

Secular variations in Precambrian seawater chemistry and the timing of Precambrian aragonite seas and calcite seas

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ABSTRACT

An extension of the seawater secular-variation model that successfully predicted the observed timing of Phanerozoic MgSO_4 vs. KCl marine evaporites and aragonite seas vs. calcite seas has been applied to the prediction of the secular variations in the major ion chemistry of seawater and aragonite seas vs. calcite seas during the Precambrian. Testing of the predictions was based on those Precambrian seafloor carbonate precipitates that have been interpreted by others to have formed originally as aragonite. Of 16 examples of Precambrian seafloor aragonite, 14 fall within the 6 periods of aragonite seas predicted for the Late Archean–Proterozoic by the model, 1 falls on the transition between an aragonite sea and calcite sea, and 1 falls in a period of calcite seas. This strong correlation supports the following predictions of the model: (1) Precambrian seawater was a saline NaCl water with $\text{Ca} > \text{HCO}_3$ since at least the Late Archean. (2) The major ion compositions of Precambrian seawater chemistry and their secular variations are in the same ranges as those of Phanerozoic seawater. (3) The Mg/Ca mole ratio in seawater has controlled the types of CaCO_3 polymorphs that have precipitated from Earth's oceans throughout the Phanerozoic and most, if not all, of the Precambrian.

Keywords: Precambrian, seawater chemistry, aragonite seas, calcite seas.

INTRODUCTION

The hypothesis that the major ion chemistry of Phanerozoic seawater has been controlled primarily by mixing of river water and mid-ocean-ridge (MOR) hydrothermal brine (Spencer and Hardie, 1990; Hardie, 1996, 2000) can account to some extent for observed secular variations in (1) the mineralogies of nonskeletal marine limestones and marine evaporites (Hardie, 1996), (2) the major ion compositions of fluid inclusions preserved in primary chevron halite in marine evaporites (Lowenstein et al., 2001), and (3) the carbonate mineralogies of reef and major sediment-producing skeletal marine organisms (Stanley and Hardie, 1998, 1999). I extend the approach to predicting the secular variations in Precambrian seawater chemistry and aragonite sea–calcite sea oscillations back to the Late Archean. Precambrian seafloor carbonate precipitates reported to be pseudomorphous after aragonite were used to test the predictions.

NATURE OF PRECAMBRIAN SEAWATER

Kempe and Degens (1985) proposed that the Precambrian global ocean before 1 Ga was a “soda ocean” ($\text{HCO}_3 > \text{Ca}$) with a very high pH. Grotzinger and Kasting (1993) argued that pseudomorphs after CaSO_4 minerals as far back as ca. 2 Ga ruled out an alkaline ocean after the late Paleoproterozoic. They postulated that in the absence of evidence for gypsum prior to ca. 2 Ga, Earth's ocean may have been an alkaline Na–Cl– HCO_3 -rich water with $\text{HCO}_3 > \text{Ca}$, capable of precipitating halite but not gypsum. However, Simonson et al. (1993) reported pseudomorphs after gypsum associated with halite casts in the 2.6 Ga Carawine Dolomite of the Hamersley Basin, Australia, and Lowe (1983) reported pseudomorphs after gypsum of Early Archean

age (3.45 Ga) in Western Australia. Of all sedimentary deposits, evaporites are the most susceptible to recycling (15 times in 3 b.y., Garrels and Mackenzie, 1971); the earlier the deposits were formed, the higher the probability of their being erased from the depositional record. Thus, here it is assumed that the sparse evidence for bedded CaSO_4 evaporites before 2 Ga is the result of selective removal. An additional but critical assumption is that Precambrian seawater was never a “soda ocean” of any kind, but instead was always a near-neutral NaCl brine with $m\text{Ca} > m\text{HCO}_3$. The essence of the argument is as follows. There is wide agreement that Earth's primordial atmosphere was swept away by the solar wind generated during our Sun's *T Tauri* phase (when the solar system was ≤ 1 m.y. old?) and replaced within ~ 100 m.y. by a secondary atmosphere made up of juvenile gases released from Earth's interior (e.g., Walker, 1977). On the basis of the amounts of volatiles such as $\text{H}_2\text{O}_{(g)}$, $\text{CO}_{2(g)}$, and $\text{HCl}_{(g)}$ (the latter now Cl ions) stored in today's ocean waters and in the form of limestones, evaporites, and organic matter, Garrels and Mackenzie (1971, p. 290) estimated that at 600 °C Earth's secondary atmosphere would have had $p\text{H}_2\text{O} = 300$ atm, $p\text{CO}_2 = 45$ atm, and $p\text{HCl} = 10$ atm. As the temperature cooled to 200 °C, most of the HCl would have been dissolved in the newly condensed rain water, whereas most of the CO_2 would have remained in the atmosphere. Garrels and Mackenzie (1971, p. 290) noted that “the reactivity of the ocean-atmosphere system would have been awesome. Gaseous HCl is almost impossible to contain in modern experimental apparatus utilizing the most refractory materials known; an ocean at 200 °C containing 1 mol/L of dissolved HCl and 0.5 mol/L of CO_2 would react vigorously with the newly formed crust.” Such a global-scale acid-base titration would have converted Earth's primordial igneous crust into an aluminosilicate “soil” and an “instant” saline NaCl ocean with $\text{Na} \approx \text{Ca} > \text{Mg} > \text{K}$ and a near-neutral pH (Garrels and Mackenzie, 1971, p. 293–296; see also Lafon and Mackenzie, 1974). This primordial ocean, like today's ocean, would have had $m\text{Ca} > m\text{HCO}_3$ because the dominance of HCl over CO_2 dissolved in the primordial acid rain would have produced far more $\text{CaCl}_{2(aq)}$ than $\text{CaHCO}_{3(aq)}$ in the primordial weathering process.

METHOD OF PREDICTING SECULAR VARIATIONS IN PRECAMBRIAN SEAWATER CHEMISTRY

To predict secular variations in Phanerozoic seawater, Hardie (1996) used the Spencer and Hardie (1990) MOR brine + river water mixing model combined with Gaffin's (1987) secular variation in seafloor generation rate over the Phanerozoic Eon to determine the secular variations in MOR/river-water (RW) flux ratios back to the Cambrian Period. However, because Gaffin's data do not extend beyond the Cambrian, some other means of determining secular variation in the rate of ocean-crust production back to the Archean is needed. For this purpose Engel and Engel's (1970) estimates of secular oscillations in Precambrian granite-pluton production in North America have been used as a proxy. Granite plutonism and ocean-crust production are coupled crust-forming processes operating at opposite ends of a moving plate, so secular variations in rates of granite plutonism at convergent boundaries should be coupled to secular variations in rates of ocean-crust production at MORs. For the Phanerozoic, Hardie (1996, Fig. 2 therein) showed that the secular variations in Gaffin's (1987) ocean-crust pro-

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duction and Engel and Engel's (1970, their Fig. 5) relative abundance of North American granite-pluton production have been in phase. On the basis of this finding, the granite data were linearly scaled to the ocean-crust data by equating Engel and Engel's Cretaceous production maximum at 115 Ma and Holocene production minimum at 0 Ma with those of Gaffin (1987). The resulting Precambrian ocean-crust production curve allowed calculation of the secular variation in the MOR/RW flux ratio throughout the Proterozoic back into the Late Archean (2.8 Ga).

A modified version of the Hardie (1996) model of calculating seawater chemistry from the MOR/RW flux ratio was used in this paper. This modified method assumes that the major ion chemistry of MOR brine is buffered by basalt and seawater interactions at greenschist-actinolite facies temperatures (Hardie, 2000). The critical interactions are (1) the conversion of plagioclase to albite and epidote (which controls Na/Ca in the brine, Berndt et al., 1989), (2) the alteration of olivine, pyroxene, and glass to Mg-chlorite and/or actinolite (which removes almost all the Mg from the hot seawater), and (3) the precipitation of anhydrite (which removes SO_4 from the upward-circulating brine). Potassium is problematical because it is not buffered by basalt and seawater interactions. It is released to the brine during hydrothermal alteration, adding to the K^+ ions provided by seawater. With this buffering, the major ion chemistry of MOR brines over geologic time would have been essentially independent of the starting composition of the seawater influx. To calculate a paleoseawater chemistry, it is only necessary to mix this buffered MOR brine with river water in proportion to the chosen MOR/RW flux ratio. The Hardie (2000) model uses a modification of the Hardie (1996) approach to calculate the MOR/RW data. Following Baker et al.'s (1995, p. 66) observation that in the modern MOR system "hydrothermal plume production is directly related to the spreading rate," it was assumed that the MOR flux was linearly related to the rate of ocean-crust production. Linear equations were fitted to the following points: (1) MOR/RW = 1 when crust production = $2.9 \text{ km}^2/\text{yr}$ (modern value, Gaffin, 1987) and (2) MOR/RW = y_{max} when crust production = $5.05 \text{ km}^2/\text{yr}$ (Cretaceous value, a maximum for the Phanerozoic, Gaffin, 1987) for a series of MOR/RW ratios with different values of y_{max} from 1.00 to 2.75. The resulting linear equations were then used to calculate the secular variation in seawater composition for each given MOR/RW = y_{max} .

Following Spencer and Hardie (1990) and Hardie (1996), I assume that (1) the concentration of major ions in average river water has been constant at Na = 0.089, K = -0.062, Ca = 0.713, Mg = 0.237, SO_4 = 0.126, HCO_3^- = 0.852, and Cl = 0.0 meq/L; (2) the "buffered" MOR brine has had the composition of the modern Reykjanes #8 brine from Iceland, i.e., Na = 430.2, K = 38.4, Ca = 78.5, Mg = 1.3, SO_4 = 0.7, HCO_3^- = 0.0, and Cl = 547.9 meq/L (see Data Repository for a discussion¹); and (3) the flux of river water was $3.75 \times 10^{16} \text{ L/yr}$, whereas the reference MOR flux was $8.45 \times 10^{13} \text{ L/yr}$. In addition, the Hardie (2000) method imposes the following mass-balance constraints on the mixing of MOR brine and river water: (1) the mass of Cl ions in the calculated paleoseawater must be the same as that in modern seawater ($739.117 \times 10^{21} \text{ meq}$, based on $262 \times 10^{20} \text{ g Cl}$), and (2) the volume of the calculated paleoseawater must be equal to that of today's ocean ($1.349 \times 10^{21} \text{ L}$). To calculate a paleoseawater composition as a function of MOR/RW flux ratio by mixing the buffered MOR brine and river water, a flux ratio is first chosen; e.g., a MOR flux 50% greater than today's flux would be equivalent to an MOR/RW ratio of 1.50. This new MOR flux would be 1.50×8.45

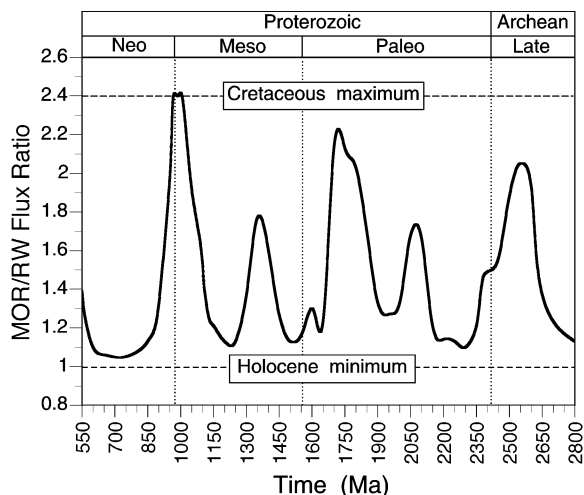


Figure 1. Predicted secular variations in mid-ocean-ridge/river-water (MOR/RW) flux ratios during Proterozoic and latest Archean based on granite-abundance data of Engel and Engel (1970).

$\times 10^{13} \text{ L/yr}$, whereas the river-water flux would remain at $3.75 \times 10^{16} \text{ L/yr}$. These values are then used in conjunction with the compositions of MOR brine and river water (in meq/L) to calculate the masses (in meq/yr) of each major ion produced by simple mixing of MOR brine with river water. This approach results in a very large excess of Ca^{2+} and HCO_3^- ions. Equal molar proportions of Ca^{2+} and HCO_3^- are removed until saturation with calcite at 25°C is achieved. Mixing is carried out until the total chloride mass reaches that of the modern oceans. This step simply involves calculating the time required to accumulate $739.117 \times 10^{21} \text{ meq}$ of chloride ions, assuming that the given MOR and river-water input fluxes were time independent. The resulting masses of each ion are then divided by the volume of ocean water ($1.349 \times 10^{21} \text{ L}$) to recover the concentrations (in meq/L) normalized to the Cl concentration of modern seawater. As in the Hardie (1996) method, the selection of the best y_{max} value was made by comparison between predicted and observed secular variation in the mineralogy of Phanerozoic evaporite and nonskeletal carbonate deposits. A very good fit was found for the curve with an MOR/RW maximum of 2.4 at 115 Ma.

PRECAMBRIAN SEAWATER CHEMISTRY AND THE TIMING OF PRECAMBRIAN ARAGONITE SEAS AND CALCITE SEAS

The preceding model, based on the curve with a maximum MOR/RW flux ratio of 2.4 during the Cretaceous, predicts that five major oscillations in MOR/RW flux ratio occurred during the Proterozoic Eon (Fig. 1). From the curve of the MOR/RW flux ratio in Figure 1, the major ion chemistry of Precambrian seawater was calculated as a function of time. The calculated secular variations in the concentrations of Ca, Mg, K, and SO_4 ions in Precambrian seawater are shown graphically in Figure 2, and the variations in Mg/Ca mole ratios are shown in Figure 3 (for tabulated values, see footnote 1). By using Mg/Ca = 2 as the boundary criterion for calcite seas (Mg/Ca ≤ 2) vs. aragonite seas (Mg/Ca > 2) (Hardie, 1996; Stanley and Hardie, 1999, Fig. 3), calcite is predicted to have been precipitated in the intervals 925–1105 Ma, 1310–1425 Ma, 1675–1875 Ma, 2025–2125 Ma, and 2375–2630 Ma, and aragonite ($\pm \text{Mg}$ -calcite) in the intervals < 550 –925 Ma, 1105–1310 Ma, 1425–1675 Ma, 1875–2025 Ma, 2125–2375 Ma, and 2630–2750 Ma (Fig. 3). Field data that can be used to test the predicted secular variations in Precambrian seawater compositions are the reported occurrences of Precambrian nonskeletal seafloor precipitates (crystal fans, early cements, and ooids) interpreted to originally have

¹GSA Data Repository item 2003114, discussion of the mid-ocean-ridge hydrothermal brine and a table of major ion chemistry variations, is available online at www.geosociety.org/pubs/ft2003.htm or on request from editing@geosociety.org, or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301-9140, USA.

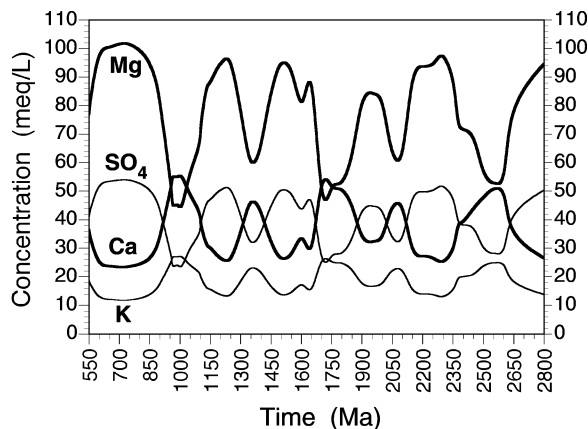


Figure 2. Predicted secular variations in concentrations of Mg, SO₄, Ca, and K ions in seawater.

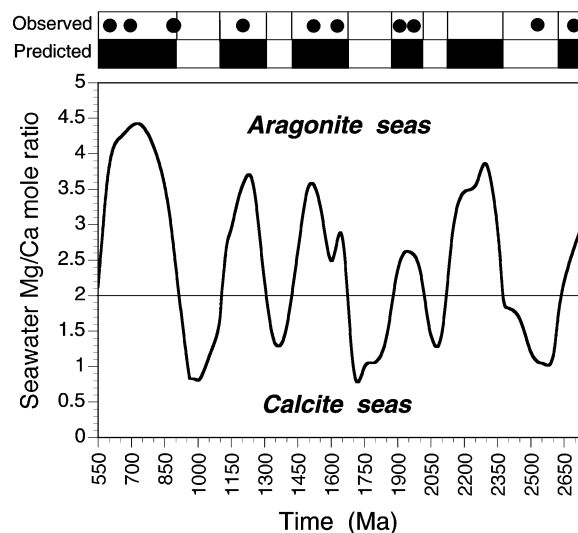


Figure 3. Predicted secular variation in Mg/Ca mole ratio of Precambrian seawater. Bars at top of diagram show periods predicted to be aragonite seas (black boxes) and reported timing of aragonite seafloor precipitates in Precambrian carbonate deposits (black circles; see Table 1). Black circle at 1640 Ma represents four different basins; black circle at 2700 Ma represents two different basins; Katakaturuk Dolomite at older than 545 Ma but younger than 800 ± 20 Ma is not plotted, but fits into aragonite sea predicted for Neoproterozoic (Table 1).

been aragonite (Table 1). If these interpretations of an originally aragonite mineralogy are correct, then the observed temporal distribution of aragonitic seafloor precipitates fits well with the predicted timing of Proterozoic aragonite seas, as illustrated in Figure 3. Of the 16 Precambrian aragonite examples listed in Table 1, 14 fall within aragonite sea periods predicted for the Proterozoic–Late Archean by the model, 1 straddles the Neoproterozoic–Mesoproterozoic aragonite sea–calcite sea boundary, and 1 falls within a calcite sea period (Fig. 3).

This last example is the 2.52–2.55 Ga Campbellrand–Malmani carbonate deposit of the Transvaal Supergroup of South Africa (Sumner and Grotzinger, 2000). The supratidal and intertidal facies of this deposit carry “halite pseudomorphs” associated with “small fanning pseudomorphs” (Sumner and Grotzinger, 2000, p. 124), pointing to periods of highly evaporitic conditions. Furthermore, for the equivalent-age Carawine Dolomite (ca. 2.55 Ga) of the Hamersley Basin, Australia (once joined with the Transvaal Basin), Simonson et al. (1993) identified dolomite pseudomorphs after gypsum associated with halite molds. They also identified (1) prismatic “zebraic dolomite cement” pseudomorphous after calcite rather than aragonite and (2) domes 4.4 m wide and 1.2 m high with cores composed of concentric layers of radiating prismatic crystals (3–20 cm long, now chert, quartz, or dolomite) as originally having been aragonite, but they found it “worrisome” that the crystal morphologies lack the “distinctive square-tipped terminations” of radiating prismatic aragonite crystals. Simonson et al. (1993) noted that the Campbellrand carbonates of the Transvaal Basin have many of these same features. It is significant that the Miocene Solifera Series of Sicily carries beds of radiating prismatic gypsum crystals that form domes 0.5–4 m in diameter and 0.5–1 m in height that bear a remarkable resemblance in shape and scale to the Carawine

Dolomite “aragonite domes” as well as to the crystal fans illustrated by Sumner and Grotzinger (2000) (cf. their Fig. 3A with Fig. 23 in Hardie and Eugster, 1971, and their Fig. 8A with Figs. 4, 5, and 6 in Hardie and Eugster, 1971). On the basis of all this, a credible case can be made for gypsum rather than aragonite as the original mineral of both the Campbellrand–Malmani and Carawine beds of radiating pseudomorphs.

NOTES AND CONCLUSIONS

1. Prismatic aragonite and gypsum, despite belonging to different crystal systems, have very similar crystal morphologies with very similar interfacial angles, making it difficult to differentiate between their pseudomorphs without the aid of accurate measurement of interfacial angles. Unfortunately, in studies of Precambrian pseudomorphs, measurement of interfacial angles has not been widely used to distinguish an aragonite from a gypsum precursor. A notable exception is the study of Walker et al. (1977, Fig. 2), who used interfacial angle measurements to reinterpret acicular pseudomorphs in the 1.4–1.6 Ga Mc-

TABLE 1. INFERRED PRECAMBRIAN ARAGONITE SEAFLOOR PRECIPITATES

Age (Ma)	Type of precipitate	Location	Source
ca. 600	Fans	Mackenzie Mts., Canada	James et al. (2001)
ca. 600	Fans	Adelaide Geosyncline, Australia	Kennedy (1996)
ca. 600–700	Ooids	Hedmark Group, Norway	Tucker (1983)
> 545 < 800	Ooids, fans	Katakaturuk Dolomite, Alaska	Clough and Goldhammer (2000)
900	Fans	Atar Group, Mauritania	Grotzinger and James (2000)
1000–1200	Ooids	Belt Supergroup, Montana	Tucker (1984)
1483	Fans	Billyakh Group, Siberia	Bartley et al. (2000)
1640	Fans	McArthur Basin, Australia	Winefield (2000)
1640	Fans	McArthur Basin, Australia	Winefield (2000)
1640	Fans	Mt. Shillinglaw Fm., Australia	Winefield (2000)
1640	Fans	Victoria Basin, Australia	Winefield (2000)
1900	Fans	Rocknest Fm., Canada	Grotzinger and Read (1983)
1970	Fans	Kilohgok Basin, Canada	Grotzinger and Friedmann (1989)
2520–2550	Fans	Transvaal Supergroup, South Africa	Sumner and Grotzinger (2000)
2700	Fans	Steep Rock Group, Canada	Hofmann (1971); Grotzinger (1989)
2700	Fans	Cheshire Fm., Zimbabwe	Grotzinger (1989); Sumner and Grotzinger (2000)

Arthur Group, Northern Territory, Australia, as after gypsum rather than the aragonite precursor of earlier workers.

2. The paucity of reports of Precambrian low-Mg calcite seafloor precipitates during times of calcite seas is puzzling. Has concentration on the spectacular fan morphology of Precambrian pseudomorphs after aragonite and gypsum caused workers to overlook primary calcite precipitates?

The correlation of observed and predicted timing of Precambrian aragonite seafloor precipitates (Fig. 3) provides strong support for the following conclusions:

Precambrian seawater was a saline NaCl water with near-neutral pH and $\text{Ca} > \text{HCO}_3$ since at least the Late Archean and very probably since the initial interaction of Earth's condensed $\text{H}_2\text{O-HCl-CO}_2$ -rich secondary atmosphere with the primordial crust.

Major ion compositions of Precambrian seawater chemistry and their secular variations predicted here are in the same ranges as those predicted for Phanerozoic seawater.

The Mg/Ca mole ratio in seawater has controlled the types of CaCO_3 polymorphs that have precipitated from Earth's oceans throughout the Phanerozoic and most, if not all, of the Precambrian. Precipitation of Precambrian abiotic aragonite, like that of Phanerozoic abiotic aragonite, occurred whenever the chemistry of seawater was favorable, specifically when the Mg/Ca mole ratio was $> \sim 2$. Far more testing of this postulate is required. In particular, the current criteria for distinguishing between pseudomorphs after aragonite and gypsum must be reexamined, and a search must be made of those Precambrian carbonates deposited in periods predicted to have been calcite seas (Fig. 3) for evidence of primary low-Mg calcite precipitates.

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REFERENCES CITED

- Baker, E.T., German, C.R., and Elderfield, H., 1995, Hydrothermal plumes over spreading-center axes: Global distributions and geological inferences, *in* Humphris, S.E., et al., eds., *Seafloor hydrothermal systems: Physical, chemical, biological, and geological interactions*: American Geophysical Union Geophysical Monograph 91, p. 47–67.
- Bartley, J.K., Knoll, A.H., Grotzinger, J.P., and Sergeev, V.N., 2000, Lithification and fabric genesis in precipitated stromatolites and associated peritidal carbonates, Mesoproterozoic Billyakh Group, Siberia, *in* Grotzinger, J.P., and James, N.P., eds., *Carbonate sedimentation and diagenesis in the evolving Precambrian world*: SEPM (Society for Sedimentary Geology) Special Publication 67, p. 59–73.
- Berndt, M.E., Seyfried, W.E., and Janecky, D.R., 1989, Plagioclase and epidote buffering of cation ratios in mid-ocean ridge hydrothermal fluids: Experimental results in and near the supercritical region: *Geochimica et Cosmochimica Acta*, v. 53, p. 2283–2300.
- Clough, J.G., and Goldhammer, R.K., 2000, Evolution of Neoproterozoic Katakuruk Dolomite ramp complex, northeastern Brooks Range, Alaska, *in* Grotzinger, J.P., and James, N.P., eds., *Carbonate sedimentation and diagenesis in the evolving Precambrian world*: SEPM (Society for Sedimentary Geology) Special Publication 67, p. 209–241.
- Engel, A.E.J., and Engel, C.G., 1970, Continental accretion and the evolution of North America, *in* Cloud, P., ed., *Adventures in Earth history*: San Francisco, W.H. Freeman and Co., p. 293–312.
- Gaffin, S., 1987, Ridge volume dependence on seafloor generation rate and inversion using long term sealevel change: *American Journal of Science*, v. 287, p. 596–611.
- Garrels, R.M., and Mackenzie, F.T., 1971, *Evolution of sedimentary rocks*: New York, Norton, 397 p.
- Grotzinger, J.P., 1989, Facies and evolution of Precambrian carbonate depositional systems: Emergence of the modern platform archetype, *in* Crevello, P.D., et al., eds., *Controls on carbonate platform and basin development*: Society of Economic Paleontologists and Mineralogists Special Publication 44, p. 79–106.
- Grotzinger, J.P., and Friedmann, J.S., 1989, Occurrence of thick crusts of former botryoidal aragonite, Rifle and Beechey Formations (1.97 Ga), Kilohigok basin, N.W.T.: Geological Association of Canada Program with Abstracts, v. 14, p. A77.
- Grotzinger, J.P., and James, N.P., 2000, Precambrian carbonates: Evolution of understanding, *in* Grotzinger, J.P., and James, N.P., eds., *Carbonate sedimentation and diagenesis in the evolving Precambrian world*: SEPM (Society for Sedimentary Geology) Special Publication 67, p. 3–20.
- Grotzinger, J.P., and Kasting, J.F., 1993, New constraints on Precambrian ocean composition: *Journal of Geology*, v. 101, p. 235–243.
- Grotzinger, J.P., and Read, J.F., 1983, Evidence for primary aragonite precipitation, lower Proterozoic (1.9 Ga) dolomite, Wopmay orogen, northwest Canada: *Geology*, v. 11, p. 710–713.
- Hardie, L.A., 1996, Secular variation in seawater chemistry: An explanation for the coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y.: *Geology*, v. 24, p. 279–283.
- Hardie, L.A., 2000, A new method of predicting paleoseawater compositions: *Geological Society of America Abstracts with Programs*, v. 32, no. 7, p. A-68.
- Hardie, L.A., and Eugster, H.P., 1971, The depositional environment of marine evaporites, a case for shallow, clastic accumulation: *Sedimentology*, v. 16, p. 187–220.
- Hofmann, H.J., 1971, Precambrian fossils, pseudo fossils, and problematica in Canada: *Geological Survey of Canada Bulletin* 189, 146 p.
- James, N.P., Narbonne, G.M., and Kyser, T.K., 2001, Late Neoproterozoic cap carbonates: Mackenzie Mountains, northwestern Canada: Precipitation and global glacial meltdown: *Canadian Journal of Earth Sciences*, v. 38, p. 1229–1262.
- Kempe, S., and Degens, E.T., 1985, An early soda ocean?: *Chemical Geology*, v. 53, p. 95–108.
- Kennedy, M.J., 1996, Stratigraphy, sedimentology, and isotope geochemistry of Australian Neoproterozoic postglacial cap dolostones: Deglaciation, $\delta^{13}\text{C}$ excursions, and carbonate precipitation: *Journal of Sedimentary Research*, v. 66, p. 1050–1064.
- Lafon, G.M., and Mackenzie, F.T., 1974, Early evolution of the oceans: A weathering model, *in* Hay, W.W., ed., *Studies in paleoceanography*: Society of Economic Paleontologists and Mineralogists Special Publication 20, p. 205–218.
- Lowe, D.R., 1983, Restricted shallow-water sedimentation of Early Archean stromatolitic and evaporitic strata of the Strelley Pool Chert, Pilbara block, Western Australia: *Precambrian Research*, v. 19, p. 239–283.
- Lowenstein, T.K., Timofeeff, M.N., Brennan, S.T., Hardie, L.A., and Demicco, R.V., 2001, Oscillations in Phanerozoic seawater chemistry: Evidence from fluid inclusions: *Science*, v. 294, p. 1086–1088.
- Simonson, B.M., Schubel, K.A., and Hassler, S.W., 1993, Carbonate sedimentology of the early Precambrian Hamersley Group of Western Australia: *Precambrian Research*, v. 60, p. 287–335.
- Spencer, R.J., and Hardie, L.A., 1990, Control of seawater composition by mixing of river waters and mid-ocean ridge hydrothermal brines, *in* Spencer, R.J., and Chou, I.-M., eds., *Fluid-mineral interactions: A tribute to H.P. Eugster*: Geochemical Society Special Publication 19, p. 409–419.
- Stanley, S.M., and Hardie, L.A., 1998, Secular oscillations in the carbonate mineralogy of reef-building and sediment-producing organisms driven by tectonically forced shifts in seawater chemistry: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 144, p. 3–19.
- Stanley, S.M., and Hardie, L.A., 1999, Hypercalcification: Paleontology links plate tectonics and geochemistry to sedimentology: *GSA Today*, v. 9, no. 2, p. 1–7.
- Sumner, D.Y., and Grotzinger, J.P., 2000, Late Archean aragonite precipitation: Petrography, facies associations, and environmental significance, *in* Grotzinger, J.P., and James, N.P., eds., *Carbonate sedimentation and diagenesis in the evolving Precambrian world*: SEPM (Society for Sedimentary Geology) Special Publication 67, p. 123–144.
- Tucker, M.E., 1983, Sedimentation of organic-rich limestones in the late Precambrian of southern Norway: *Precambrian Research*, v. 22, p. 295–315.
- Tucker, M.E., 1984, Calcitic, aragonitic and mixed calcitic-aragonitic ooids from the mid-Proterozoic Belt Supergroup, Montana: *Sedimentology*, v. 31, p. 627–644.
- Walker, J.C.G., 1977, *Evolution of the atmosphere*: New York, Macmillan Publishing Co., 318 p.
- Walker, R.N., Muir, M.D., Diver, W.L., Williams, N., and Wilkins, N., 1977, Evidence of major sulphate evaporite deposits in the Proterozoic McArthur Group, Northern Territory, Australia: *Nature*, v. 265, p. 526–529.
- Winefield, P.R., 2000, Late Paleoproterozoic seafloor cements, *in* Grotzinger, J.P., and James, N.P., eds., *Carbonate sedimentation and diagenesis in the evolving Precambrian World*: SEPM (Society for Sedimentary Geology) Special Publication 67, p. 145–159.

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