LATE ARCHEAN ARAGONITE PRECIPITATION: PETROGRAPHY, FACIES ASSOCIATIONS, AND ENVIRONMENTAL SIGNIFICANCE

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ABSTRACT: Large crystal pseudomorphs, composed of limestone and dolomite, that radiate upward to form centimeter- to meter-tall fans are known from every well-preserved Late Archean carbonate platform on earth. In many cases these crystal fans are an important facies, constituting as much as 50% of the observed volume of carbonate rock. Texturally, the fans are composed of elongate blades consisting of a mosaic of crystals with randomly oriented optic axes. In some pseudomorphs, trains of inclusions define the fibrous character of the precursor mineral, and the blades exhibit blunt terminations when draped by micritic sediment. Some of these pseudomorphs contain strontium concentrations of up to 3700 ppm. Associated facies include strongly elongate giant stromatolites, hummelry cross-stratified sandstones, ooid-intraclast packstone to grainstone, small domal stromatolites, and several thinly laminated micritic facies that may display desiccation cracks.

Previously, some of these crystal fans have been interpreted as calcite- and dolomite-replaced pseudomorphs after gypsum, formed under restricted conditions resulting from evaporative concentration of seawater. However, replacement textures and elevated strontium concentrations suggest that the crystal fans are more the result of neomorphism of large botryoids of aragonite that formed thick crusts directly on the sea floor. Furthermore, occurrence of the crystal fans in direct association with strongly elongate giant stromatolites and hummelry cross-stratified sediments suggests precipitation of the fans in open marine, wave- and current-swept environments. Although evaporation of seawater may have contributed to the growth of fans in some peritidal environments, most occurrences are not associated with any other indicators of evaporitic conditions such as halite or gypsum pseudomorphs.

The interpretation of most reported occurrences of Late Archean gypsum pseudomorphs as aragonite pseudomorphs indicates that calcium sulfate precipitation from Late Archean seawater was rare, and that precipitation of aragonite as thick crusts on the sea floor was significantly more abundant than during any subsequent time in earth history. Rapid aragonite precipitation rates and the paucity of calcium sulfate precipitation can be accounted for in a model for Late Archean seawater featuring, relative to present-day seawater, higher supersaturation with respect to calcium carbonate and high HCO₃⁻ concentrations.

INTRODUCTION

Ocean chemistry varies on time scales ranging from thousands to billions of years. Many of these changes are tracked by changes in the chemistry of carbonates and other minerals that precipitate from seawater (e.g., Broecker and Peng, 1987; Grotzinger, 1989; Hardie, 1996; Opdyke and Wilkinson, 1993; Sandberg, 1985b; Wilkinson et al., 1985; Wilkinson and Given, 1986). Recent changes are relatively easy to constrain because the chemistry of seawater is similar to that in the modern oceans. However, developing constraints on ocean chemistry becomes increasingly difficult with increasing age because pH is even lower for the very high pCO₂ suggested by climate models for the Archean atmosphere (e.g., Owen et al., 1979; Walker, 1985; Kasting, 1987). Furthermore, occurrence of the crystal fans in direct association with strongly elongate giant stromatolites and hummelry cross-stratified sediments suggests precipitation of the fans in open marine, wave- and current-swept environments. However pH is even lower for the very high pCO₂ suggested by climate models for the Archean atmosphere (e.g., Owen et al., 1979; Walker, 1985; Kasting, 1987).
nificant quantities of gypsum (Grotzinger, 1989, 1994), suggesting that \([\text{HCO}_3^-] > 2[\text{Ca}^{2+}]\) (Grotzinger and Kasting, 1993), which produces a very different interpretation for the carbonate chemistry of Archean through Mesoproterozoic seawater. Both predict halite precipitation, and neither predicts the precipitation of \(\text{Na}_2\text{CO}_3\), in contrast to the “soda ocean” model. Grotzinger and Kasting (1993) suggest that the paucity of calcium sulfate minerals might also be due to critically low concentrations of sulfate, due to lower \(\text{pO}_2\) at that time. Given the diversity of predicted minerals for various chemical models, the identification of the primary precipitates from ancient seawater can provide constraints on the viability of each model.

Archean carbonates commonly contain large crystal pseudomorphs that radiate upward in centimeter- to meter-tall fans that have been interpreted as either gypsum (e.g., Bertrand-Sarfati, 1976; Martin et al., 1980; Walter, 1983; Holland, 1984; Abell et al., 1985; Hofmann et al., 1985; Wilks, 1986) or aragonite (e.g., Hofman, 1971; Bertrand-Sarfati and Eriksson, 1977; Martin et al., 1980; Simonson et al., 1993). Given the dependence of Archean seawater models on the chemistry and timing of mineral precipitates, it is important to document the primary mineralogy of these pseudomorphs, the range of depositional environments in which they precipitated, and their morphological diversity. Here, we document the occurrences, depositional environments, modes of growth, and crystal characteristics of fanning, botryoidal, and fringing pseudomorphs from various depositional environments in the 2.55 to 2.52 Ga Campbellrand–Malmani carbonate platform, South Africa; –2.7 Ga Belingwe Greenstone Belt, Zimbabwe; –2.6 Ga Bulawayo Greenstone Belt, Zimbabwe; and –2.7 Ga Steeprock Group, Ontario.

**GEOLOGICAL AND DEPOSITIONAL SETTINGS**

**Campbellrand–Malmani Carbonate Platform**

The 2550–2520 Ma (Barton et al., 1994; Walraven and Martini, 1995; Altermann, 1996; Sumner and Bowring, 1996) Campbellrand and Malmani subgroups, Transvaal Supergroup, South Africa, are correlative and compose a ~1.5 km-thick carbonate platform that is preserved over 190,000 km² and was probably deposited over >600,000 km² on the Kaapvaal Craton (Fig. 1; Button, 1973; Eriksson and Truswell, 1974; Beukes, 1980, 1987, Sumner, 1995). It was deposited on the transgressive fluvial to marine Black Reef sandstones (Button, 1973; Clendenin et al., 1991) and the Schmidtsdrif Subgroup (Beukes, 1987), and it is overlain by the thick Kuruman and Penge iron formations, which were deposited after drowning of the carbonate platform. Preservation of the Campbellrand–Malmani platform for 800 km perpendicular to strike, the thickness of all the associated systems tract architecture, and the presence of basinal facies, indicate that the platform formed in a pericratonic, probably passive-margin setting and thus represents precipitation from seawater (Beukes, 1987; Sumner, 1995).

Structural disruption of the Campbellrand–Malmani carbonate platform is limited to gentle warping over most of the craton with locally steeper dips around the Bushveld Complex and intense folding and faulting coincident with the western boundary of the Kaapvaal craton (Stowe, 1986; Beukes and Smit, 1987). Metamorphic alteration is limited, with most outcrops below greenschist facies equivalent metamorphism except around the Bushveld Complex (Button, 1973; Miyano and Beukes, 1984). Early, fabric-retentive dolomite replaced most of the Malmani Subgroup, whereas a significant volume of the Campbellrand Subgroup still consists of limestone.

Eight lithofacies assemblages have been defined for the platform (Fig. 2; Sumner, 1995). 1) **Slope and basinal lithofacies** include rhythmites with interbedded turbidites, chert and dolostone breccias, carbonaceus shales, iron-formation, and tuffaceous turbidites. The presence of turbidites as well as possible debris-flow breccias near the platform margin strongly supports a basinal depositional environment for this lithofacies assemblage (Beukes, 1980, 1987). 2) **The deep subtidal microbialite lithofacies** assemblage consists of a variety of “fenestrate microbialites,” which are a newly characterized group of microbial structures that consist of three components: draping, mat-like laminae; vertically oriented structures called supports; and voids filled with carbonate cements (Sumner, 1997b, 2000). The fenestrate microbialites show diverse morphologies due to varying proportions and relationships among the laminated mat, supports, and cement-filled voids, in addition to physicochemical processes. The delicate morphology of the microbialites, the lack of evidence for scouring, and the absence of clastic carbonate all suggest a deep subtidal, sub-wave-base depositional environment for the microbialite assemblage (Sumner, 1997a, 1997b). 3) **The subtidal giant stromatolite lithofacies** consists of giant elongate mound stromatolites composed of columnar stromatolites, smooth to peaked laminae, and fanning pseudomorphs. The giant, elongate mound stromatolites range from 2 to 10 meters wide and from 5 to >45 meters long (Truswell and Eriksson, 1972; Button, 1973; Eriksson et al., 1976; Eriksson and Truswell, 1974; Eriksson, 1977; Beukes, 1987). Giant elongate mound stromatolites are common in Precambrian carbonate platforms, and above-wave-base, open marine subtidal depositional environments for them have been well established (e.g., Hoffman, 1969; Button, 1973; Truswell and Eriksson, 1973; Eriksson and Truswell, 1974; Grotzinger, 1986a, 1986b; Pelechaty and Grotzinger, 1988). Isolated crystal fans and continuous layers of crystal fans within the giant mound stromatolites previously have been interpreted as domal stromatolites with a radiating internal fabric (Truswell and Eriksson, 1973; Eriksson, 1977) and as gypsum rosettes (Bertrand-Sarfati, 1976). 4) **The lagoonal lithofacies** assemblage contains fenestral microbial laminites and small domal stromatolites. An abundance of local truncation surfaces and the lack of cross-stratification and channeling suggest a shallow subtidal depositional environment with little agitation. The stratigraphic position of these lithofacies platformward of a rimmed margin suggests a lagoonal depositional environment (Fig. 2; Beukes, 1987). 5) **The intertidal to shallow subtidal lithofacies** assemblage is dominated by columnar stromatolites, oolitic and non-oolitic grainstones, and large fanning and fringing pseudomorphs. An abundance of erosional unconformities, rare channeling, and ripple, small dune, and low-angle cross-stratification in grainstones suggest a lower intertidal to shallow subtidal depositional environment. 6) **The supratidal to upper intertidal lithofacies** assemblage consists of domal stromatolites, intraclast and ooid grainstones, intraclast breccias, tepee structures, small fanning pseudomorphs, halite pseudomorphs, and...
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minor micrite. Grainstones contain wave-ripple stratification, desiccation cracks, intraclasts, and channels. The sedimentary structures support a shallow intertidal to supratidal depositional environment. 7) The **grainstone-dominated lithofacies** assemblage consists of beds of oolitic grainstones, non-oolitic grainstones, and wavy-laminated dolomite. They commonly are re-crystallized to the extent that primary sedimentary features are difficult to identify. However, rare wave, interference, climbing, and current ripples are present. Hummocky cross-stratification and trough cross-stratification also are present locally. The range in cross-stratification styles suggests deposition in environments ranging from shallow subtidal to supratidal. 8) Rare quartz sands, siltstones, and siliciclastic shales are associated with exposure surfaces and form a lithofacies assemblage consisting of shallow marine to fluvial siliciclastic deposits.

**Crystal pseudomorphs.**—Pseudomorph fans are abundant across the Campbellrand–Malmani carbonate platform from the platform margin to the interior and in open subtidal to evaporitic supratidal environments (Fig. 2). All of the fanning pseudomorphed crystals grew upward from bedding planes (Fig. 3) or outwards from the sides ofstromatolites as botryoids (Fig. 4). The pseudomorphs consist of millimeter- to centimeter-wide linear zones of clear calcite, dolomite, and/or recrystallized chert that exclude all surrounding sediment. They radiate from a single nucleation point and reach lengths of over 50 cm. Commonly, they are draped by laminated sediment that infilled inter-pseudomorph space and produced stromatolite-like domes (Fig. 3A–C). Rare pseudomorphs are not draped by sediment, and inter-pseudomorph space is filled with calcite cement.

Pseudomorph fans typically are spaced from centimeters to tens of meters along specific bedding planes. In shallow subtidal environments of the giant stromatolite and intertidal to shallow subtidal lithofacies assemblages, 3–50 cm-thick beds of closely spaced pseudomorph fans are common. In these beds, the crystal fans grew into each other; the most inclined pseudomorphed crystals abut crystals in neighboring fans whereas more vertically oriented crystals continued to grow upward (Fig. 3B). These beds have variable sediment influx. Beds with a high influx of sediment relative to growth rate of the original crystals are characterized by small pseudomorph fans and thick layers of draping sediment. Usually, growth of the precursor crystals was terminated by thick layers of sediment, but rarely the most vertically oriented crystals projected above the sediment layer and continued to grow. In beds with lower sediment influx, pseudomorphed crystals that radiated at a low angle to bedding commonly are overlain by a layer of sediment that terminated their growth whereas more vertically oriented crystals continued to grow (Fig. 5A–C). Some fans grew as giant botryoids on bedding planes and lack elastic carbonate between the original crystals. The pseudomorphs in these fans radiate 180° outward from the nucleation sites and abut pseudomorphs from neighboring fans (Fig. 5E). Individual pseudomorphs diverge outward, and small crystal fans are present in the intervening space. Remaining inter-pseudomorph space is filled with calcite cement rather than detrital carbonate.

Where fans are very closely spaced, only the most upright crystals continued to grow, and a fringe of crystals oriented perpendicular to bedding developed (Figs. 3D, E, 5C, D). Similarly, some thinly laminated beds contain crystal pseudomorphs that were elongate perpendicular to bedding without a botryoidal geometry. These pseudomorphs of fine fibrous crystals extend through multiple laminae (Button, 1973; Eriksson, 1977). They always are oriented perpendicular to bedding and parallel to each other. Laminated sediment fills space between
the crystals (Figs. 3D, 5C). These textures are common in the giant stromatolite lithofacies and are present in supratidal deposits.

Commonly, crystal fringes grew off the sides of stromatolites in shallow subtidal depositional environments and in the reef-like margin of the platform (Fig. 4; Bertrand-Sarfati and Eriksen, 1977). These pseudomorphs consist of parallel fine fibers that grew perpendicular to the stromatolite surface. They sometimes coat the entire stromatolite, but more frequently grew as <1 mm to 10 cm thick lenticular to botryoidal coatings projecting into inter-stromatolite troughs (Fig. 4). The fibrous fringes often are coated by later fibrous calcite marine precipitates, including herringbone calcite (a marine cement texture; Sumner and Grotzinger, 1996), or are overlain by grainstone.

**Cheshire Formation, Belingwe Greenstone Belt**

The Belingwe Greenstone Belt, Zimbabwe, unconformably overlies a gneissic basement complex, as old as 3.6 Ga (Bickle et al., 1975; Martin, 1978; Nisbet, 1987). The volcanics-dominated “lower greenstone assemblage”, the Mtshingwe Group, is overlain unconformably by an “upper greenstone assemblage”, the ~2.7 Ga (Hawkesworth and Bickle, 1976) Ngezi Group (Macgregor, 1951; Laubscher, 1963; Bickle et al., 1975). The Ngezi Group consists of three units (Fig. 6): the predominantly sedimentary Manjeri Formation, the volcanic Reliance and Zeedersbergs formations, and the predominantly sedimentary Cheshire Formation. The Cheshire Formation is distributed along the main synclinal axis of the Belingwe greenstone belt. It is about 2.5 km thick and consists of a heterogeneous succession of sedimentary rocks including conglomerate, sandstone, silstone, limestone, and minor banded iron-formation (Martin, 1978). Thicker and more abundant conglomerates characterize the eastern flank of the syncline. They pass laterally across depositional strike into thinner and finer-grained conglomerates toward the western flank of the syncline. Cheshire carbonates are developed in the western flank and pinch out to the east (Martin, 1978).

The Cheshire carbonates occur in a mixed siliciclastic and carbonate interval approximately 500 m thick. The principal outcrop belt studied by Martin et al. (1980) contains stromatolitic limestones, locally interbedded with siltstone and sandstone, and coarse limestone breccia. Martin et al. (1980) described the stromatolitic facies as a series of shallowing-upward cycles that are one to a few meters thick and extend laterally for at least several kilometers. The cycles consist of two subfacies: 1) well-laminated, stromatolitic limestone and dolomitic limestone, with minor chert, and rare argillaceous limestone; and 2) well-preserved upward-fanning bundles of crystal pseudomorphs that were interpreted as calcite pseudomorphs after either aragonite (Martin et al., 1980) or sulfates (Martin et al., 1980; Walter, 1983).

We studied these outcrops to refine the sedimentologic framework in which the carbonates were deposited, as well as better define the tectonic setting of the basin (see also Grotzinger et al., 1993). Our work involved mapping and logging of detailed measured sections from the main stromatolite outcrop. The lower part of the Cheshire Formation comprises siltstones and shales with rarer interstratified fine- to medium-grained sandstone beds. Sandstone beds are dominated by planar lamination, ripple cross-lamination, and low-angle planar stratification. In some cases, they contain well-developed hummocky cross-stratification. Other beds consist of centimeter-scale interstratified sandstones and shales that form lenticular to wavy bedding. In these beds, thin sandstones are dominated by symmetrical to slightly asymmetrical ripples with internal stratification exhibiting bundled, chevron-type upbuilding. Ball-and-pillow structures, convolute bedding, and small slump structures are common, particularly near the tops of thicker sandstone beds. Amalgamated sandstone beds form units up to 2.5 m thick.

Upwards in the section, partially dolomitized limestones become interstratified with siliciclastic facies, forming discrete beds 20–50 cm thick. The limestones contain fine-grained oolites, numerous beds of upward-radiating fans of pseudomorphed crystals, and uncommon simple domal stromatolites. Pseudomorph fans commonly form small mounds that are overlapped by rippled oolites. The proportion of siliciclastic facies decreases upward in the section, and carbonate beds thicken.
reaching up to 3 m thick, and are dominated by small mounds of fanning pseudomorphs. Ultimately, siliciclastic facies give way to a 50-m-thick continuous carbonate interval called the "main stromatolitic outcrop" (Martín et al., 1980).

The bedding characteristics and assemblages of sedimentary structures in the Cheshire Formation below the main stromatolitic outcrop typically are associated with wave- or storm-dominated open marine shelf settings (Clifton et al., 1971; de Raaf
et al., 1977; Dott and Bourgeois, 1982; Arnott, 1993). Sediment deposition seems to have been greatest during times of strong unidirectional to oscillatory flows, interspersed with more prolonged intervals of settling from suspension and reworking by gentle wave-produced currents. Siliciclastic facies of the lower Cheshire Formation suggest a shallow subtidal environment, with water depths on the order of 5–50 m. The oolite facies is consistent with these depths; only thin oolitic sheets formed, rather than the thick lenticular units characteristic of shoals. These facies assemblages are most consistent with subtidal deposition of pseudomorph fan facies under normal marine conditions in an open, wave-swept shelf setting. There is no evidence to indicate that the pseudomorph fans in the lower Cheshire Formation formed in a restricted lagoonal setting as proposed by Martin et al. (1980).

The main stromatolite outcrop comprises asymmetric cyclic limestones with stromatolites and fans of pseudomorphs (Martin et al., 1980). Cycles typically are bounded by erosional surfaces with up to a few centimeters of relief that are overlain and draped by centimeter-thick beds of shale, transgressive lag deposits consisting of oolite–intraclast grainstone/packstone, and rare flat-pebble conglomerate (Fig. 7). In several cases, pseudomorph fans and stromatolites nucleated directly on the erosional surfaces, but most appear to have grown on lag deposits. Pseudomorph fans form beds 10–200 cm thick that alternate with small domal to columnar stromatolites 2–10 cm wide and 5–20 cm high. Pseudomorphs grew off of stromatolitic laminae and vice versa. These facies are gradationally overlain by a crinkly laminite facies composed of submillimeter- to millimeter-thick microsparitic laminae that have a constant thickness normal to layering. The crinkly laminites commonly are truncated by a minor erosional surface, and the cyclic facies motif is repeated (Fig. 7). Transition styles between facies suggest that cycle boundaries occur at the bases of pseudomorph fan and stromatolitic units, coincident with stratigraphic thicknesses with evidence for erosion and draping overlap. Because the pseudomorph fan and stromatolite beds usually are overlain gradually by the crinkly laminite facies, which is truncated by the erosion surfaces, the crinkly laminite facies represents the top of any given cycle. This interpretation is distinct from that reported by Martin et al. (1980), who placed cycle boundaries at the top of pseudomorph fan and stromatolitic beds, which were interpreted as the final stage of deposition in evaporative cycles.

Our reinterpretation of the Cheshire cycles suggests a non-evaporitic depositional environment. Rather, the sedimentary characteristics best fit the shallow flooding of subaerial exposure surfaces followed by deposition of shale, ooids, and intraclasts in a zone of active wave reworking; surfaces of this type with overlying lag deposits are extremely common in the record of shallow marine carbonate platforms (e.g., James, 1984). The crystal fan facies would have a shallow subtidal origin, consistent with open marine environmental interpretations for the pseudomorph fans in the lower Cheshire Formation. The transition to crinkly laminite facies is interpreted as shallowing to the peritidal zone, where deposition occurred in a more restricted setting. The crinkly laminite facies is similar to other peritidal laminites of early Precambrian age that show monotonous, fine lamination, often with extreme lateral continuity, which suggests a precipitated origin (Grotzinger and Rothman, 1996). However, the crinkly laminite facies differs somewhat from other peritidal laminites in that it shows remarkable local surface roughness across a broad range of length scales. In that sense, the facies is more comparable to the peaked laminite facies of the Paleo- and Mesoproterozoic Cowles Lake Formation, which is interpreted as a shallow subtidal facies (Jackson, 1989; Grotzinger and Rothman, 1996). With the reinterpretation of crystal pseudomorphs replacing aragonite rather than gypsum, combined with the absence of casts and molds of standard evaporite minerals, we find no evidence that would contradict the interpretation that the pseudomorph fan facies developed in a shallow subtidal setting that ranged from open marine shelf, to somewhat more restricted, peritidal conditions.
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FIG. 5.—Various geometries of fanning pseudomorphs. A) Pseudomorph fans draped by laminated sediment tend to nucleate on specific surfaces. Where closely spaced, neighboring fans interpenetrate and the original crystals competed for growth space. Note that more inclined crystals commonly were buried by sediment earlier than more vertically oriented ones. B) Thick layers of sediment often bury fans. Sometimes the most vertically oriented pseudomorphed crystals project through thick sediment layers and new fans nucleated on them. In rare cases where crystals projected significantly above the sediment-water interface, pseudomorphs acted as nucleation sites for digitate stromatolites. C) In areas with abundant fine-grained sediment and closely spaced fans, thin, fibrous pseudomorphs project through multiple laminae, often resulting in beds with a strong vertical fabric at right angles to a fine horizontal lamination. D) Some beds consist entirely of closely spaced pseudomorphs. A fanning geometry is apparent only at the bases of the beds where fans nucleated. The tops of the beds consist of nearly vertically oriented pseudomorphs. E) Some beds consist entirely of widely spaced fanning pseudomorphs. The individual pseudomorphs radiate out at 180°. New fans nucleated on the sides of the precursor crystals as they diverged outward. Calcite cement typically fills the remaining pore space.

Crystal pseudomorphs.—Pseudomorph fans form a substantial fraction of the carbonates in the Cheshire Formation. In the lower Cheshire Formation, they commonly form localized buildups or lithoherms and laterally continuous beds (Fig. 8). The lithoherms have widths of tens of centimeters to tens of meters and up to 20 cm of synoptic relief. They are onlapped by wavy-laminated grainstone or siltstone (Fig. 8A), and grainstone commonly fills space between individual pseudomorphs. In most cases, pseudomorph fans nucleated on a single surface and grew into each other laterally, resulting in vertically oriented pseudomorphs in the upper parts of the beds (Fig. 5C, D). In rare cases, however, new fans nucleated within a bed, producing upward-diverging pseudomorph orientations throughout the bed. In the main stromatolitic outcrop, the pseudomorphed crystals nucleated on erosional surfaces, lag deposits, or stromatolitic laminae. Pseudomorphed fans that nucleated on erosional surfaces or lag deposits usually form continuous layers of fans. However, some beds contain widely spaced, 5–10 cm tall pseudomorphed crystals that nucleated on highs on the underlying bed and are separated by grainstone with rare intraclasts. Crystal pseudomorphs are intimately associated with stromatolitic laminae. In many cases, stromatolitic laminae coat the tops of the crystals and mimic the relief of the underlying crystals. Centimeter–diameter digitate stromatolites grew off of the tips of some individual pseudomorphed crystals (Fig. 8C), and troughs between both the pseudomorphs and digitate stromatolites are filled with oolitic grainstone. Some crystal fans nucleated on the tops of columnar stromatolites, and rare pseudomorph fans are present between stromatolitic laminae, commonly, but not always, forming continuous layers (Fig. 7).

BELINGWE GREENSTONE BELT

(NGEZI GROUP; 2.7 Ga)

FIG. 6.—Generalized stratigraphy of the Ngezi Group in the Belingwe Greenstone Belt illustrating relative position of the Cheshire Formation. After Martin (1978) and Martin et al. (1980).
Fig. 7.—Representative stratigraphic section of the Cheshire Formation, from the "Main Stromatolite Outcrop" of Martin et al. (1980). This interval forms the uppermost 10 m of the outcrop, and is directly overlain by a siliciclastic-rich interval, containing fine sandstones and siltstones similar to the lower Cheshire Formation. Note cyclic repetition of facies, with fans and grainstones directly overlying cycle boundaries, interpreted as subaerial exposure and transgressive surfaces.
**Huntsman Limestone, Bulawayo Greenstone Belt**

The ~2.6 Ga (Hawkesworth and Bickle, 1976) Bulawayo greenstone belt, Zimbabwe, contains a thick succession of mafic and ultramafic lavas interspersed with thin units of felsic volcanics, phyllites, banded iron formation, and rare carbonate (Wilson, 1979). In general, outcrop is poor and little is known about this belt. However, local occurrences of limestone are present and are clearly part of the thick succession of mafic and ultramafic rocks. These carbonates have been studied only in a very general way starting with their discovery by Macgregor (1941) and followed by hand-sample descriptions of stromatolites (Schopf et al., 1971; Walter, 1983).

In 1993, excellent exposures were available for study at Huntsman Quarry because of a long drought, which lowered water levels in the normally flooded pits. We measured two short sections that revealed a diverse suite of structures including stromatolites, fenestrate microbialites, abundant fanning pseudomorphs, and laminated clastic carbonates. The stratigraphically lower section from the southeast pit (Fig. 9) consists predominantly of beds of fanning pseudomorphs with calcite cement crusts and interbeds of fenestral carbonate and rare micritic sediment. These facies are typically arranged into decimeter-thick cycles. The base of each cycle consists of light tan pseudomorph fans that darken upward. They are capped by 0.1–5 cm-thick crusts of herringbone calcite that form either continuous layers or digitate stromatolites. The crusts are dark and abruptly overlain by light pseudomorph fans. In several cycles, micritic layers filled the relief on top of the herringbone calcite crusts before the nucleation of new pseudomorphed crystals. No evidence of erosion or dissolution was observed along these surfaces. The origin of fenestral beds that are occasionally interbedded with these cycles is unknown, but may be due to microbial mat growth.
Fig. 9.—Stratigraphic sections of the Huntsman limestone. The southeast pit contains abundant layers of fanning pseudomorphs and fenestral limestone. The north pit contains abundant pseudomorph fans intergrown with fenestrate microbialites. Because of abundant shearing and recrystallization, microbial structures are commonly recognized only by the presence of dish-shaped voids preserved as sparry calcite in darker limestone.
The upper section is from the west face of the north pit (Fig. 9). It starts with beds of fanning pseudomorphs with rare fenestral interbeds. After a recrystallized massive interval, the large domal stromatolites described by Macgregor (1941) are developed. Internal textures are poorly preserved, but faint laminations occasionally are visible. Above the giant domes, abundant fenestral microbial structures with scattered fanning pseudomorphs are the dominant lithofacies. The microbial structures consist of laminated mat, supports, and dish-shaped voids that are similar to cuspatate fenestral microbialites of the deep subtidal microbialite lithofacies assemblage in the Campbellrand–Malmani carbonate platform (Sumner, 1997a, 1997b). Because of extensive recrystallization, often only the dish-shaped voids are visible because of their light color relative to the laminated mat and supports. However, in less altered beds, the microbialite structure is well preserved. Upward in the section, beds of vertically oriented pseudomorphs are interfretted with beds of fenestral microbialites. The pseudomorphs in these beds commonly are draped by black laminae that are vertically separated by one to several millimeters of white calcite that appears to fill centimeter-long, bedding-parallel fenestrae. The sides of these fenestrae are defined by the edges of pseudomorphs, whereas the tops and bottoms are defined by the dark laminae. Upward in the section, pseudomorphed fan lithoherms developed, and one layer of columnar stromatolites with a herringbone calcite internal texture was deposited. The top of the upper section is extensively sheared, and few sedimentary features are preserved.

The lack of cross-stratification and a larger stratigraphic context for the Huntsman limestone makes interpretation of the depositional environment equivocal. However, facies in the upper section are consistent with a subtidal depositional environment (Macgregor, 1941). The delicate fenestral microbialites were probably deposited below wave base or during episodes of low agitation (Sumner, 1997a, 1997b), whereas the large domal stromatolites may have been deposited above wave base (Macgregor, 1941). No sedimentary structures suggesting intertidal or restricted depositional environments were observed.

Crystal pseudomorphs.—In the Huntsman Limestone, the pseudomorph fans commonly nucleated at the bases of 3–20 cm-thick beds that usually consist solely of pseudomorphs (Fig. 10A), and rarely contain small amounts of draping sediment. Lithoherms consisting solely of pseudomorph fans developed synoptic relief of up to 20 cm. The fans in the lithoherms commonly nucleated along specific surfaces, overgrowing the underlying pseudomorphs. They range in height from 1 to 20 cm.

Pseudomorphs associated with the fenestral microbialites are poorly preserved because of extensive recrystallization and strain. We identified only widely separated pseudomorphs in microbialite-rich beds, where they project through the fenestral microbialites irrespective of the microbial textures (Fig. 10B). Walter (1983) described an acicular crystal texture corresponding to our fanning pseudomorphs that projected through both the microbial mat and the dish-shaped voids. He reported that the acicular texture was pervasive, which suggests that it may be more common than we observed. Walter (1983) suggested that the voids in the microbialites were due to separation of laminae from the force of crystallization of the acicular pseudomorph growth. However, the microbial structures are identical to cuspatate microbialites in the Campbellrand–Malmani platform, where voids are filled with isopachous calcite cements (Sumner, 1997b, 2000). Thus, the voids are probably a result of microbial processes rather than precipitation of primary crystals. We did not observe any evidence that growth of the original crystals affected the microbialite textures by producing voids, forming surfaces that were colonized by mats, or disrupting the lateral continuity of the mat.

Beds of vertically oriented pseudomorphs that are interfretted with microbialites commonly are draped by black laminae and contain oblong, bedding-parallel fenestrae distinct from those in the microbialite beds (Fig. 10C). The fenestrae-filling calcite typically is extensively recrystallized, so its origin is unknown. However, the texture of the laminae is similar to the laminated mat in the fenestral microbialites, which suggests that they may have been microbial mats. If so, these beds may have consisted of vertically oriented crystals that were draped by microbial mats, leaving voids beneath the mats and between the crystals that were later filled with calcite cement. In this case, the original crystals may have formed a surface on which microbial mats grew.

Steeprock Group

The ~2.7 Ga Steeprock Group, Ontario, Canada, unconformably overlies much older crystalline basement and consists of a platform of siliciclastic sands and conglomerate, carbonate, and altered iron-formation, followed by a "typical" greenstone belt sequence of thick pyroclastic ashrock, mafic volcanics, and turbiditic sediments (Jollife, 1966; McIntosh, 1972). The contact between the ashrock and overlying thick mafic volcanics is strongly sheared, suggesting that the volcanics have been thrust over Steeprock platform sediments (Hoffman, 1989). Carbonates in the Steeprock Group have been studied for over 100 years from regional, economic, paleontologic, and sedimentologic perspectives (Smyth, 1891; Walcott, 1912; Lawson, 1913; Jollife, 1955; Hofmann, 1971; Walter, 1983; Wilks and Nisbet, 1985; Wilks, 1986).

The Steeprock carbonates were deposited on a veneer of fluvial (Wilks, 1986) and possibly shallow marine siliciclastic sediments that covered the exposed crystalline basement (Fig. 11). The carbonates are up to 500 m thick and extend continuously along strike for 12 km, with the exception of one locality where the entire unit has been cut out beneath a major karstic unconformity developed at the top of the sequence (Wilks, 1986; Hoffman, 1989). The upper karstic carbonates are overlain by a carbonate soil-like sequence containing the minerals goethite, gibbsite, hematite, and kaolinite, as well as including lenses of pisolithic ferruginous bauxite (Jollife, 1955; Wilks, 1986). This deeply weathered soil unit is overlain by a sequence of altered probable banded iron-formation, which is thought to have accumulated subaqueously, following transgression of the paleosol and foundering of the platform (McIntosh, 1972; Wilks, 1986).

A crude stratigraphy (Fig. 11) based on stromatolite morphology has been defined for the Steeprock carbonates (Wilks and Nisbet, 1985; Wilks, 1986). Grainstones apparently are absent from the sequence, which is dominated by stromatolitic lithologies. Small domal stromatolites up to 15 cm wide with up to 10 cm synoptic relief occur near the base of the sequence and are associated with units containing microbial laminites and
irregular to wavy-laminated stromatolites (Wilks and Nisbet, 1985; Wilks, 1986). Digitate columnar stromatolites and linked conical stromatolites are developed locally, and pseudomorphs after a fibrous, radiating precursor mineral are present (Hofmann, 1971). These pseudomorphs were first described and interpreted by Walcott (1912) as biogenic structures, and assigned the name Atikokania. Subsequently, these were reinterpreted to be crystal structures identical to the pseudomorphs described here. Hofmann (1971) suggested gypsum or aragonite as a precursor mineralogy, but later authors have favored only the gypsum interpretation, on the basis of the large size of the crystals, which extend for up to 25 cm (Walter, 1983; Wilks, 1986). Overlying carbonates contain large, elongate stromatolite mounds up to 3 m wide and 5 m long, and with up to 1 m of synoptic relief (Wilks, 1986). Stromatolites form biostromes that extend across most outcrops. Lamination in stromatolites is defined by variations in the organic content of the carbonate, as well as fenestrae that are up to 3 cm long (Wilks, 1986). Walter (1983) noted that the laminae are defined in part by the presence of acicular crystal fibers, similar to those of the "Atikokania" facies.

The overall stratigraphy of the Steeprock carbonate sequence has been interpreted by Wilks (1986) as a subtidal, shallowing-upward depositional package, with smaller stromatolites at the base and larger stromatolites at the top. However, many documented Proterozoic shallowing-upward sequences contain larger-scale stromatolites that are overlain by smaller varieties (Cecile and Campbell, 1978; Grotzinger, 1986a; Beukes, 1987). Thus, the Steeprock sequence probably deepens upward. A subsequent fall in relative sea level exposed the top of the platform and a karstic unconformity developed.

**Crystal pseudomorphs.**—Continuous sections were not measured at Steeprock, but fans of pseudomorphs, identical to Atikokania, are abundant as laterally continuous beds interstratified with columnar stromatolites and fenestrate microbialites. In beds, the crystal fans typically nucleated very close to each other and grew continuously upward for 1 to 160 cm. The fanlike geometry is predominant at the very bases of beds, and upward, the pseudomorphs are predominantly parallel and vertically oriented (Figs. 5D, 12). Pseudomorphs draped with sediment were not observed.

Pseudomorphs fans commonly are found within fenestrate microbialites that form wavy layers with alternating void-rich and void-poor microbialites (Fig. 12B; Sumner, 2000). Rare layers of cuspatate fenestrate microbialites with dish-shaped voids are present, but most of the fenestrate microbialites have 0.5–5 mm equant rather than dish-shaped voids and form a net-like texture. Void-rich, net-like microbialites contain abundant equant voids separated by supports draped by thin mat layers. The supports commonly show small amounts of compactional fold-
timing. Void-poor microbialites contain abundant compacted supports draped by filmy laminae. Voids are rare in the compacted microbialites and are flattened parallel to the filmy laminae where present. In some cases, pseudomorphs project through the microbialites. They are more abundant or better preserved in void-poor microbialite layers that show evidence for post-growth compaction than in less compacted microbialites. In the compacted microbialites, the pseudomorphs are typically densely spaced with few to no identifiable gaps between them. In some samples, the pseudomorphs form fans that grew against one another (Fig. 12). The microbial laminae dome up over the centers of the fans and have a trough-filling geometry where neighboring fans intersect. The pseudomorphs project through the microbial components without directly affecting the morphology of the microbialites. The microbialites are encased in the pseudomorphs, and the laminated mat and supports continue from pseudomorph to pseudomorph without deflecting upward or downward at the pseudomorph boundaries (Sumner, 2000). In addition, the supports and pseudomorphed crystals are not always oriented parallel to each other. At the sides of fans, the pseudomorphs radiate slightly outward whereas the supports are oriented more vertically. Compaction probably modified the original orientation of the supports, but they are not oriented parallel to the elongation of the pseudomorphs, which implies that their orientation was not affected by precipitation of the precursor mineral.

The origin of the carbonate in the void-rich microbialites is unclear. Pseudomorphs are less abundant in them, because of either poor preservation or precipitation of fewer precursor crystals. Sumner (2000) interprets the differences in void-rich and void-poor net-like microbialites as due to variable synsedimentary compaction. In void-rich microbialites, carbonate precipitation probably occurred on the supports during growth of the microbialites, giving them rigidity. In contrast, there was probably little contemporaneous precipitation on void-poor microbialites, allowing them to compact. However, Walter (1983) reports acicular crystals projecting through voids in what look to be void-rich microbialites, suggesting that originally the pseudomorphed crystals did precipitate within both void-rich and void-poor microbialites.

**Timing and Environments of Pseudomorph Precipitation**

In all four carbonate platforms studied, the pseudomorph fans grew upward or outward from depositional surfaces. The abundance of beds of crystal pseudomorphs up to 160 cm thick and lacking evidence for detrital carbonate demonstrates that they did not grow within sediment. The growth of lithoherms consisting solely of fans and surrounded by siltstone, grainstone, and intraclasts demonstrates that they could form current-resistant highs on the sea floor. In addition, the growth of digitate stromatolites on the tips of individual pseudomorphs demonstrates that some crystals projected above the sea floor and formed sites favorable for stromatolite growth. Sediment that draped growing fans or infilled troughs between fans was deposited contemporaneously with or after growth of the pseudomorphed crystals. Thus, most of the pseudomorphs replace a primary mineral that grew directly from ambient seawater at or projecting above the sediment–water interface.

The timing of precipitation of the fine, vertically oriented pseudomorphed crystals that project through laminated sediment is more difficult to interpret. The primary crystals probably did not project far above the sedimentary surface because traction transport of sediment would have broken off the fine crystals. In contrast, they may have precipitated either at or just below the sediment–water interface.

The timing of precipitation of pseudomorphed crystals preserved in fenestrate microbialites is also somewhat ambiguous. The primary crystals show no evidence of having influenced the growth morphology of the microbialites, which implies that the precipitation of the original crystals may have occurred below the mat surface and encased the mat as they grew upward. In addition, the evidence for compaction in some microbialites containing abundant pseudomorphs suggests that crystal growth occurred below the mat surface after minor compaction of the microbialites (Sumner, 2000). In contrast, the beds of pseudomorphed crystals in the upper Bulawayo section that appear draped by mats may have provided a surface for microbial colonization, and thus influenced the texture of the microbial structures. Even where the pseudomorphed crystals may have grown below a microbial mat, there is no evidence for preexisting sediment that was replaced by growth of the crystals. The textural evidence suggests that the crystals formed the original sediment within microbial mats consisting of organic residue with abundant water-filled voids. Thus, the pseudomorphs likely reflect the primary precipitation of the precursor mineral from microbiolally modified seawater.

The environments in which the pseudomorph precursor precipitated are diverse, ranging from agitated subtidal to evaporitic facies. Depositional environments are best constrained in the Campbellrand–Malmani carbonate platform, where preser-
FIG. 12.—Fibrous pseudomorphs from the Steep Rock carbonates. A) Field photo of fans. Coin is 2 cm in diameter. B) Two pseudomorph fans project through microbialites and abut each other in the trough near the white tension crack.

vation of the platform for 800 km across strike allows evaluation of the extent of restriction during growth of the fans. Fans are abundant throughout the platform, including the wave-swept subtidal giant stromatolite facies belt in the ramp that developed at the base of the platform and during a major transgression in the middle of the platform (Fig. 2). In addition, the fans are present throughout the reef margin. The presence of fans in these agitated, open marine environments implies that they precipitated from open seawater and not solely from evaporitically concentrated waters. Fans that grew in more restricted facies of the Campbellrand–Malmani carbonate platform tend to be substantially smaller, suggesting that crystal precipitation in restricted facies had different morphological characteristics, possibly because of a higher influx of detrital carbonate. In the Cheshire Formation, pseudomorph fans also are abundant in open-shelf, agitated depositional environments, as well as possibly more restricted environments. Although similar evaluations of the extent of restriction are not as reliable for the Bulawayo and Steep Rock greenstone belt carbonates, facies studied are consistent with near-wave-base subtidal deposition. Thus, precipitation of the precursor mineral in these four carbonates of diverse age probably reflects global Late Archean seawater chemistry.

PSEUDOMORPH CHARACTERISTICS

Petrographic Characteristics

The fanning and botryoidal crystal pseudomorphs now consist of calcite, dolomite, and chert. Their morphology is defined
by trains of inclusions and their relationships to the surrounding sediment. Where the pseudomorphs are draped by fine sediment, they have flat to feathery terminations. In addition, they have hexagonal cross sections. Petrographic preservation is best in pseudomorphs now consisting of calcite.

Calcite replacement of the original crystals can be texturally classified into four petrographic facies (Fig. 13): 1) inclusion-rich, equant mosaic; 2) scattered inclusion, interlocking mosaic; 3) elongate mosaic; and 4) equant mosaic. The optically best preserved pseudomorphs are replaced by an inclusion-rich, equant mosaic of calcite. This petrographic facies contains abundant trains of inclusions that run parallel to elongation in the pseudomorphs and preserve the original fibrous character of the precursor mineral. They crosscut calcite crystal boundaries. The optically unoriented calcite crystals are 50–250 μm in diameter and are equant to rarely elongate parallel to inclusion trains. Crystal boundaries are usually planar compromise boundaries with rare irregular to interlocking boundaries. Some crystals overstep the edges of pseudomorphs and replace both the primary mineral and inter-pseudomorph fill. The scattered inclusion, interlocking mosaic petrographic facies contains fewer inclusions, which are scattered throughout with only very faint linear trends parallel to pseudomorph elongation. The optically unoriented calcite crystals are about 300 μm in diameter and are sometimes elongate parallel to pseudomorph elongation. They have well defined, interlocking crystal boundaries.

Commonly, well defined crystals contain about four subdomains with slightly different extinction orientations and indistinct domain boundaries. The elongate mosaic petrographic facies lacks inclusions defining original crystal structure. The optically unoriented calcite crystals are variable in size but are typically smaller than 175 x 500 μm and are elongate parallel to pseudomorph elongation. Rare crystals contain subdomains with slightly different extinction, which are also elongate parallel to pseudomorph elongation. The crystals have irregular boundaries that tend to be more linear when parallel to pseudomorph elongation. The equant mosaic petrographic facies includes most other replacement textures that do not preserve characteristics of the primary minerals. The equant crystals vary in size and are optically unoriented.

All four petrographic facies are abundant in the pseudomorphs from the Campbellrand–Malmani carbonate platform. The facies grade laterally into each other. Individual pseudomorphs sometimes contain all four facies and often contain the scattered inclusion, elongate, and equant mosaics. Pseudomorphs from the Cheshire Formation typically consist of scattered inclusion mosaic facies that grades into equant mosaics. Pseudomorphs from the Huntsman limestone and the Steeprock Group are poorly preserved and consist of equant mosaics. The pseudomorphs from the Steeprock Group typically contain bimodal mosaics with 80% of crystals <50 μm in diameter and 20% >200 μm in diameter.

![Figure 13](image-url)

**Fig. 13.—Photomicrographs of fibrous pseudomorphs in sample BT 22 from the Campbellrand–Malmani platform. A) The right half of the pseudomorph consists of the inclusion-rich, equant mosaic whereas the left half consists of the scattered inclusion, interlocking mosaic. B) Same view under crossed polarizers. C) Pseudomorph consisting of the elongate mosaic facies. The high Sr measured in sample BT 22 came from this area. D) Same view under crossed polarizers. Scale bar is 500 μm long for all photographs.**
Primary Mineralogy

Several of the petrographic characteristics of the fanning pseudomorphs strongly suggest an aragonite precursor mineralogy. First, the relict morphological characteristics of the original crystals are most consistent with an aragonite precursor: the fibrous nature of the primary mineral and the blunt to feathery terminations of the pseudomorphs are typical of aragonite (Loucks and Folk, 1976; Mazzullo, 1980; Sandberg, 1985a; Peryt et al., 1990). Gypsum crystals usually have well-developed crystal faces (e.g., Hardie et al., 1983; Lowenstein, 1988), none of which were observed. Second, optically unoriented, equant to elongate calcite crystals with unit extinction are characteristic of calcite replacement of aragonite (Assereto and Folk, 1980; Mazzullo, 1980; Sandberg, 1985a). Gypsum and anhydrite typically are replaced by calcite in a dissolution–precipitation process, so preservation of inclusions defining the internal texture of a gypsum precursor is not expected (e.g., Harwood, 1980; Folk et al., 1993). Also, secondary calcite mosaics filling gypsum molds would show either a void-filling geometry or an equant neomorphic texture rather than elongation parallel to pseudomorph elongation. Solution-collapse features, which can be associated with replaced gypsum pseudomorphs, were not observed in any of the Archean carbonates described. Thus, a combination of the primary crystal morphology and the petrographic textures of the pseudomorphs are inconsistent with gypsum as the precursor mineral.

The pseudomorph characteristics also are inconsistent with recrystallized primary calcite cements. Recrystallization of fibrous calcite usually produces optically oriented neomorphic calcite mosaics (Assereto and Folk, 1980; Mazzullo, 1980; Sandberg, 1985a) rather than the unoriented mosaics observed. These recrystallized calcite textures are present adjacent to, but not within, the pseudomorphs. Also, the hexagonal cross sections of the pseudomorphs are consistent with either gypsum or twinned aragonite (e.g., Sandberg, 1985a; Buick and Dunlop, 1987; Riccioni et al., 1996) but are not characteristic of fibrous calcite.

Strontium Concentrations

Aragonite commonly contains high [Sr] whereas calcite and gypsum typically contain less strontium, because the strontium partition coefficient for aragonite is 1.13 (Kinsman, 1969; Kinsman and Holland, 1969) whereas the partition coefficients for calcite and gypsum are <0.1 (Katz et al., 1972; Lorens, 1981) and 0.2 (Kushnir, 1980), respectively. Marine aragonite commonly contains tens of thousands of ppm strontium initially, and thousands of ppm strontium can be preserved in aragonite pseudomorphs during conversion of aragonite to calcite at low water-to-rock ratios (e.g., Katz et al., 1972; Sandberg, 1985a). Concentrations of several thousand ppm are rare in primary calcite and would not be expected in recrystallized calcite because of Sr loss during recrystallization. Similarly, gypsum replaced by calcite should not contain high [Sr] because of the relatively low distribution coefficient of Sr into gypsum, and substantial volumes of water are necessary to alter gypsum to calcite, which would further dilute the [Sr] of the secondary calcite. Thus, high preserved [Sr] supports the interpretation of an aragonite precursor to the pseudomorphs. Low [Sr] may reflect either high water-to-rock ratios or a different precursor mineral.

Strontium concentrations of pseudomorphs from the Campbellrand–Malmani platform were measured using an electron microprobe with a 15 keV beam acceleration, 5 nA beam current, and a 10 µm spot size. Counting times were 10 s for Ca, Mg, and Fe and 30 s for Sr and Mn. Yield weights were calculated for stoichiometric carbonate using [Ca], [Mg], [Mn], [Fe], and [Sr] and were 98–103%. The Sr, Mn, and Fe detection limits were 400 ppm, 600 ppm, and 1200 ppm, respectively. Analyses were performed on 1–4 pseudomorphs in each of six samples and on fibrous calcite cement in one sample. [Sr]
in each pseudomorph and the calcite cement was measured at six spots separated by 15–50 μm. The calcite cement (sample MV104-1) contained less than or equal to 600 ± 400 ppm Sr, and pseudomorphs in the same sample contained up to 900 ± 400 ppm Sr, although most analyses were below the detection limit (Table 1). Highest [Sr] were measured in an area of sample BT 20 consisting of the elongate mosaic facies replacing a botryoidal pseudomorph, where concentrations from 1800 to 3700 ± 400 ppm were measured. [Sr] varied from 1800 ppm to 3200 ppm over a distance of <50 μm. Strontium concentrations greater than 900 ± 400 ppm were also measured in the scattered-inclusion interlocking-mosaic facies in both botryoidal and fanning crystal pseudomorphs. Concentrations are extremely variable and jump from >900 ppm to below the detection limit in a distance of <50 μm. This local heterogeneity demonstrates that water–rock interactions were variable over very small distances during recrystallization of the original crystals.

The preservation of several thousand ppm Sr in the pseudomorphs supports an aragonitic precursor. The composition of recrystallized calcite cements associated with less well preserved pseudomorphs overlaps [Sr] in the pseudomorphs, so results do not unambiguously demonstrate that the pseudomorphs contain higher [Sr] than associated calcite. However, the high concentrations in better preserved pseudomorphs and local heterogeneity are supportive of an aragonitic precursor that recrystallized to calcite with variable but low water-to-rock ratios. This distribution of Sr would not be expected with the large water-to-rock ratios required for calcite replacement of gypsum.

**DISCUSSION**

**Other Archean Occurrences**

Similar aragonite pseudomorphs have been reported from two other Archean carbonates. In the 2.6 Ga Carawine Dolomite, Hamersley Basin, Australia, pseudomorphs are found in shallow-water, low-energy depositional environments and consist of prismatic pseudomorphs forming sediment-draped fans and acicular pseudomorphs forming fringes and botryoids (Fig. 14; Simonson et al., 1993). The prismatic pseudomorphs are 3–20 cm long, have hexagonal cross sections, and show irregular crystal terminations. Neighboring pseudomorphs show evidence of competitive growth. The replacing dolomite and chert appear to have filled molds of the original crystals (Simonson et al., 1993). Acicular pseudomorphs are up to 4 cm long and are closely spaced forming parallel to botryoidal masses. Some of these masses were reworked and abraded (Simonson et al., 1993). Morphologically, the acicular pseudomorphs are similar to the prismatic pseudomorphs, but petrographically, they show replacement rather than dissolutional textures (Simonson et al., 1993). Simonson et al. (1993) interpret these pseudomorphs as replacing aragonite, which is consistent with our aragonitic interpretation for the pseudomorphs described here. The aragonite pseudomorphs are distinct from stubby pseudomorphs that Simonson et al. (1993) interpreted as gypsum on the basis of their growth geometry and chevron crystal terminations. The possible gypsum pseudomorphs were found in three layers, each <2 cm thick. At one location, they occur in conjunction with hollow-faced cubes, interpreted as halite pseudomorphs.

Fanning crystal pseudomorphs are also present in the 2925–2940 Ma Uchi Greenstone Belt at Red Lake, Ontario (Hofmann et al., 1985). They form fans up to 1.2 m in diameter that consist of chert and carbonate. The pseudomorphs are centimeter- to decimeter-wide bundles of acicular crystals that nucleated on bedding planes and grew upward. Neighboring fans have interpenetrating pseudomorphs indicative of competitive growth (Hofmann et al., 1985). The pseudomorphs were interpreted as replacing either gypsum or aragonite (Hofmann et al., 1985). They are morphologically more similar to the pseudomorphs documented here, and we propose that they replace aragonite rather than gypsum.

**Aragonite Precipitation Rates**

The growth of crystal fans >1 m high in beds lacking evidence for detrital sediment requires that there was little sediment influx during aragonite precipitation, aragonite precipitation rates were very high, or a combination of both. If crystal growth rates were not substantially higher than modern aragonite precipitation rates, long intervals of no sediment influx are required. Maximum aragonite cement precipitation rates estimated from modern reefs are about 25 mm/100 yr or 1 cm/40 yr (Grammer et al., 1993; Grammer et al., 1996). If Late Archean aragonite precipitation occurred at the same rate, it would take a 10 cm fan 400 yr to precipitate and a 1 m fan 4000 yr to precipitate. It is unrealistic to expect no sediment influx into agitated shallow subtidal to intertidal depositional environments for hundreds to thousands of years. Also, in many cases, grainstones filled space between aragonite pseudomorphs and finer sediment draped some fans, demonstrating the availability of at least some detrital sediment. Thus, to get the observed decimeter heights of Archean aragonite fans, aragonite precipitation must have been substantially faster than it is in modern reefs. Rapid precipitation may have been a result of higher than modern supersaturation of seawater with respect to aragonite (Grotzinger, 1989; Grotzinger and Kasting, 1993).

Older Late Archean carbonates, i.e., those from Steep Rock, Belingwe, Bulawayo, and Uchi greenstone belts, tend to have larger aragonite fans and more fan lithoherms that are associated with grainstones than the younger Campbellrand–Malmani and Carawine carbonates, which have aragonite pseudomorph fans and fine crystals draped by fine-grained sediment. Fans in the Campbellrand–Malmani platform rarely are associated with grainstones. If the thickness of aragonite fan beds reflects crystal growth rates, aragonite supersaturation may have been higher around 2.7–2.6 Ga than around 2.6–2.5 Ga. Alternatively, if the thickness of aragonite fan beds reflects sediment influx, a difference in production of grainstones and/or grain transport is required. A paucity of large aragonite fans in Proterozoic and Phanerozoic carbonates could be due to either a decrease in aragonite precipitation rate or an increase in deposition of detrital carbonate. Each effect, either by itself or in combination, would allow burial of any aragonite crystals that started to grow on the sea floor. Thus, it appears that the Campbellrand–Malmani and Carawine carbonates reflect a transition from more abundant and large aragonite pseudomorphs in older Late Archean carbonates to the rare pseudomorphs found in unusual environments in Proterozoic and Phanerozoic carbonates.
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### Implications for Seawater Chemistry

The reinterpretation of most of the reported occurrences of Late Archean gypsum pseudomorphs as aragonite pseudomorphs implies that gypsum precipitation from Late Archean seawater was rare. Although rare gypsum pseudomorphs are present in one Late Archean carbonate deposit (e.g., Simonson et al., 1993), the sedimentological contexts of observed halite casts in the Carawine Dolomite and Campbellrand–Malmani carbonate platform do not allow for the precipitation and subsequent dissolution of substantial volumes of gypsum prior to halite precipitation (e.g., Simonson et al., 1993; Sumner, 1995). The lack of abundant Late Archean gypsum pseudomorphs or solution-collapse features within sediments below or laterally equivalent to those containing halite casts implies that gypsum was not a volumetrically important evaporite mineral.

Either low [SO\(_4^{2-}\)] or high HCO\(_3^-\) can explain the absence of abundant gypsum (Grotzinger and Kasting, 1993). With an oxidizing surface ocean, SO\(_2^-\) should have been abundant, allowing gypsum precipitation unless much of seawater Ca\(^{2+}\) was removed through carbonate precipitation (Grotzinger and Kasting, 1993). This situation would imply [HCO\(_3^-\)] > 2[Ca\(^{2+}\)]. However, prior to the rise in atmospheric oxygen, this argument is complicated by the possibility of low oceanic [SO\(_4^{2-}\)], which would also have limited gypsum precipitation. Currently, the [SO\(_4^{2-}\)] of Archean seawater is poorly constrained, so low [SO\(_4^{2-}\)] cannot be eliminated as the reason gypsum precipitation was rare. However, high [HCO\(_3^-\)] is consistent with the necessary rapid aragonite precipitation rates, as is high [Ca\(^{2+}\)]. Even if HCO\(_3^-\) was high, the presence of rare gypsum pseudomorphs in the Carawine Dolomite indicates that gypsum saturation was attained at least locally. Thus, the possibility that [HCO\(_3^-\)] was much greater than 2[Ca\(^{2+}\)] for all of Late Archean time in all environments is unlikely. Rather, it seems more likely that [HCO\(_3^-\)] was close to 2[Ca\(^{2+}\)], which is consistent with simultaneous saturation of siderite and calcite (Grotzinger and Kasting, 1993). This would allow for locally minor gypsum precipitation when and where [HCO\(_3^-\)] locally dropped below 2[Ca\(^{2+}\)].

The paucity of gypsum is also consistent with the “soda ocean” model, which implies [HCO\(_3^-\)] > 2[Ca\(^{2+}\)]. However, this model is not consistent with the accumulation of large carbonate platforms dominated by CaCO\(_3\) precipitation. Widespread aragonite precipitation in open marine environments suggests that bulk seawater was capable of precipitating substantial volumes of aragonite, especially by about 2.5 Ga, when the Campbellrand–Malmani carbonate platform was deposited. Kempe and Kazmierczak (1994) suggest that the “soda ocean” [Ca\(^{2+}\)] was between 8 × 10\(^{-4}\) and 1 × 10\(^{-4}\) mol/l. At these low [Ca\(^{2+}\)], it is difficult to accumulate significant quantities of CaCO\(_3\) in reasonable lengths of time. For example, the Campbellrand–Malmani carbonate platform is over 1 km thick and is preserved over 190,000 km\(^2\) (Beukes, 1987; Button, 1973; Sumner, 1995). Even assuming that 25% of the volume of the platform is noncarbonate and ignoring the eroded part of the platform, which originally covered more than 600,000 km\(^2\) (Button, 1973; Beukes, 1987; Sumner, 1995), more than 10\(^{18}\) mol Ca\(^{2+}\) are required even if the entire platform was dolomitized soon after deposition. At 10\(^{-4}\) mol Ca\(^{2+}\)/l, more than 10\(^{22}\) l of seawater would be necessary to provide sufficient Ca\(^{2+}\) for accumulation of the preserved part of the platform. The current volume of the ocean is 1.37 × 10\(^{18}\) l. Thus, in order for the Campbellrand–Malmani carbonate platform to have accumulated from a “soda ocean,” high fluxes of Ca\(^{2+}\) from weathering would be required to rapidly replenish seawater Ca\(^{2+}\). If Ca\(^{2+}\) is delivered to the oceans in rivers, carbonate precipitation would be concentrated at the mouths of rivers draining siliciclastic interiors. In the case of the Campbellrand–Malmani carbonate platform, the development of a rimmed margin, the widespread deposition of subtidal lithofacies across the entire platform, and the lack of siliciclastic sediment from a weathering craton imply that precipitation occurred from seawater as opposed to the mixing of river water with seawater. Thus, the low Ca\(^{2+}\) concentrations required by the “soda ocean” are unrealistic given abundant calcium carbonate accumulation by 2.5 Ga.

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**Table 1.** Continued MICROPROBE ANALYSES OF ARAGONITE PSEUDOMORPHS

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<th>MgCO(_3) (mol%)</th>
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Concentration below detection limit.
CONCLUSIONS

Abundant aragonite precipitated from Late Archean seawater, forming fans of crystals meters tall. This precipitation occurred in diverse depositional environments ranging from evaporitic to open marine subtidal shelves. The crystals grew directly on the sea floor and projected up into open water, sometimes forming lithoherms that were resistant to abrasion during deposition of surrounding grainstones. Precipitation of large aragonite crystals on the sea floor requires that: 1) later Archean seawater was supersaturated with respect to aragonite; 2) aragonite precipitation rates were rapid relative to the influx of detrital carbonate; and 3) aragonite precipitation was more rapid than the fastest rates observed in modern reefs. In addition, a decline in the abundance and size of aragonite fans from the older (2.7–2.6 Ga) to the younger (2.6–2.5 Ga) Late Archean carbonates studied suggests that there were secular variations in aragonite precipitation rates in Late Archean time.

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REFERENCES


