Demise of Ediacaran dolomitic seas marks widespread biomineralization on the Siberian Platform

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ABSTRACT

The trigger for biomineralization of metazoans in the terminal Ediacaran, ~550 million years (Ma) ago has been suggested to be the rise of oxygenation or an increase in sea water Ca concentration, but geochemical and fossil data have not been fully integrated to demonstrate cause and effect. Here we combine the record of macrofossils with early marine carbonate cement distribution within a relative depth framework for terminal Ediacaran to Cambrian successions on the eastern Siberian Platform, Russia to interrogate the evolution of sea water chemistry and biotic response. Prior to ~545 Ma the presence of early marine ferroan dolomite cement suggests dominantly ferruginous anoxic ‘aragonite-dolomite seas’, with a very shallow oxic chemocline that supported
mainly soft-bodied macrobiota. After ~545 Ma, marine cements changed to
aragonite/high-Mg calcite, and this coincides with the appearance of widespread
aragonite and high-Mg calcite skeletal metazoans suggesting a profound change in sea
water chemistry to ‘aragonite seas’ with a deeper chemocline. By early Cambrian Stage
3, the first marine low-Mg calcite cements appear coincident with the first low-Mg calcite
metazoan skeletons suggesting a further shift to ‘calcite seas’. We suggest that this
evolution of sea water chemistry was caused by enhanced continental denudation that
increased the input of Ca into oceans so progressively lowering Mg/Ca which, combined
with more widespread oxic conditions, facilitated the rise of skeletal animals and in turn
influenced the evolution of skeletal mineralogy.

INTRODUCTION

The appearance and diversification of diverse animal skeletons in the late
Ediacaran to early Cambrian (550 – 520 Ma) suggests an external trigger such as a
change in seawater chemistry or rise in predation (Knoll, 2003). Abiotic factors proposed
include the increased availability of oxygen (Towe, 1970) or a rise in the concentration of
calcium in seawater (Brennan and Lowenstein, 2004). Uncertainty persists, however, as
to both the record of shallow marine oceanic redox during this interval, and the
relationship to changes in sea water chemistry.

Most early metazoan skeletons were calcium carbonate (CaCO₃), forming as
aragonite, low-Mg calcite and high-Mg calcite (Zhuravlev and Wood, 2008), which were
also major abiotic precipitates (e.g. Corsetti et al., 2003). By contrast, dolomite
(CaMg(CO₃)₂), has a highly ordered crystal lattice with slow kinetic growth rates, does
not readily form in modern oceans despite supersaturation, and has never been
documented as a biomineral. This is of note because early metazoan skeletal clades often co-opt carbonate minerals in concert with ambient ocean chemistry driven mainly by inferred changing seawater Mg/Ca (Porter, 2007; Zhuravlev and Wood, 2008).

Here we analyze an underutilized proxy for seawater chemistry – the mineralogy and trace element chemistry of early marine carbonate cements. This avoids bulk sampling which can lead to an averaging or contamination of redox signal, and also allows analysis of shallow carbonate settings where Ediacaran-Cambrian skeletal metazoan biodiversity was highest. Mimetic preservation by dolomite (i.e. retention of original crystallographic orientation) of originally aragonite/high-Mg calcite grains (Tucker, 1982; Corsetti et al., 2006) and dolomite cements (Hood and Wallace, 2015) provide evidence that early marine dolomite precipitation dominated Cryogenian to early Ediacaran oceans (~740-~630 Ma). This is inferred to be due to widespread low oxygen or stratified oceans and high Mg/Ca seawater (Hood et al., 2011). The presence of high iron (ferroan) concentrations in early dolomite cements (Hood and Wallace, 2015), and ferroan dolomite concretions in shales further indicates that these oceans were anoxic and ferruginous (Spence et al., 2016). These so-called ‘aragonite-dolomite seas’ (Hood et al., 2011) are thought to have been largely replaced by ‘aragonite seas’ by the early Ediacaran (Corsetti et al., 2006; Hardie, 2003). Here we present evidence, however, for the continuation of ‘aragonite-dolomite seas’ very close to the Ediacaran/Cambrian boundary on the Siberian Platform.

**GEOLOGICAL SETTING**

We consider the stratigraphic distribution of carbonate minerals and macrofossils across three Ediacaran-Cambrian sections on the Yudoma River, Uchur–Maya Region.
1) Yudoma-Maya confluence, 2) Nuuchchalakh valley, and 3) Kyra-Ytyga river (Fig. 1). These sections encompass the entire Ediacaran Yudoma Group which is unconformably overlain by the lower Cambrian Pestrotsvet Formation (Fig. 1) (see Supplementary Information). The Yudoma Group is subdivided into the Aim (stratigraphic thickness, 45 - 95 m) and Ust’-Yudoma (150 - 205 m) formations (Khomentovsky, 1985).

The sections record a shelf-edge transect from proximal to the shore (Yudoma-Maya confluence), to increasingly distal settings toward the northeast. Sequences are dominated by clastics proximally and carbonates distally (Khomentovsky, 1985). We use sequence stratigraphy to place lithological and macrofossil distribution within a framework of changing relative sea level (Fig. 1). Aim Formation sequences are composed of Transgressive Systems Tracts (TST) of mainly dolomitised siltstones and shales (Fig. DR1), followed by thick (up to ~150 m) Highstand Systems Tracts (HST) of shallow marine dolostones and subordinate limestones. Dolomite dominates these successions, except in the mainly HSTs of the Aim Formation and the uppermost 10–70 m of the Ust’-Yudoma Formation where the lithology switches to limestone. Limestone then persists into the lower Cambrian Pestrotsvet Formation (Fig. 1), and continues to dominate throughout the Cambrian over the entire Siberian Platform (Ashtashkin et al., 2003).

MACROFOSSIL DISTRIBUTION

The distribution of fossils is closely related to lithology in these successions (Fig. 1). Macrofossils in the Aim Formation are restricted to TST and early HST facies, and consist almost exclusively of soft-bodied biota: Gaojiashania (Fig. 2A), Beltanelliformis...
brunsae (Fig. 2B), Aspidella terranovica, Beltanelliformis brunsae, Shaanxilithes and Palaeopascichnus (Zhuravlev et al., 2009, 2012; Ivantsov, 2016). Thrombolites occur in the HST limestones in the Aim Formation, and microbial structures are abundant throughout, particularly in the dolomitic parts of the Ust’-Yudoma Formation.

Calcereous macrofossils are restricted to carbonate lithologies. Suvorovella aldanica (Fig. 2D) and Majaella verkhoianica (Khomentovsky, 1985) occur in the latest HST dolostone at the top of the Aim Formation. Suvorovella is very similar in size and morphology to Aspidella found in the underlying sandstones. The terminal Ediacaran Cloudina (Fig. 2E) and Anabarites (Fig. 2F) both appear 50 m below the top of the Ust’-Yudoma Formation within the HST limestones (Zhuravlev et al., 2012). Rare dolomitised megasphaeromorph acritarchs occur just below this level (Fig. 2D). In the uppermost 8 m of light–gray dolomitic limestone of the Ust’–Yudoma Formation at Kyra-Ytyga river, a characteristic upper Nemakit–Daldynian Purella cristata Zone (= Fortunian, lowermost Cambrian) skeletal assemblage appears, including protoconodonts, anabaritids (Zhuravlev et al., 2012), the hyolithid Allatheca, and trace fossil Diplocraterion.

EVIDENCE FOR EARLY DOLOMITIZATION

Several observations suggest that dolomitization of these sections was very early, and rapid. First, siltstone clasts from shallower depths are dolomitized within a non-dolomitised matrix (Fig. DR1C) suggesting dolomitization occurred prior to reworking. Second, organic-walled acritarchs are preserved in folded, but uncompressed, form by encrustations of very fine crystalline dolomite (Figs. 2D). Third, cavities in dolostones are lined with dolomite cements. In a subtidal-intertidal dolomitic grainstone, grains and Suvorovella skeletal material are preserved as molds with a pronounced micrite envelope
with no breakage or compaction features (Fig. 3A). These molds are now filled with, and
encrusted by, isopachous rims of fibrous dolomite and a later generation of dolomite rhombs (Figs. 3B). We infer an originally aragonitic or high-Mg calcite mineralogy for *Suvorovella* and other grains, with rapid dissolution occurring post-micritisation as evidenced by the symmetrical growth of early marine cement crusts from micrite substrates.

Dolomite cements are fibrous and radial, with a length-slow character (a high angle between the c-axis and the greatest growth direction), and have abundant inclusions which define steep rhombic patterns that follow the crystal form (Figs. 3B). Under cathodoluminescence, crystals show a well-preserved primary growth zonation of multiple dull and bright zones of rhombic patterns confined to individual crystals that do not extend across crystal boundaries (Fig. 3C, D). These features confirm the primary marine nature of these dolomite cements (Hood et al., 2011), and are distinct from burial cements and the coarsely recrystalline, dolomitic replacements of primary calcite and aragonite cements characteristic of early Cambrian carbonates (Whittaker et al., 1994; Corsetti et al., 2006).

By contrast, earliest marine intergranular cements from the limestone intervals of the Aim, latest Ust’-Yudoma and Pestrotsvet formations are exclusively low-Mg calcite. In the Aim and latest Ust’-Yudoma formations these are present as recrystallized spar, but in the Pestrotsvet Formation cements occur as fascicular optic fibrous and prismatic crystals (Fig. 3E), which are largely non-luminescent or with some blotchy bright patches, with limited preservation of primary growth zonation (Fig. 3F).

**REDOX OF EARLY CEMENTS**
Mn and Fe content of seawater is mainly controlled by redox, and cathodoluminescence zonation follows this chemical variation. Non-luminescent cements have low Fe and Mn; bright luminescent cements have high Mn but low Fe; and dull luminescent cements have moderate values of both Fe and Mn. A non-bright-dull progression is caused by carbonate precipitation in waters with decreasing Eh (Barnaby and Rimstidt, 1989).

Dolomitic isopachous crusts reveal moderate to high levels of Fe, up to 3624 ppm (mean: 1393 ppm, n = 68) and variable levels of Mn up to 552 ppm, but with the mean below the detection limit (n = 68) (see Supplementary Information). Later dolomite rhombs show higher levels of Fe (up to 6127 ppm; mean: 2733 ppm, n = 68) and Mn up to 218 ppm, mean 113 ppm (n = 68).

By contrast, the recrystallized low-Mg calcite cements from the Aim Formation show far lower levels of Fe (up to 1044 ppm; mean: 501 ppm, n = 10) but moderate to high levels of Mn (up to 602 ppm; mean: 237 ppm, n = 10). Recrystallized low-Mg cements from the Pestrotsvet Formation show very low levels of Fe (mean = 148 ppm) and moderate levels of Mn (mean = 213 ppm) except for a thin, very early Fe- and Mn-enriched crust (Fe = 4084 ppm, Mn = 1219 ppm), and later, burial, ferroan calcite zones.

This Fe-Mn abundance and behavior indicates that these cements were precipitated in variable redox conditions: dolostones with early dolomite cements under ferruginous, anoxic conditions, but limestones under dominantly non-ferruginous, sub-oxic to oxic conditions.

**DISCUSSION**
Within any one conformable sequence and traced laterally across equivalent tracts, we see evidence for exclusively aragonite or high-Mg calcite early cement precipitation, as inferred from recrystallized low-Mg calcite spar, only in very shallow proximal settings, but extensive early marine dolomite precipitation at other all water depths. The stratigraphic distribution of early dolomitization with changes in relative sea level suggests a very shallow chemocline below the upper Aim Formation. Limestone is found when accommodation space was decreasing and the sedimentary system switched to dominantly carbonate production (Figs. 1; 4B). The HST of the Ust’-Yudoma Formation is extensively dolomitised suggesting that the originally aragonitic sediments were rapidly bathed in anoxic, ferruginous seawater. In such a setting the originally aragonitic Suvorovella was rapidly dolomitised. The oxic layer was therefore restricted to proximal and very shallow coastal waters, where wave action aerated and oxygenated, or where oceans received oxidised continental waters (Fig. 4B). In the latest Ust’-Yudoma Formation (~545 Ma) all localities show a change from dolostone to limestone lithologies with aragonite or high-Mg calcite early cement precipitation, but no attendant changes in facies. This implies a change in local sea water chemistry rather than another environmental factor such water depth or hydrodynamic regime.

Given the continued absence of early dolomite in the Siberian Cambrian record we interpret this as a change in seawater chemistry from ‘aragonite-dolomite seas’ to ‘aragonite seas’ probably controlled by a marked expansion of the oxic zone associated with a lowering of the chemocline (Fig. 4A). There is a globally documented general decrease in ferruginous dolomite during the Ediacaran to early Cambrian interval (Corsetti et al., 2003; Spence et al., 2016). Individual basins probably responded variably,
with the expansion and contraction of the local oxic chemocline manifest in an oscillation between dominant early dolomite and limestone shallow marine lithologies.

The precise controls on Neoproterozoic dolomite formation is unclear as there is little experimental data to infer conditions under which mixed Fe–Ca–Mg carbonates form (Spence et al., 2016), but precipitation was probably promoted by ocean anoxia, high Mg/Ca and ferruginous conditions, and possibly by organic matter enrichment, concentrated organic surface carboxyl groups, low marine sulfate, high pH and alkalinity (Vasconcelos et al., 1995; Hardie, 2003; Roberts et al., 2013; Hood and Wallace, 2015; Spence et al., 2016). These conditions coupled with unstable and reactive phases such as aragonite would further enhance the dolomitization potential of fluids sourced from seawater (Corsetti et al., 2006).

Dramatically enhanced continental weathering occurred during the Neoproterozoic, creating a marked increase in carbonate deposition inferred to be due to a substantial input of Ca\(^{2+}\) into seawater (Peters and Gaines, 2012). Fluid inclusion data confirms that seawater Ca\(^{2+}\) increased markedly and Mg\(^{2+}\) declined slightly during the Ediacaran to early Cambrian so progressively lowering Mg/Ca by the early Cambrian (Brennan and Lowenstein, 2004). This reduction in seawater Mg/Ca is also supported by models (Hardie, 2003).

We propose that the Neoproterozoic anoxic ‘aragonite-dolomite seas’ may have ceased due to increasing oxygenation potentially combined with a reduction in organic matter preservation, as well as an increase of Ca which lowered Mg/Ca. Further decrease in Mg/Ca would favor another switch to low-Mg calcite marine precipitates, and indeed
this is documented in lower Cambrian Stage 3 (525-520 to 514 Ma) (Zhuravlev and Wood, 2008) (Fig. 4C).

We note a biotic response to this proposed progressive decline of Mg/Ca from the Ediacaran to early Cambrian in the Yudoma successions (Fig. 4D). When ferruginous dolomite dominates, we record mainly soft-bodied macrofossils in exclusively very shallow settings inferred to be above the chemocline. The variety of skeletal biota may be due to restricted habitable space with a seawater chemistry permissive for biomineralisation: the slow kinetics of dolomite make it unsuitable to be co-opted as a biomineral. Additionally, the low-Mg calcite cements of the Aim Formation have comparatively high concentrations of Mn and Fe compared to both modern marine cements (Barnaby and Rimstidt, 1989), and those in the Pestrotsvet Formation, suggesting a lower oxidation state than the earliest Cambrian.

Most skeletal macrofossils (Cloudina, Anabarites) appear with the succeeding limestones at the top of the Ust’-Yudoma Formation. This is coincident with the appearance of widespread high-Mg calcite/aragonite marine cements. We infer that biomineralisation was facilitated by a rise in oxygenation and increased concentration of Ca, which is known to enhance biologically-induced calcification (Brennan and Lowenstein, 2004). Moreover, all known Ediacaran and lowermost Cambrian (Fortunian and Stage 2) metazoans have either aragonitic or high-Mg calcitic skeletal mineralogies. But synchronous with the first low-Mg calcitic marine cements in Cambrian lower Stage 3, we record the first metazoans with low-Mg calcite skeletons (Fig. 4D; Zhuravlev and Wood, 2008).
CONCLUSIONS

We propose that the late Ediacaran to early Cambrian early diagenetic setting underwent step changes coincident with the rise of skeletal metazoans. We document a succession of early marine cements on the Siberian Platform from dominantly dolomite (pre-545 Ma), to aragonite/high-Mg calcite (~545 to ~525 Ma), to low-Mg calcite (525-520 to 514 Ma). This coincides with the first appearance of aragonite/high-Mg calcite skeletons at ~545 Ma, and low-Mg calcite skeletons at 525-520 Ma. These events may have been facilitated by the rising oxygenation state of the oceans enabling irrigation of the shallow diagenetic environment, as well as an input of Ca driven by enhanced continental weathering.

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REFERENCES CITED

249 the Siberian Platform: Cirelation chart and explanatory notes: International Union of
250 Geological Sciences Publication, v. 27, p. 1–133.
251 Barnaby, R.J., and Rimstidt, J.D., 1989, Redox conditions of calcite cementation
interpreted from Mn and Fe contents of authigenic calcites: Geological Society of
255 Brennan, S.T., and Lowenstein, T.K., 2004, Seawater chemistry and the advent of
the Neoproterozoic-Cambrian boundary: A case study from Death Valley,
259 California: Sedimentary Geology, v. 191, p. 135–150,
261 Hardie, L.A., 2003, Secular variations in Precambrian seawater chemistry and the timing
of Precambrian aragonite seas and calcite seas: Geology, v. 31, p. 785–788,
264 Hood, A.S., Wallace, M.W., and Drysdale, R.N., 2011, Neoproterozoic aragonite-
dolomite seas? Widespread marine dolomite precipitation in Cryogenian reef
267 Hood, A.S., and Wallace, M.W., 2015, Extreme ocean anoxia during the Late Cryogenian
recorded in reefal carbonates of Southern Australia: Precambrian Research, v. 261,

Programme and Abstracts: Moscow, PIN RAS, p. 36–37 [in Russian].


FIGURE CAPTIONS

Figure 1. Sections of the Ediacaran-Cambrian Yudoma Group on the Yudoma River, with inset map of Uchur–Maya region (UM) within the Siberian Platform (SP), Russia.
Yudoma-Maya confluence. 2, Nuuchchalakh valley. 3, Kyra–Ytyga river. Stratigraphic logs and fossil distribution with inferred zones and international stages. Fm, Formation; Pet., Pestrotsvet. AT = *Anabarites trisulcatus* Zone; PC = *Purella cristata* Zone; FT = Fortunian. MFS = Maximum Flooding Surfaces. *Diplo.* = *Diplocraterion*; *Shaan.* = *Shaansilithes*.


Figure 3. Early marine cements from A-D Ediacaran Yudoma Group and E,F Cambrian Pestrovset Formation. A - D, Photomicrographs of isopachous crusts of radial-slow fibrous dolomite, Aim Formation, Yudoma-Maya confluence. A: Uncompacted grains and *Suvorevella aldanica* fragment (S). B: Plane polarized image of symmetrical growth from a micrite envelope around *Suvorevella aldanica* (S) fragment, showing rhombic inclusion-rich early zones and clear latest zones. C, D, Cathodoluminescent images showing primary alternating thin dull and bright zones. Dotted line shows approximate outline of *Suvorevella aldanica* fragment. C: Radial slow isopachous crust. D: Radial
slow isopachous crust and later rhombic cements (R). E,F, Recrystallized fibrous calcite cements from Nuuchchalakh valley. E: Multiple generations interlayered with sediment. F: Cathodoluminescent image showing dominant non-luminescence except in latest generations.

Figure 4. Relationship between the evolution of Ediacaran-Cambrian seawater chemistry and skeletal metazoans. A: post-~545 million years (Ma). B: pre-~545 Ma during relative sea level changes: transgression, and regression (highstand), with inferred Mg/Ca and redox state. C: Inferred changes in oceanic $m$Mg/Ca. FT = Fortunian. AT = Anabarites trisulcatus Zone. HMC/A = high-Mg calcite/aragonite; LMC = low-Mg calcite. Fluid inclusion $m$Mg/Ca (Brennan and Lowenstein, 2004). D: Biotic response showing the first appearance of HMC/A, then LMC skeletal metazoans.

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