ca}] > [\text{DIC}]$, and Mg is a trace constituent of the solid. $\delta^{26}\text{Mg}$ is altered at the lowest W/R, followed by $\delta^{44/40}\text{Ca}$ and finally $\delta^{13}\text{C}$. (E) These calculations were performed for a variety of fluid compositions, with the W/R value at which a given isotopic system becomes fully reset plotted as a function of seawater-normalized element concentration in the altering fluid (ranging from 0.1 to 4× modern seawater concentrations for Mg, Ca and C).

Fig. 10. (A–D) Simulations of carbonate diagenesis in both an open and closed system, after Banner and Hanson (1990) and Jacobsen and Kaufman (1999), involving a fluid with modern seawater concentrations of Ca, Mg and C and a limestone with an Mg/Ca of 12.5 mmol/mol. Isotopic change can be caused by either the altering fluid having a different isotopic value than the primary formation fluid or by the expression of a different fractionation factor under diagenetic conditions (as in Fantle and DePaolo (2007) and Jacobson and Holmden (2008) for Ca). Isotopic resetting progresses from left-to-right, with increasing W/R values; ‘fully reset’ is defined as the inflection point (marked by closed circles) on the altered side of the curves. The model was run again with a meteoric fluid that lacked dissolved Mg$^{2+}$, Ca$^{2+}$ or DIC to highlight the ease of resetting $\delta^{18}\text{O}$ in these styles of models. As seawater concentrations progress $[\text{Mg}] > [\text{Ca}] > [\text{DIC}]$, and Mg is a trace constituent of the solid, $\delta^{26}\text{Mg}$ is altered at the lowest W/R, followed by $\delta^{44/40}\text{Ca}$ and finally $\delta^{13}\text{C}$. (E) These calculations were performed for a variety of fluid compositions, with the W/R value at which a given isotopic system becomes fully reset plotted as a function of seawater-normalized element concentration in the altering fluid (ranging from 0.1 to 4× modern seawater concentrations for Mg, Ca and C).
show a wide range in portion to be syn-depositional, as the Saint Ronan clasts strain the timing of this potential resetting in the basal Wonoka Fm., as they predict full resetting at the lowest W/R values (Fig. 10A and E) and do not produce linear arrays between $\delta^{13}$C$_{carb}$ and $\delta^{18}$O$_{carb}$. Wonoka Fm. carbonates, by contrast, show strong covariation between $\delta^{13}$C$_{carb}$ and $\delta^{18}$O$_{carb}$, especially for $\delta^{13}$C$_{carb}$ values less than $-5\%$ (r$^2$ values on Fig. 5). Thus, while late stage alteration models, which have sought to explain this covariation (Derry, 2010), are not viable for the Wonoka Fm. (Husson et al., 2012, 2015), explaining the observed correlations between $\delta^{13}$C$_{carb}$ and $\delta^{18}$O$_{carb}$ in South Australia and in other ‘Sharam’ excursion successions remains a challenge (Grotzinger et al., 2011).

5.4. Connections between Wonoka $\delta^{13}$C$_{carb}$ and $\delta^{44/40}$Ca

If the upper rise in $\delta^{44/40}$Ca was acquired during post-depositional dolomitization (Fig. 7D), could the basal, more positive values in $\delta^{44/40}$Ca (lowermost 100–200 m in Figs. 5 and 6B) also be the result of open-system recrystallization? In other words, did all Wonoka Fm. carbonate originally carry aragonitic $\delta^{44/40}$Ca values before being variably reset? Evidence for recrystallization and isotopic resetting in the lowermost Wonoka Fm. is particularly important to evaluate, given that the nadir in $\delta^{13}$C$_{carb}$ ($-12\%$$_{oo}^\circ$) is found in these horizons. While the current dataset cannot rule out this possibility explicitly, it does constrain the timing of this potential resetting in the basal portion to be syn-depositional, as the Saint Ronan clasts show a wide range in $\delta^{44/40}$Ca values (Fig. 5A). The Saint Ronan clasts, in fact, host the transitional basal values (i.e., between $-0.8$ and $-1.8\%$$_{oo}^\circ$) that are not present across the unit 3/4 transition in section 9 (discontinuity in the $\delta^{44/40}$Ca profile of section 9 at $\sim$160 m; Fig. 5). As section 9 is immediately adjacent to the Saint Ronan paleocanyon (Fig. 2B), the observation of transitional values in the Saint Ronan breccias suggests that the horizons directly beneath the unit 3/4 transition in section 9 have been eroded and sloughed down-slope into canyon-fill (Husson et al., 2015). Thus, in the basal carbonates, unlike in the upper Wonoka Fm., any potential transformation to more positive $\delta^{44/40}$Ca values must have occurred before those carbonates were eroded and re-deposited in the Saint Ronan canyon-fill.

Even if basal $\delta^{44/40}$Ca values are reset, the implications for $\delta^{13}$C$_{carb}$ are unclear. In addition to simple diagenetic models which suggest that $\delta^{13}$C$_{carb}$ is more rock-buffered during fluid-rock interactions than $\delta^{44/40}$Ca (Fig. 10E), the relationship between $\delta^{13}$C$_{carb}$ and relatively heavy $\delta^{44/40}$Ca is not constant throughout the Wonoka Fm. dataset. Namely, the base shows a negative correlation between $\delta^{13}$C$_{carb}$ and $\delta^{44/40}$Ca, with the nadir in $\delta^{13}$C$_{carb}$ associated with the most positive $\delta^{44/40}$Ca values, while the top shows a positive correlation (Fig. 7A). This switch in the $\delta^{13}$C$_{carb}$-$\delta^{44/40}$Ca relationship occurs despite a consistent, positive relationship between $\delta^{44/40}$Ca and [Mn] (Fig. 7C), a traditional indicator of diagenetic alteration (Brand and Veizer, 1981). The observed enrichments in [Mn] in the Wonoka Fm. are considerable; basal horizons have Mn abundances of $\sim$7000 ppm (Fig. 5E and G), whereas core-top foraminifera calcite tests are $\sim$10 ppm (Boyle, 1983), modern corals range between 0.01 and 0.5 ppm (Shen et al., 1991), and Phanerozoic carbonates classified as ‘well-preserved’ (mainly based on high, aragonitic concentrations of Sr) are generally less than 200 ppm (Brand and Veizer, 1981). Mn abundances in the upper-most Wonoka Fm., however, where $\delta^{13}$C$_{carb}$ values range between $0\%$$_{oo}^\circ$ and $+8\%$$_{oo}^\circ$, are also impressively high ($\sim$7000 ppm; Fig. 5E and G). Although the upper-most Wonoka Fm. is dolomitized (Fig. 6D), the implied formation (or alteration) fluid Mn concentrations are comparable even when considering the different Mn distribution coefficients for calcite and dolomite ($k_{D,calc}^{calc}$/k$_{D,calc}^{dol}$ $\approx$0.8; Kretz, 1982). Thus, in the Wonoka Fm., relatively high [Mn] values (and lower $\delta^{44/40}$Ca values) are not always associated with low $\delta^{13}$C$_{carb}$ values.

Regardless of [Mn] or Ca isotope evidence for diageneis in the basal Wonoka Fm., the best preserved interval of the Wonoka Fm., based upon aragonitic values for both [Sr] and $\delta^{44/40}$Ca, occurs between 200 and 500 m (Fig. 6B and F) where $\delta^{13}$C$_{carb}$ values are between $-8\%$$_{oo}^\circ$ and $-7\%$$_{oo}^\circ$. As aragonite is heavier in $\delta^{13}$C$_{carb}$ relative to calcite by $\sim$2$\%$$_{oo}^\circ$ (Romanek et al., 1992), the recorded Wonoka $\delta^{13}$C$_{carb}$ are equivalent to $-10\%$$_{oo}^\circ$ to $-9\%$$_{oo}^\circ$, if the primary polymorph forming from seawater had been calcite. This difference in $\delta^{1}$C between aragonite and calcite may therefore help explain some, but not all, of the $\sim$4–5$\%$$_{oo}^\circ$ rise in $\delta^{13}$C$_{carb}$ over the lowermost 100–200 m of the Wonoka Fm. (Fig. 6G), as the $\delta^{44/40}$Ca values shift from calcite to aragonitic values (Fig. 6B). These $\delta^{13}$C$_{carb}$ values ($\sim$4–5$\%$$_{oo}^\circ$ below the canonical $-5\%$$_{oo}^\circ$ value for mantle carbon) are extremely negative relative to other intervals of Earth history (Halverson et al., 2007). Geochemical evidence from $\delta^{44/40}$Ca and [Sr] measurements, however, strongly suggest that these anomalous $\delta^{13}$C$_{carb}$ values are primary products of the Ediacaran surface environment.

Reasons for why the geochemistry of the Wonoka Fm. records a switch to (or improved preservation of) a primary aragonite polymorph, and any connection to $\delta^{13}$C$_{carb}$, are not immediately apparent. Global forcings could be considered, with the basal drop in Wonoka Fm. $\delta^{44/40}$Ca values indicative of a switch from calcite to aragonite in the favored marine CaCO$_3$ precipitate. These scenarios do not necessarily require $\delta^{44/40}$Ca change in the global seawater pool; the Wonoka Fm. may represent local
geochemical preservation of the newly preferred polymorph. Changing seawater Mg/Ca, driven by changes in global tectonics and seafloor spreading rates, traditionally has been invoked to explain long-term (~100 Myr) oscillations between aragonite and calcite seas (Hardie, 1996; Lowenstein et al., 2001). Such a forcing is unlikely to affect a calcite to aragonite switch over this 100–150 m thick interval, which is predicted to represent 1–8 Myr of time under the current end-member estimations of the duration of the full δ13C_carb excursion (Le Guerroué et al., 2006b; Bowring et al., 2007). Increasing temperature has been shown experimentally to favor aragonite precipitation, even at low Mg/Ca values (Morse et al., 1997). In the context of carbon injection models for the ‘Shuram’ excursion (Rothman et al., 2003; Bristow and Kennedy, 2008), however, one may expect the switch to aragonite to be coeval with the nadir in δ13C_carb, whereas in the Wonoka Fm., the apparent switch to aragonite lags the most negative δ34S_carb values.

Recent experimental work has shown that the presence of SO42− encourages aragonite formation; however, if Mg/Ca is above 2, aragonite forms even if SO42− is absent from the formation fluid (Bots et al., 2011). Therefore, if rising [SO42−] levels in the Ediacaran, a model that has been proposed and interrogated by numerous sulfur isotope studies (Fike et al., 2006; McFadden et al., 2008; Li et al., 2010; Sahoo et al., 2012), are a trigger for the formation of Wonoka aragonite, Mg/Ca levels must be below 2 during Wonoka Fm. deposition. Mg/Ca values from fluid inclusions in halite of the Ara Gp. of Oman, which overlies the Shuram Fm. and is dated by U–Pb ash bed geochronology to be ~547 Ma; (Bowring et al., 2007), are 3–5 (Lowenstein et al., 2001). Thus, the viability of seawater Mg/Ca being less than 2 depends upon how much the ‘Shuram’ excursion pre-dates deposition of the Ara Group, and how quickly seawater Mg/Ca can evolve. Evaluating models which seek to explain the preservation of these aragonitic geochemical signals, and its connection to ‘Shuram’ excursion, would be well served by similar datasets from other Ediacaran sections, and thus test whether the strong δ34S_carb-δ44/40Ca relationships observed in the Wonoka Fm. are observed globally.

Regardless of the driver for a switch to aragonite, the preservation of aragonitic δ44/40Ca values in the Wonoka Fm. is noteworthy. While the preservation potential of aragonite Ca isotope values in modern carbonate platform and periplatform sediments is a topic of active research, the first-order expectation is that it should be low, as neomorphism to calcite occurs almost immediately after deposition (Reid and MacIntyre, 1998). This widespread diaGenesis may be early enough such that Ca remains open to seawater, thereby allowing δ44/40Ca of the transformed sediment to be reset to higher, calcitic values (Fantle and Higgins, 2014). Thus, given constraints from modern settings, geochemical signatures in the middle portion of Wonoka Fm. stratigraphy – between 200 and 500 m, where δ44/40Ca is as low as −1.9‰ (Fig. 6B) – are very well preserved, despite δ13C_carb values of −8 to −7‰. Considering the differences in ε13C between carbonate polymorphs, these δ13C_carb values would be equivalent to ~ −10‰ if recorded in calcite. If such negative δ13C_carb are the result of an admixture of primary aragonite and authigenic calcite (Schrag et al., 2013), the authigenic end-member is required to be extremely depleted in δ13C_carb. For example, if primary carbonate has a δ13C_carb of 0‰, and a δ44/40Ca value of −2.0‰ (aragonite end-member in a calcite-sink sea; Fig. 4B), and authigenic calcite has a δ44/40Ca value of −0.7‰ (heavier than the global sink of −1.1‰ owing to a smaller δ44/40 during pore-space carbonate precipitation; Fantle and DePaolo, 2007), its δ13C_carb would be required to be −104‰ to produce an admixture with δ13C_carb of −8 and δ44/40Ca value of −1.9‰. In addition to being 30 to 40‰ more negative than any documented authigenic carbonate (Campbell et al., 2002; Bristow and Grotzinger, 2013), tiny variations in the amount of this diagenetic end-member would cause huge variations in the δ13C_carb of the resulting mixture. The δ44/40Ca profile of the Wonoka Fm., however, varies less than 0.5–1.0‰ across the entire basin (Husson et al., 2015; see also Fig. 6G). An admixture of authigenic calcite, therefore, is not a tenable hypothesis to explain values of −8‰ to −7‰ in the Wonoka Fm. of South Australia, and in turn must be products of the Ediacaran marine environment.

Whether such values are reflective of the secular evolution of the global DIC pool, or are the result of more local processes that are happening in Ediacaran basins around the world, remains to be established (Grotzinger et al., 2011). In this regard, independent estimates of age and duration of the Ediacaran excursions is that they are found in disparate marine basins (Fig. 5; Husson et al., 2012, 2015) and other Ediacaran chemostратigraphic datasets (Grotzinger et al., 2011). Whether explained by a fundamentally local or global carbon cycle process, a defining observation of these Ediacaran excursions is that they are found in disparate marine basins (Fig. 1A) and are unique in Earth history. Thus, any successful model must address why such excursions are pervasive worldwide and restricted in time to the Ediacaran Period.
6. CONCLUSIONS

In the Ediacaran-aged Wonoka Formation, large, stratigraphically coherent changes in 4 canyon-shoulder sections are observed in $\delta^{26}\text{Mg}$ and $\delta^{44/40}\text{Ca}$. In both systems, based upon constraints from modern ocean budgets, the changes are too large to explain via evolving global seawater reservoirs of Mg and Ca, and relationships with abundances of Mg and Sr suggest a mineralogical control. For magnesium, a stratigraphic transition from limestone to dolostone explains the $\sim 1\%_{\text{ro}}$ rise in $\delta^{26}\text{Mg}$. For calcium, the initial $\sim 1.2\%_{\text{ro}}$ negative excursion is driven by increasing preservation of primary aragonite geochemistry, with the following $\sim 1.2\%_{\text{ro}}$, positive recovery at the top related to post-depositional transformation to dolostone that follows a facies-organized pattern of alteration. The most pristine samples in the Wonoka dataset, preserving $\sim 7000$ ppm Sr concentrations and distinctly aragonitic values of $\delta^{44/40}\text{Ca}$, have $\delta^{34}\text{C}_{\text{arb}}$ of $-8\%_{\text{ro}}$ to $-7\%_{\text{ro}}$, thereby providing strong geochemical evidence that extremely negative $\delta^{34}\text{C}_{\text{arb}}$ are primary products of the Ediacaran marine environment, given the preservation potential of $\delta^{44/40}\text{Ca}$ and $\delta^{34}\text{C}_{\text{arb}}$ deduced from simple models of rock diagenesis and end-member calculations.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2015.03.012.

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