Seawater chemistry and the advent of biocalcification

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ABSTRACT

Major ion compositions of primary fluid inclusions from terminal Proterozoic (ca. 544 Ma) and Early Cambrian (ca. 515 Ma) marine halites indicate that seawater Ca^{2+} concentrations increased approximately threefold during the Early Cambrian. The timing of this shift in seawater chemistry broadly coincides with the "Cambrian explosion," a brief drop in marine $^{87}Sr/^{86}Sr$ values, and an increase in tectonic activity, suggesting a link between the advent of biocalcification, hydrothermal mid-ocean-ridge brine production, and the composition of seawater. The Early Cambrian surge in oceanic $[Ca^{2+}]$ was likely the first such increase following the rise of metazoans and may have spurred evolutionary changes in marine biota.

Keywords: seawater, evaporites, fluid inclusions, biomineralization, Cambrian explosion.

INTRODUCTION

One of the most dramatic and confounding events in evolutionary and geologic history was the sudden onset of biomineralization in the Early Cambrian during the "Cambrian explosion" (Knoll and Carroll, 1999; Conway-Morris, 2000) (Fig. 1). Explanations for this event include (1) a response to increased predation (Stanley, 1976), (2) detoxification (Simkiss, 1977, 1989) due to increased seawater $[Ca^{2+}]$ (Kempe and Kazmierczak, 1994), and (3) increased atmospheric oxygen concentration (Cloud, 1976). Here we present new data—38 analyses of evaporated seawater in fluid inclusions from terminal Proterozoic (ca. 544 Ma, 24 analyses) and Early Cambrian (Toyonian, ca. 515 Ma, 14 analyses) marine halites—to help answer this unresolved issue in Earth's history. These analyses indicate that the major ion composition of seawater changed between 544 Ma and 515 Ma, highlighted by a large increase in $[Ca^{2+}]$. This increase in the seawater $[Ca^{2+}]$ may have created a chemical environment favorable for the initial development of calcium carbonate and calcium phosphate hard parts, which have dominated marine biota ever since.

GEOLOGIC SETTING

Primary fluid inclusions from chevron halites of the terminal Proterozoic Ara Group (southern Oman) (Brasier et al., 2000) and the Early Cambrian (Toyonian) Angarskaya Formation (eastern Siberia) (Andreev et al., 1986) were analyzed by using the environmental scanning electron microscope–energy-dispersive spectrometer (ESEM-EDS) method of Timofeeff et al. (2000).

The terminal Proterozoic halite samples are from the E3 halite unit (Mattes and Conway-Morris, 1990) of the Ara Group (South Oman Basin, core depth of 3010.5 m). The underlying C3 carbonate unit, equivalent to the A3-C unit of Amthor et al. (2003), contains the marine fossils *Cloudina* and *Namacalathus* (Mattes and Conway-Morris, 1990; Amthor et al., 2003). The repeated cycles of conformable marine carbonates and restricted-marine evaporites (sulfates, halites, and potassium salts) and the halite $[Br^-]$ of 59–109 ppm suggest that the parent waters of the Ara Group halites were seawater (Schröder et al., 2003).

The Early Cambrian halites are from the Lower Rock Salts of the Gazhenka Member (S6 unit) of the Angarskaya Formation (Eastern Siberian Basin, near Bratsk; core depth of 805 m). The Gazhenka Member overlies the marine carbonate Olemka Member (RVII unit) of the upper Botomian Bulayskaya Formation (Zharkov, 1984). The stratigraphic succession—marine carbonates overlain by the anhydrite and halite—and high $[Br^-]$ in fluid inclusion brines within the Lower Rock Salts (Horita et al., 2002) suggest that the parent waters of the
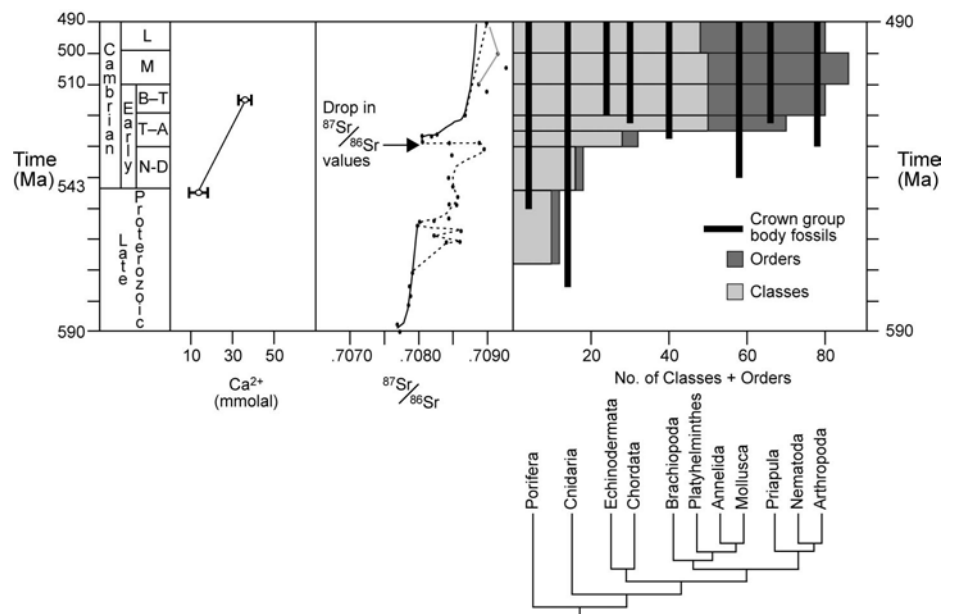
Figure 1. Geological and biological changes in oceanic realm during terminal Proterozoic and Cambrian. Stages in Early Cambrian are Nemakit-Daldynian (N-D), Tommotian–Atdabanian (T–A), and Botomian–Toyonian (B–T); Middle (M) and Late (L) Cambrian are also shown. There was dramatic increase in diversity of animal classes and orders starting in Tommotian time (from Knoll and Carroll, 1999). Phylogeny and corresponding crown group first appearances (time line) show diversification of animal clades (from Knoll and Carroll, 1999). Crown groups are "the last common ancestor of all living members of a clade plus all its descendants" (from Knoll and Carroll, 1999, p. 2136). Decrease in marine $^{87}Sr/^{86}Sr$ ratios ca. 530 Ma during otherwise increasing trend in $^{87}Sr/^{86}Sr$ ratios likely indicates increase in mid-ocean-ridge spreading rates (Walter et al., 2000; Nicholas, 1996). Bars indicate possible ranges of oceanic $[Ca^{2+}]$ determined in this study; open circles represent average values (Table 1) used for computer simulations shown in Figure 2. Concentrations are millimolal (millimoles per 1 kg H_2O).
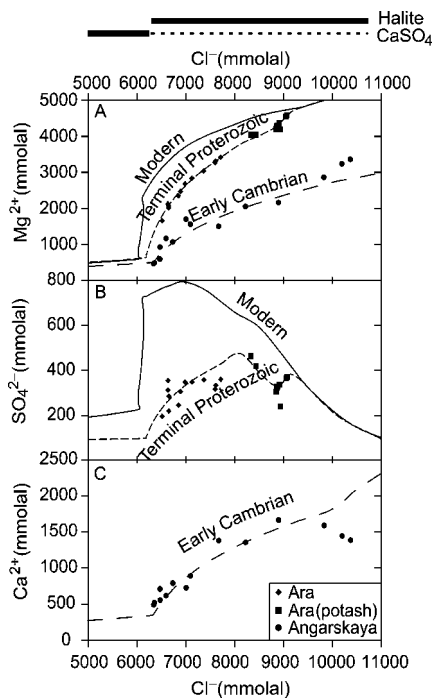
Figure 2. Plots of (A) [Mg²⁺], (B) [SO₄²⁻], and (C) [Ca²⁺] vs. [Cl⁻] (mmolal, millimoles per 1 kg H₂O) in brine inclusions. Fluid inclusions from terminal Proterozoic (Ara Group) and Early Cambrian (Angarskaya Formation) define evaporation paths different from those produced during evaporation of present-day seawater. Evaporation paths reflect initial concentrations of major ions, evaporative concentration, and loss of certain species to mineral precipitation (i.e., Na⁺ and Cl⁻ to halite). Large change in slope of each evaporation path at ~6000 mmolal Cl⁻ represents onset of halite precipitation. There is no present-day seawater evaporation path on Ca²⁺ vs. Cl⁻ plot; during evaporation of present-day seawater, essentially all of Ca²⁺ is removed prior to halite saturation because of precipitation of calcium sulfate. Some terminal Proterozoic fluid inclusions, indicated by square symbols, contain highly concentrated brines in equilibrium with sylvite [KCl] and carnallite [KMgCl₃·6H₂O] (i.e., brines evaporated into potash field). Best-fit curves through data were generated with Harvie-Møller-Weare computer model (Harvie et al., 1984) by using composition of terminal Proterozoic and Early Cambrian seawater (Table 1). Bars above plots show timing of precipitation of CaSO₄ and halite; dashed CaSO₄ line indicates minor precipitation within halite field.

Major ion	Terminal Proterozoic (ca. 544 Ma)	Early Cambrian (ca. 515 Ma)	Present day
Na⁺	479	450	485
K⁺	11	9	11
Ca²⁺	14 (9.5–18.5)	37 (33.5–40)	11
Mg²⁺	52	44	55
Cl⁻	581	605	565
SO₄²⁻	20.5 (16–25)	8 (4.5–11)	29
Mg²⁺/Ca²⁺	~4	~1	5

Note: The Ca²⁺ and SO₄²⁻ values represent the average of the possible end-member concentrations (in parentheses). All concentrations are mmolal (i.e., millimoles per 1 kg H₂O).

brine interface. Only single-phase fluid inclusions within growth bands were analyzed to ensure that the inclusions had not been altered after being trapped within the halite. Therefore, the entrained fluids analyzed in this study were pristine surface brines. The brines were marine in origin; therefore, the brine inclusions are samples of evaporated terminal Proterozoic and Early Cambrian seawater.

FLUID-INCLUSION ANALYSES

The 38 fluid-inclusion analyses were done with an ESEM-EDS, which allows direct observation and analysis of the surface of frozen fluid inclusions. Detection limits are 0.5 wt% for Na⁺ and 0.1 wt% for Mg²⁺, Ca²⁺, K⁺, SO₄²⁻, and Cl⁻, with typical precisions between 2% and 7% and accuracies better than 7% (Timofeeff et al., 2000). This method has been verified by analyzing primary fluid inclusions in modern marine chevron halites (Timofeeff et al., 2001). In that study, the analyses of the brine inclusions from modern halite samples yielded major ion compositions that accurately reflected the chemistry of evaporated present-day seawater.

The Ara Group samples contained Ca²⁺-depleted Na-Mg-K-SO₄-Cl brines; these ionic components are similar to those in modern evaporated seawater and fluid-inclusion brines trapped in modern marine halites (Lowenstein et al., 2001; Timofeeff et al., 2001). The Angarskaya Formation samples contained SO₄²⁻-depleted Na-Mg-K-Ca-Cl brines; these ionic components are similar to those in other early Paleozoic (Cambrian, Silurian, Devonian) fluid inclusions in marine halites (Lowenstein et al., 2001; Brennan and Lowenstein, 2002; Horita et al., 2002). Other reported fluid-inclusion analyses from the Cambrian halites of the Eastern Siberian Basin also have Na-Mg-K-Ca-Cl compositions (Kovalevich et al., 1998; Horita et al., 2002); this chemistry is consistent with that of the fluid inclusions analyzed in this study (Table DR1[1]).

[1]GSA Data Repository item 2004082, Table DR1, brine-inclusion compositions, is available online at www.geosociety.org/pubs/ft2004.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

Compositional plots (Fig. 2) outline distinct evaporation paths for the terminal Proterozoic and Early Cambrian fluid inclusions. Terminal Proterozoic and in particular Early Cambrian fluid inclusions are below the evaporation path of modern seawater on the Mg²⁺ versus Cl⁻ plot, which indicates that these ancient seawaters were relatively depleted in [Mg²⁺] compared to present-day seawater (Fig. 2A). Similarly, the [SO₄²⁻] of terminal Proterozoic fluid inclusions are below the modern seawater evaporation path (Fig. 2B). However, in all Early Cambrian fluid inclusions, the [SO₄²⁻] were below detection (<~15 millimolal [millimoles per 1 kg H₂O, or "mmolal"]) (Timofeeff et al., 2000). Unlike modern and terminal Proterozoic evaporated seawater, in which [Ca²⁺] is severely depleted by the precipitation of CaSO₄, [Ca²⁺] in Early Cambrian fluid inclusions are as high as 1670 mmolal (Fig. 2C). These results indicate that Cambrian seawater was on the Ca²⁺-rich side of the Ca-SO₄ chemical divide, such that [Ca²⁺] > [SO₄²⁻] + [½HCO₃⁻] (Hardie and Eugster, 1970). During evaporation and precipitation of CaCO₃ and CaSO₄, HCO₃⁻ and SO₄²⁻ were essentially removed from the brine, leaving Ca²⁺ as a dominant cation during later evaporative concentration. In contrast, modern and terminal Proterozoic seawater plot on the SO₄²⁻-rich side of the Ca-SO₄ chemical divide. In summary, fluid-inclusion analyses indicate that Early Cambrian seawater was enriched in [Ca²⁺] and depleted in [Mg²⁺] and [SO₄²⁻] relative to terminal Proterozoic seawater.

SEAWATER COMPOSITIONS

Brine-inclusion chemistries and the evaporation paths that they define (Fig. 2) can be used in conjunction with the Harvie-Møller-Weare (HMW) computer model (Harvie et al., 1984) to back-calculate the compositions of terminal Proterozoic and Early Cambrian seawater. The HMW computer program calculates the concentrations, in molalities, of all the major ions at each evaporation step along with the number of moles of salts precipitated during each evaporation step.

Early Cambrian and terminal Proterozoic seawater (Table 1) were modeled using the

Angarskaya Formation halites analyzed in this study were seawater.

The samples chosen for analysis were all chevron halites, which are structures with upward-oriented crystal faces defined by bands of primary fluid inclusions that were trapped as the crystal precipitated. These structures indicate that the halite has not recrystallized since forming at the sediment-

Major ion ratio	Terminal Proterozoic (ca. 544 Ma)	Early Cambrian (ca. 515 Ma)
Mg^{2+}/SO_4^{2-}	8.0	–
K^+/SO_4^{2-}	1.7	–
Mg^{2+}/Ca^{2+}	–	1.5
K^+/Ca^{2+}	–	0.3

fluid-inclusion chemistries. Early Cambrian "first halites" with low $[Mg^{2+}]$ (~470 mmolal, Fig. 2A) were used to calculate the Mg^{2+} of Early Cambrian seawater because this ion behaves conservatively during evaporative concentration. This $[Mg^{2+}]$, 470 mmolal, divided by the concentration factor at initial halite saturation, 10.6, gives $[Mg^{2+}]$ = 44 mmolal in Early Cambrian seawater. Early Cambrian fluid inclusions have Mg^{2+}/Ca^{2+} = 1.5 (Table 2), which gives $[Ca^{2+}]$ = 29 mmolal in Early Cambrian seawater (44/29 = 1.5). Similarly, Early Cambrian brine inclusions have K^+/Ca^{2+} = 0.3 (Table 2), which gives $[K^+]$ = 9 mmolal in Early Cambrian seawater (9/29 = 0.3). The $[Ca^{2+}]$ determined from these ratios, however, does not account for $[Ca^{2+}]$ lost during earlier precipitation of $CaSO_4$. Modern seawater has a $[Ca^{2+}] \times [SO_4^{2-}]$ product of ~300 mmolal^2 (Horita et al., 2002). If we assume that Early Cambrian seawater had a $[Ca^{2+}] \times [SO_4^{2-}]$ product between 150 and 450 mmolal^2 (Horita et al., 2002; Lowenstein et al., 2003) and that all SO_4^{2-} was consumed by the precipitation of $CaSO_4$, then the $[Ca^{2+}]$ in Early Cambrian seawater can be determined via the equation (29 mmolal + x) x = 300 ± 150, where 29 mmolal is the $[Ca^{2+}]$ in the fluid inclusions and x is the original $[SO_4^{2-}]$. Based on this equation, the $[Ca^{2+}]$ of Early Cambrian seawater was between 33.5 and 40 mmolal (average = 37 mmolal). The Ca^{2+} lost via precipitation of $CaCO_3$ is not considered here, as HCO_3^- is a minor component of seawater relative to Ca^{2+}. The $[Na^+]$ and $[Cl^-]$ in Early Cambrian seawater were determined by charge balance, assuming that Early Cambrian salinity was the same as present-day seawater (Johnson and Goldstein, 1993). The chemistry of the calculated Cambrian seawater (Table 1), when its evaporation is modeled with the HMW computer model (Harvie et al., 1984), yields the best-fit curves shown in Figures 2A and 2C.

Terminal Proterozoic seawater brine inclusions are below the modern seawater path on the Mg^{2+} versus Cl^- plot (Fig. 2A), but above the path of the Early Cambrian brine inclusions. The $[Mg^{2+}]$ of terminal Proterozoic seawater was therefore greater than in Early Cambrian seawater, but less than present-day seawater values, i.e., between 55 and 44 mmolal. The evaporation path, generated by

the HMW computer model that best fit the fluid-inclusion data (Fig. 2A), had an $[Mg^{2+}]$ = 52 mmolal. Terminal Proterozoic fluid inclusions average Mg^{2+}/SO_4^{2-} = 8 (Table 2), which gives $[SO_4^{2-}]$ = 6.5 mmolal (52/6.5 = 8). Similarly, terminal Proterozoic fluid inclusions average K^+/SO_4^{2-} = 1.7 (Table 2), which gives $[K^+]$ = 11 mmolal for terminal Proterozoic seawater (11/6.5 = 1.7). The $[SO_4^{2-}]$ determined from these ratios does not account for $[SO_4^{2-}]$ lost during earlier precipitation of $CaSO_4$. Again, if we assume that terminal Proterozoic seawater had a $[Ca^{2+}] \times [SO_4^{2-}]$ product between 150 and 450 mmolal^2 and that all Ca^{2+} was consumed by the precipitation of $CaSO_4$, then the terminal Proterozoic seawater $[SO_4^{2-}]$ can be determined via the equation (6.5 mmolal + x) x = 300 ± 150, where 6.5 mmolal is the $[SO_4^{2-}]$ in the fluid inclusions and x is the original $[Ca^{2+}]$. Based on this equation, terminal Proterozoic seawater $[SO_4^{2-}]$ was between 16 and 25 mmolal (average = 20.5 mmolal). The $[Na^+]$ and $[Cl^-]$ for terminal Proterozoic seawater were determined by charge balance assuming that terminal Proterozoic seawater salinity was equal to present-day seawater salinity (Johnson and Goldstein, 1993). The chemistry of the calculated terminal Proterozoic seawater (Table 1), when its evaporation is modeled with the HMW computer model (Harvie et al., 1984), yields the best-fit curves through the fluid-inclusion data in Figures 2A and 2B.

The modeled values (Table 1) indicate that the $[Ca^{2+}]$ in seawater increased almost three-fold (14–37 mmolal) during the Early Cambrian (Table 1). In contrast, over the same period, $[SO_4^{2-}]$ decreased more than twofold (20.5–8 mmolal), and $[Mg^{2+}]$ decreased ~20% (Table 1).

CONCURRENT PHENOMENA

Changes in the major ion composition of seawater coincided with other Early Cambrian global phenomena. Estimates of mid-ocean-ridge (MOR) spreading rates during this interval range up to 300 mm/yr (Kirschvink et al., 1997), which is 3–10 times greater than any modern MOR spreading rates. A considerable negative excursion in the $^{87}Sr/^{86}Sr$ ratio of seawater (Fig. 1) occurred between ca. 532 and 528 Ma (Nicholas, 1996; Walter et al., 2000). This excursion apparently reflects enhanced MOR hydrothermal brine flux (Nicholas, 1996). Such an interpretation is consistent with the seawater secular variation model of Hardie (1996, 2003) that proposes that long-term fluctuations in the major ion chemistry of seawater are driven by changes in ocean-crust production that, in turn, modify ratios of MOR hydrothermal brine flux to river water flux.

CAMBRIAN CALCIUM CRISIS?

The rise of seawater $[Ca^{2+}]$ in the Early Cambrian coincided with the onset of widespread biomineralization (Fig. 1). Calcification in modern organisms can be affected by changes in ambient $[Ca^{2+}]$. Decalcified coccolithophorids, for example, will grow new coccoliths in aqueous solutions with high $[Ca^{2+}]$ (~10^{-2} molar), but show no such growth at lower $[Ca^{2+}]$ (10^{-3} to 10^{-4} molar) (Blackwelder et al., 1976). Furthermore, the Mg^{2+}/Ca^{2+} ratio (Riding, 1982; Stanley and Hardie, 1998) and $[Ca^{2+}]$ (Arp et al., 2001) of seawater appear to influence biocalcification in organisms such as cyanobacteria (Riding, 1982; Arp et al., 2001), coccolithophorids (Stanley and Hardie, 1998; Arp et al., 2001), and coralline algae (Stanley et al., 2002). Calcifying cyanobacteria are abundant in the Phanerozoic rock record during times of high oceanic $[Ca^{2+}]$ (Hardie, 1996; Arp et al., 2001; Lowenstein et al., 2001), and the first appearance of widespread calcifying cyanobacteria (Riding, 1982) coincides with our proposed $[Ca^{2+}]$ spike in the Early Cambrian. Coccolithophorids were not part of the Cambrian explosion; however, they were most abundant in the Late Cretaceous (Stanley and Hardie, 1998; Arp et al., 2001), another period of elevated seawater $[Ca^{2+}]$ (Stanley and Hardie, 1998; Lowenstein et al., 2001). Coralline algae produce skeletons of high-Mg calcite, but experiments in artificial seawater with a low Mg^{2+}/Ca^{2+} ratio of ~1 show that these algae will produce low-Mg calcite (Stanley et al., 2002). Biologically induced calcification, exhibited by the above organisms, appears to be affected by changes in the ambient $[Ca^{2+}]$ and Mg^{2+}/Ca^{2+} ratio, whereas biologically controlled calcification, which was the prevalent mode of the Cambrian explosion, is a far more complex problem.

The idea that biomineralization might be a metabolic detoxification process induced by increases in intracellular $[Ca^{2+}]$ was proposed by Simkiss (1977). During the Early Cambrian, the ambient oceanic $[Ca^{2+}]$ may have risen to such a degree that cells could no longer effectively exclude or expel the Ca^{2+} ions, causing intracellular $[Ca^{2+}]$ in certain marine organisms to reach toxic levels (Simkiss, 1977, 1989; Kempe and Kazmierczak, 1994). Furthermore, high $[PO_4^{3-}]$ in Early Cambrian seawater may have amplified the uptake of Ca^{2+} by organisms (Kempe and Kazmierczak, 1994). Opportunistic organisms may have modified existing cellular waste-removal systems by binding Ca^{2+} as relatively insoluble minerals (calcium carbonate or calcium phosphate), which could have been the starting point of the complex process that eventually

led to shell production (Simkiss, 1977, 1989; Kempe and Kazmierczak, 1994).

Fluctuations in the major ion chemistry of seawater likely occurred many times in the 4 b.y. of Earth's history prior to the Cambrian explosion (Hardie, 2003), but the Early Cambrian was probably the first time metazoans were subjected to such high $[Ca^{2+}]$ in seawater. It is estimated that metazoan diversification began ca. 1 Ga (Knoll and Carroll, 1999), but early metazoans were small (Knoll and Carroll, 1999; Conway-Morris, 2000). Widespread evidence of trace fossils beginning ca. 610 Ma (Knoll and Carroll, 1999; Conway-Morris, 2000) suggests that metazoans became larger and more abundant in the Late Proterozoic. We propose that the first major pulse in seawater $[Ca^{2+}]$ following the rise of the metazoans occurred during the Early Cambrian, triggering the metabolic changes that led to pervasive biocalcification. That the rise of biocalcifying organisms occurred in all extant phyla during a spike in oceanic $[Ca^{2+}]$ concentrations seems to be more than a coincidence.

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