Rise in seawater sulphate concentration associated with the Paleoproterozoic positive carbon isotope excursion: evidence from sulphate evaporites in the ~2.2–2.1 Gyr shallow-marine Lucknow Formation, South Africa

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ABSTRACT

Past oceanic sulphate concentration is important for understanding how the oceans’ redox state responded to atmospheric oxygen levels. The absence of extensive marine sulphate evaporites before ~1.2 Gyr probably reflects low seawater sulphate and/or higher carbonate concentrations. Sulphate evaporites formed locally during the 2.22–2.06 Gyr Lomagundi positive δ13C excursion. However, the ~2.2–2.1 Gyr Lucknow Formation, South Africa, provides the first direct evidence for seawater sulphate precipitation on a carbonate platform with open ocean access and limited terrestrial input. These marginal marine deposits contain evidence for evaporite molds, pseudomorphs after selenite gypsum, and solid inclusions of Ca-sulphate in quartz. Carbon and sulphur isotope data match the global record and indicate a marine source of the evaporitic brines. The apparent precipitation of gypsum before halite requires ≳2.5 mM L−1 sulphate concentration, higher than current estimates for the Paleoproterozoic. During the Lomagundi event, which postdates the 2.32 Gyr initial rise in atmospheric oxygen, seawater sulphate concentration rose from Archean values of ≲200 μM L−1, but dropped subsequently because of higher pyrite burial rates and a lower oceanic redox state.


Introduction

Extensive marine sulphate beds are abundant in Phanerozoic and Neo-proterozoic shallow-marine evaporite deposits, signalling a modern precipitation sequence where carbonate is followed by gypsum/anhydrite and halite. They are less abundant in early Mesoproterozoic rocks, but become rare in sedimentary successions older than 1.2 Gyr (Pope and Grotzinger, 2003). Inferred Archean sulphate evaporites (e.g. Buick and Dunlop, 1990) may rather represent localized precipitation of barite and Ca-sulphate, often from hydrothermal fluids (Runnegar et al., 2001). This trend in sulphate deposition was explained by lower oceanic sulphate concentration under a more reducing atmosphere and ocean, and/or higher oceanic carbonate concentration because of higher atmospheric CO2 levels in the Archean and Paleoproterozoic (Grotzinger and Kasting, 1993). In the latter case, no calcium would be available to evaporative environments because of enhanced carbonate precipitation.

Some Paleoproterozoic primary sulphate evaporites apparently formed in marginal marine settings during the 2.22–2.06 Gyr Lomagundi positive δ13C excursion (e.g. Cameron, 1983; El Tabakh et al., 1999; Melezhik et al., 2005). However, because of their depositional setting in either isolated basins or basins with a restricted connection to the ocean, they may reflect local environments influenced by terrestrial run-off or volcanic deposits rather than a seawater composition (Grotzinger, 1994; Pope and Grotzinger, 2003). Whereas the initial rise in atmospheric oxygen is reasonably well constrained between 2.47–2.32 Gyr (Bekker et al., 2004a), changes in ocean redox state remain poorly constrained. The isotopic record and sulphate concentration therefore provide an important constraint on the redox state of the ocean and atmosphere (e.g. Holser et al., 1988). Originally, the initial rise in atmospheric oxygen was linked to high relative burial rates of organic carbon during the Lomagundi event, but more probably the rise of atmospheric oxygen preceded the Lomagundi event by almost 100 Myr (Bekker et al., 2004a). The relation between rising atmospheric oxygen levels, the Lomagundi isotope excursion, and seawater sulphate levels is significant for the understanding how ocean redox state responded to atmospheric oxygenation. This paper provides detailed new evidence for the deposition of sulphate evaporites in Paleoproterozoic shallow-marine rocks from South Africa, including an assessment of their depositional context and their marine or non-marine nature. Field observations and new carbon and sulphur isotope data constrain the nature of the sulphate source to the rocks under study and to the contemporaneous ocean.

Stratigraphy and sedimentology

The Paleoproterozoic Lucknow Formation (Transvaal Supergroup) gradually overlies shales and red beds of the Mapedi Formation (Fig. 1; Beukes and Smit, 1987). Conglomerates and sandstones of the Neylan...
Formation rest with an erosional unconformity on the Lucknow Formation (Fig. 1c; van Niekerk, 2006). The depositional age of the Lucknow Formation cannot be constrained directly, but it is estimated at 2.20–2.10 Gyr. Lavas of the Ongeluk Formation (age 2222 ± 12 Myr) are separated from the Lucknow Formation by an unconformity (Fig. 1c; Cornell et al., 1996), and the youngest detrital zircons found in the Lucknow Formation give an age of 2228 ± 25 Myr (van Niekerk, 2006). Lucknow carbonates have highly positive δ13C values (Master et al., 1993; Swart, 1997; Bekker et al., 2001) consistent with their deposition during the Lomagundi excursion (Karhu and Holland, 1996; Melezhik et al., 1999). The correlative Silvertown to Magaliesberg succession in the Transvaal Basin ~500 km to the northeast (Beukes et al., 2002; Coetzee et al., 2006) is older than the intrusive Bushveld Complex (2061 ± 2 Myr; Walraven, 1997). The Hartley Formation lavas overlying the Lucknow Formation were dated at 1928 ± 4 Myr (Fig. 1c; Cornell et al., 1998).

The Lucknow Formation consists of shales, micritic and stromatolitic dolostones, ferruginous wackes, mature quartz-arenites, and dolarenites and dolorudites (Table 1). Low-grade greenschist facies metamorphism is indicated by the presence of chlorite in siliciclastic rocks. The micritic and stromatolitic dolostones and shales were deposited under largely quiet-water conditions in a relatively shallow-water setting (Table 1). Finer-grained wackes, with lenticular-wavy bedding, wave ripples and mud cracks probably record deposition on sand and mud flats (Table 1; cf. Button and Vos, 1977). Although these sedimentary structures are consistent with tidal deposition, no diagnostic features for tidalites were observed. The coarse dolostones, quartz-arenites and coarser wackes with rip-up clasts represent episodic higher-energy events and were deposited as large-scale channels and/or bars (Table 1; cf. Fedo and Cooper, 1990). Paleocurrent data are unimodal and they are directed west–southwest, i.e. basinwards from the craton (cf. van Niekerk, 2006).

Siliciclastic rocks of the Lucknow Formation represent fluvo-deltaic deposits with sand bars and channels of a braided delta (cf. Fedo and Cooper, 1990). The base of the formation is formed by bars and channels prograding over marine muds of the Mapedi Formation (Fig. 2; van Schalkwyk and Beukes, 1986; Beukes and Smit, 1987; van Niekerk, 2006). Up section, progradation and/or shifting of sand bars and ephemeral channels led to the episodic filling of associated lagoons and flats (cf. Button and Vos, 1977). When siliciclastic input was cut off, carbonate and evaporite deposition occurred (Fig. 2).

**Textural evidence for sulphate evaporite deposition**

**Molds and quartz nodules**

Molds occur in shales, ferruginous wackes, and micritic dolostones. On exposed bedding surfaces, they are usually weathered hollow with irregular outlines; but, on fresh surfaces, they correspond to pre-compactional quartz nodules. Flared corners (Fig. 3a) and triangular outlines of molds are relatively rare. One quartz-arenite bed with wave ripples contained clusters of mm-sized quartz nodules concentrated in troughs between the ripple crests (Fig. 3b).

The outlines of most molds are inconclusive as to the original mineralogy. Cubic molds with flared edges resemble halite hopper crystals growing displacively in host sediment or in shallow brine pools, whereas discoidal shapes may represent former displacive sulphate minerals (Shearman, 1978). These textures are typical for syndepositional to early diagenetic evaporite precipitation from capillary
brines in sabkha or shallow saline environments (Shearman, 1978). The isolated occurrence in ripple troughs suggests syndepositional formation by slow evaporation of slack water on shallow siliciclastic flats (e.g. Benison and Goldstein, 2001, their fig. 5d).

Quartz cluster nodules

Micritic dolostone beds locally contain cm-scale, clustered, pre-compactional quartz nodules. Most nodules have irregular and flattened shapes, but some are distinctly upright and palmate (Fig. 3c,d). The palmate nodules show nodular-mosaic (chickenwire) texture (Maiklem et al., 1969), and they occur as cm-thick beds with a sharp horizontal top that may be erosive (Fig. 3c). Some of these nodules show poorly developed chevron terminations (Fig. 3d).

The original mineralogy of the irregular nodules is uncertain, but the palmate upright shapes and chevron terminations are consistent with a selenite gypsum precursor (Schreiber and Kinsman, 1975). Modern selenite gypsum typically forms in shallow hypersaline pools or salinas with less than about 10 m water depth (e.g. Schreiber and Kinsman, 1975).

Ca-sulphate inclusions in quartz nodules

Quartz in the above cluster nodules contains abundant hollow inclusions up to about 20 μm in size with stepped outlines. Some solid inclusions with rectangular and platy outlines were observed (Fig. 3e). Geochemical spectra obtained by SEM-EDS show calcium and sulphur as the only components of the solid inclusions, whereas the surrounding material consists of quartz (Fig. 3f–h).

The stepped outlines of these inclusions might result from the pinacoidal cleavage of an anhydrite precursor (Shearman, 1978). In addition, SEM-EDS spectra provide unequivocal evidence that solid inclusions represent gypsum or anhydrite. These minerals are unlikely to represent daughter minerals that precipitated during opening of fluid inclusions. The minerals fill close to 100% of the inclusion volume (Fig. 3e), and precipitation as daughter minerals would require unreasonably high sulphate concentrations in the original fluid inclusion.

Geochemical data

Thirteen micritic dolostone samples were analysed for δ13C and δ18O values. Carbonate-associated sulphate was extracted from two carbonate samples for δ34S measurements. In addition, sulphate was extracted from two quartz samples and also subjected to δ34S analysis. Major and trace element concentrations of 10 dolostone samples were determined by inductively-coupled optical-emission spectrometry (ICP-OES) and X-ray diffraction (XRF). The details of analytical procedures are given in Table 2. Values for δ13C and δ18O range from 8.7 to 10.4‰, V-PDB, and −11.9 to −4.6‰, V-PDB (Table 2), respectively. Two carbonate samples yielded δ34S values of 11.3 and 11.9‰ V-CDT, and analyses of quartz-hosted sulphate produced values of 9.2 and 14.0‰ V-CDT (Table 2). The δ13C values are probably close to original values, because of (1) little

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Table 1 Descriptions of Lucknow Formation lithofacies.

<table>
<thead>
<tr>
<th>Facies</th>
<th>Thickness, texture</th>
<th>Sedimentary Structures</th>
<th>Components, microfacies</th>
<th>Preservation, remarks</th>
<th>Depositional environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shales</td>
<td>N/A</td>
<td>Weakly laminated to massive</td>
<td>N/A</td>
<td>Rarely exposed</td>
<td>Open marine, below</td>
</tr>
<tr>
<td></td>
<td></td>
<td>to nodular and laminited; cm- and</td>
<td></td>
<td></td>
<td>storm wave base</td>
</tr>
<tr>
<td>Micritic and</td>
<td>cm and dm-thick continuous beds;</td>
<td>dm-scale dolominal and</td>
<td></td>
<td></td>
<td>Shallow protected</td>
</tr>
<tr>
<td>Stromatolitic</td>
<td>lenticular intercalations of (a) wacke and</td>
<td>columnar stromatolites</td>
<td></td>
<td></td>
<td>carbonate lagoon</td>
</tr>
<tr>
<td>dolomites</td>
<td>arenites beds, (b) dolarenites, dolorudites</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferruginous</td>
<td>cm/dm-thick beds, variable maturity and</td>
<td>Lenticular-wavy and flat</td>
<td>Quartz grain size</td>
<td>Prominent purple</td>
<td>Sand and mud flats</td>
</tr>
<tr>
<td>Wackes</td>
<td>sorting</td>
<td>bedding, trough and tabular cross-bedding,</td>
<td>between silt-coarse sand;</td>
<td>colour on weathered</td>
<td>(tidal?)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>wave ripples, mud</td>
<td>dolomitic-siliceous matrix makes up</td>
<td>surfaces</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>cracks</td>
<td>10–50% of rock; fine-grained hematite,</td>
<td></td>
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</tr>
<tr>
<td>Quartz-arenites</td>
<td>m- and dm-thick sheet-like and lenticular</td>
<td>Poorly preserved; flat</td>
<td>cm-scale fining-upward cycles from</td>
<td>m-scale fining-upward</td>
<td></td>
</tr>
<tr>
<td></td>
<td>beds with sharp contacts and, locally,</td>
<td>bedding, large-scale</td>
<td>quartz-arenites to wackes, mudstone</td>
<td>cycles from</td>
<td></td>
</tr>
<tr>
<td></td>
<td>erosive base; at least moderately well</td>
<td>trough and tabular cross-bedding,</td>
<td>clasts at cycle base</td>
<td>quartz-arenites to</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sorted, texturally and mineralogically</td>
<td>wave ripples</td>
<td></td>
<td>wackes, mudstone</td>
<td></td>
</tr>
<tr>
<td>Dolarenites and</td>
<td>cm-thick beds, commonly with erosive base</td>
<td>Massive, locally weak</td>
<td>Recrystallization, sparitic</td>
<td>Recrystallization,</td>
<td></td>
</tr>
<tr>
<td>Dolorudites</td>
<td></td>
<td>grading</td>
<td></td>
<td>sparitic</td>
<td></td>
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</tbody>
</table>

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evidence for recrystallization and metamorphic overprint in fine-crystal\linebreak line dolomite (cf. Buick et al., 1998), and (2) no correlation between \( \delta^{13}C \) and \( \delta^{18}O \), and between \( \delta^{13}C \), bulk-rock major, and trace element concentrations (Table 2).

**Discussion**

Two lines of evidence argue for a marginal marine depositional environment with access to the open ocean. First, the above depositional environments are relatively extensive on a km-scale and pass southward to a storm-dominated muddy shelf. Second, (Beukes et al., 2002) correlated the Lucknow and Mapedi formations with the marine Silverton and Magaliesberg formations of the Transvaal Basin. These two structural basins were once parts of the same depositional basin. The stratigraphic successions share a similar sequence stratigraphic, chemostratigraphic and geochronologic framework (Swart, 1999; Beukes et al., 2002).

Carbon isotope data for the Lucknow Formation are consistent with the contemporaneous global record (Table 3; Master et al., 1993; Karhu and Holland, 1996; Melezhik et al., 1999; Swart, 1999; Bekker et al., 2001, 2005), and suggest that a seawater signature dominated \( \delta^{13}C \) values of inorganic carbon at the depositional site of the Lucknow Formation. Positive \( \delta^{13}C \) excursions are generally interpreted to reflect high relative burial rates of organic carbon on a global scale, coupled with excessive oxygen release to the atmosphere (e.g. Karhu and Holland, 1996). However, the restricted nature of many Lomagundi-age carbonate deposits allows alteration of a global signal by local factors, such as high microbial productivity and evaporation (Melezhik et al., 1999). Carbon isotope data presented here show a relatively small range of variation (8.4–11.3\%) consistent with a limited impact of local microbial productivity or hypersaline conditions on carbon isotope systematics.

The S isotope composition of Archean seawater sulphate was close to 0\% (Strauss, 1993, 2004), consistent with limited biological sulphur isotope fractionation at sulphate con-

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Fig. 2 Simplified stratigraphic section of the Lucknow Formation and the top of the underlying Mapedi Formation in the northern locality of the study area. Occurrences of evaporitic textures are shown and a stratigraphic subdivision is given along the left side (see text for discussion). The right column shows the measured \( \delta^{13}C \) and \( \delta^{34}S \) values.
Paleoproterozoic sulphate evaporites, South Africa  •  S. Schröder et al.

Petrographic evidence for the former presence of evaporites in the Lucknow Formation. (a) Molds in partly silicified shale with variable shapes, including discoidal (1) and rectangular forms with flared edges (2). (b) Quartz-arenite with wave ripples (ripple crests indicated by arrows). Clusters of quartz nodules occur preferentially in ripple troughs. (c) Clustered quartz nodules with nodular-mosaic texture (white) in Fe-rich dolomitic matrix. Note that nodules have a relatively sharp and horizontal top surface (between arrows). (d) SEM photograph of quartz nodule (qz) in dolomite (do) from the same sample as (c). The nodule has a distinct palmate outline (dashed line). (e) SEM photograph of quartz nodule with rectangular solid inclusions (inc) containing Ca and S. The dashed rectangle indicates the area shown by SEM-EDS maps (f)-(h). (f–h) Geochemical maps obtained by SEM-EDS for the area in (c), showing the distribution of elements Si, Ca and S, respectively. Light grey tones correspond to higher element concentrations.

centrations < 200 µm L⁻¹ (Canfield, 1998; Habicht et al., 2002). Early Paleoproterozoic sulphates have elevated δ³⁴S values of ~10‰ (Table 3), suggesting that bacterial sulphate reduction and pyrite deposition in anoxic settings might have shifted the δ³⁴S of seawater sulphate. This is consistent with an increase in the seawater sulphate reservoir (Canfield, 1998) and its residence time above Archean levels. Detrital pyrites are lacking in sedimentary successions deposited on continental margins after ~2.3 Gyr (Barley et al., 2005; Bekker et al., 2005), suggesting that enhanced oxidative continental weathering provided sulphate to the ocean.

The lack of sulphate evaporites in Archean and earliest Paleoproterozoic rocks is generally ascribed to high carbonate and/or low sulphate concentrations in contemporaneous seawater (Grotzinger and Kasting, 1993). Deposits formed during the c. 2.22–2.06 Gyr Lomagundi carbon isotope excursion (Table 3) contain silica or carbonate pseudomorphs after Ca-sulphate (e.g. this study; El Tabakh et al., 1999), or preserved sulphate minerals (e.g. Cameron, 1983; Melezhik et al., 2005). Essentially, all of these occurrences formed in restricted and small-scale marginal marine environments with potential major influence of continental factors (cf. Hardie, 1984), lack thick sulphate beds and predate major bedded sulphate evaporites by 900 Myr (cf. Pope and Grotzinger, 2003). Sulphate evaporites of the Lucknow Formation provide the first direct evidence for Lomagundi-age sulphate precipitation from seawater on a carbonate platform with open access to the ocean and without strong influence of terrestrial run-off from underlying deeply-weathered mafic volcanics. Given the globally consistent isotopic record (Table 3), it is probable that most, if not all, of these deposits were largely sourced from seawater. Consequently, we infer that seawater during the Lomagundi event contained sufficiently high sulphate concentration and, by implication, oxygen levels to allow precipitation of sulphate evaporites.

At modern seawater sulphate concentration, gypsum starts precipitating from brines 3.5x more concentrated than seawater (Holser, 1979). With decreasing sulphate concentration and Ca-sulphate solubility product, higher concentration factors are required for sulphate precipitation. At low sulphate concentrations that require a concentration factor of ~11 to reach oversaturation, anhydrite and halite will co-precipitate. If carbonate precipitation preceded this, the solubility product of Ca²⁺ and SO₄²⁻ at this point is ~25 (mM L⁻¹)² (Holland, 1984). This situation could apply to the displacive evaporite molds in peripheral areas of the Lucknow lagoons, although it is not clear whether the minerals formed from the same brine. In contrast, the observed selenite pseudomorphs indicate gypsum precipitation in standing evaporating pools before halite, requiring ≥2.5 mM L⁻¹ sulphate at modern calcium concentrations of ~10 mM L⁻¹ (Holland, 1984; Grotzinger and Kasting, 1993). Calcium limitation because of carbonate precipitation from bicarbonate-oversaturated seawater (Grotzinger and Kasting, 1993) would require even higher minimum sulphate concentra-
Table 2 Bulk-rock geochemical and isotope data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Material analysed</th>
<th>Analysis type*</th>
<th>Mg (wt. %)</th>
<th>Ca (wt. %)</th>
<th>Mn (ppm)</th>
<th>Sr (ppm)</th>
<th>Fe (ppm)</th>
<th>$\delta^{13}$C (%/V-PDB)</th>
<th>$\delta^{18}$O (%/V-PDB)</th>
<th>$\delta^{34}$S (%/V-CDT)</th>
</tr>
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<tbody>
<tr>
<td>LO-1</td>
<td>Quartz cluster nodule</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>9.2</td>
<td>2.0</td>
<td>-6.6</td>
</tr>
<tr>
<td>LO-3</td>
<td>Micritic dolomite</td>
<td>ICP-OES</td>
<td>2.0</td>
<td>4.2</td>
<td>109</td>
<td>13</td>
<td>629</td>
<td>10.4</td>
<td>-6.6</td>
<td>nd</td>
</tr>
<tr>
<td>LO-4</td>
<td>Dolarenite – clast</td>
<td>ICP-OES</td>
<td>3.6</td>
<td>8.7</td>
<td>150</td>
<td>28</td>
<td>988</td>
<td>9.8</td>
<td>-7.8</td>
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<tr>
<td>LO-5 (1)</td>
<td>Dolarenite – clast</td>
<td>ICP-OES</td>
<td>5.9</td>
<td>9.9</td>
<td>444</td>
<td>34</td>
<td>2598</td>
<td>8.8</td>
<td>-11.9</td>
<td>nd</td>
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<tr>
<td>LO-5 (2)</td>
<td>Dolarenite – recrystallized clast</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td>9.2</td>
<td>-11.8</td>
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<tr>
<td>LO-12</td>
<td>Micritic dolomite</td>
<td>ICP-OES</td>
<td>3.0</td>
<td>5.1</td>
<td>237</td>
<td>di</td>
<td>725</td>
<td>10.1</td>
<td>-6.9</td>
<td>nd</td>
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<tr>
<td>LO-13 (1)</td>
<td>Micritic dolomite</td>
<td>ICP-OES</td>
<td>2.8</td>
<td>5.7</td>
<td>94</td>
<td>di</td>
<td>725</td>
<td>10.1</td>
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<tr>
<td>LO-13 (2)</td>
<td>Cement vein</td>
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<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td>10.3</td>
<td>-8.2</td>
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<td>115</td>
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<td>14.1</td>
<td>209</td>
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<td>Dolarenite – clast</td>
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<td>nd</td>
<td>nd</td>
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<td>nd</td>
<td>nd</td>
<td>10.3</td>
<td>-5.6</td>
<td>nd</td>
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<td>LH-3</td>
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<td>ICP-OES</td>
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<td>17.5</td>
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<td>LH-12</td>
<td>Quartz cluster nodule</td>
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<td>nd</td>
<td>nd</td>
<td>nd</td>
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<td></td>
<td>$\delta^{13}$C notation: absolute reproducibility in % (1σ)</td>
<td>±1.8</td>
<td>±1.1</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>XRF: relative reproducibility in % (1σ)</td>
<td>±0.8</td>
<td>±0.3</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>ICP-OES: relative reproducibility in % (1σ)</td>
<td>±0.2</td>
<td>±0.2</td>
</tr>
</tbody>
</table>

*Bulk-rock analysis of major and trace elements (for carbonates only); nd, not determined; dl, below detection limit.

Extractions and isotope measurements were performed in the stable isotope laboratory at the Geologisches-Paläontologisches Institut, Westfälische Wilhelms-Universität Münster, Germany. Analyses were performed in an automated on-line system attached to a ThermoElemental Delta Plus XL mass spectrometer. For carbonate $\delta^{13}$C and $\delta^{18}$O measurements, CO$_2$ was liberated via phosphorylation at 75°C (Wächter and Hayes, 1985). Results are expressed in the standard delta notation as per mil differences to the V-PDB standard.

Extraction of trace sulphate occurred by sequential wet chemical extraction with NaCl and HCl solutions, and de-ionized water (cf. Goldberg et al., 2005; Kampschulte and Strauss, 2004). Dissolved sulphate was precipitated as BaSO$_4$ following standard procedures (e.g. Sullivan et al., 1994).

Results are given in $\delta^{34}$S notation as per mil differences to the V-CDT standard.

Bulk-rock element concentrations were determined at the Spectrau analytical facility, University of Johannesburg. For ICP-OES analysis, samples were microwave digested using a mixture of HNO$_3$, HCl, H$_2$O$_2$, and HBrF$_4$ followed by dilution in 1% HNO$_3$. Element concentrations were further determined by XRF on fused glass beads and pressed powder pellets (cf. Schröder et al., 2006).
<table>
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<tr>
<th>Name of unit, location</th>
<th>Age (in Gyr)</th>
<th>Tectonic setting</th>
<th>Evaporite evidence</th>
<th>$^{13}$C&lt;sub&gt;Carb&lt;/sub&gt; values (% V-PDB)</th>
<th>$^{34}$S values (% V-CDT)</th>
<th>References</th>
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<td>Gordon Lake Formation, Huronian Supergroup (Lake Huron, Canada)</td>
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<td>Barite beds, silicified and pristine anhydrite and gypsum nodules and layers</td>
<td>5.0–8.2</td>
<td>11.7–15.6</td>
<td>Cameron (1983), Chandler (1988), Bennett et al. (1989), Bekker et al. (2006)</td>
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<tr>
<td>Kona Dolomite, Chocolay Group (Michigan, USA)</td>
<td>c. 2.3–2.22</td>
<td>Intracratonic basin open to passive margin</td>
<td>Pseudomorphs after gypsum and anhydrite</td>
<td>5.0–9.5</td>
<td>11.4–16.0</td>
<td>Taylor (1972), Clark (1974), Wohlabough (1980), Hemzacek et al. (1982), Hemzacek (1987), Perry et al. (1984), Feng (1986), Bekker et al. (2006)</td>
</tr>
<tr>
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<td>8.0–10.3</td>
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<tr>
<td>Lower Nash Fork Formation, Snowy Pass Supergroup (Medicine Bow Mountains, Wyoming, USA)</td>
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<td>Molds after anhydrite nodules and gypsum crystals</td>
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<td>Tulomozero Formation, Upper Jatulian Group (Lake Onega, Russia)</td>
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<tr>
<td>Bubble Well Member, Juderina Formation, Yerrida Group (Nabberu Province, Western Australia)</td>
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<td>Back–arc basin</td>
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<td>El Tabakh et al. (1999), Krapez and Martin (1999), Lindsay and Brasier (2002)</td>
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<td>Lucknow Formation, Postmasburg Group (South Africa)</td>
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<tr>
<td>Joshe Formation, Deweras Group (Magondi Belt, Zimbabwe)</td>
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<tr>
<td>Dewhara Formation, Avavali Group (Rajasthan, India)</td>
<td>c. 2.1</td>
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<td>Barite layers</td>
<td>5.1–11.1&lt;sup&gt;1&lt;/sup&gt;</td>
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<td>Passive margin</td>
<td>Anhydrite layers and veins</td>
<td>−1.7–5.5</td>
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<td>Vinogradov et al. (1976), Zolotarev et al. (1989), Velikoslavinsky et al. (2003), Guliy and Wada (2003)</td>
</tr>
</tbody>
</table>

<sup>1</sup>Data for the overlying Jhamarkotra Formation.
(Canfield, 1998; Bekker et al., 2006; Slack et al., 2007). Consistent with this interpretation are dominant halite but rare sulphate pseudomorphs in the ~1.88 Gyr Stark Formation, Canada (Pope and Grotzinger, 2003). During the Lomagundi event, localized precipitation of sulphate before halite was possible either in the water column or below the sediment-water interface, but thick extensive beds of sulphate evaporites became a characteristic feature of evaporite deposition only after further oxidation of the surface environment at ~1.25 Gyr (Kah et al., 2004).

Acknowledgements
The research was funded through an NRF postdoctoral fellowship for S. Schroeder (SFP 2005072200010), and by the Agouron Institute. Participation of A. Bekker was supported by the NASA-Ames Research Center, NASA, and PRF/ACS grants to H.D. Holland and, at a later stage, by NSF grant EAR-05-45484, NASA Astrobiology Institute award No. NNA04CC09A, and NSERC Discovery Grant to AB. The authors thank D. Bedorf, N. Downer and A. Fugmann for valuable laboratory assistance, as well as J. Gutzmer, S. Lugli and B.C. Schreiber for comments and discussions to improve an earlier draft. Constructive criticism by Editor M. Coleman and three anonymous reviewers is gratefully acknowledged.

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Received 31 March 2007; revised version accepted 12 January 2008