Fractionation between inorganic and organic carbon during the Lomagundi (2.22–2.1 Ga) carbon isotope excursion

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1. Introduction

Subsequent to its discovery within carbonates of the Paleoproterozoic Lomagundi Group, Zimbabwe (Schidlowski et al., 1975, 1976), the positive carbon isotope excursion in shallow-marine sedimentary carbonates, later named the Lomagundi Event, has been observed in a number of Paleoproterozoic basins worldwide (e.g. Baker and Fallick, 2002).
Another related issue is the relatively common assumption that the isotopic fractionation between organic and carbonate carbon ($\delta^{13}C$) during the Precambrian was constant (e.g. Eichmann and Schidlowski, 1975; Schidlowski and Aharon, 1992). This assumed constant fractionation is used as a test for post-depositional alteration (e.g. Knoll et al., 1986; Kaufman and Knoll, 1995) and for the reconstruction of carbonate carbon isotopic values from the organic carbon isotope record (e.g. Calver, 2000; Karlstrom et al., 2000; Walter et al., 2000; Kaufman and Xiao, 2003). In both cases, fractionation between 25 and 30% is commonly used as a canonical range of values despite the observation of temporal variations in this parameter in the Neoproterozoic and Phanerozoic rock record (Hayes et al., 1999). Large DIC and DOC reservoirs as well as redox stratification in the Precambrian ocean should have had a dramatic effect on isotopic fractionation between carbonate and organic carbon, possibly leading to the decoupling of their records both locally and globally.

To address these issues, we present new $\delta^{13}C$ data on both the carbonate and organic fractions in subtidal carbonates of the 2.22–2.06 Ga Silverton Formation (Pretoria Group, South Africa) and the corrrelative Sengoma Argillite Formation, Segwagwa Group across the border in Botswana (Figs. 1 and 2). These data are compared to the $\delta^{13}C_{org}$ values in the underlying organic-rich shales of the Sengoma Argillite Formation. Buick et al. (1998) found a positive $\delta^{13}C_{Carb}$ excursion in carbonates of the lower part of the Silverton Formation from the northeastern part of the Transvaal Basin (Button, 1973; Fig. 2) within the contact-metamorphic aureole of the 2.06 Ga Bushveld Complex, which they correlated to the 2.22–2.1 Ga Lomagundi carbon isotope excursion. Because both the Silverton–Sengoma carbonates and Sengoma shales were deposited during the Lomagundi Event, $\delta^{13}C_{Carb}$ and $\delta^{13}C_{org}$ data will be used to test whether the carbonate and organic carbon records are coupled, and whether enhanced methane cycling alone can account for the massive and prolonged shift in $\delta^{13}C_{Carb}$ values recorded in shallow-marine carbonates between 2.22 and 2.1 Ga.

1.1. Regional geology and stratigraphy

The Silverton Formation belongs to the Neoproterozoic Pretoria Group (Fig. 1) deposited in the open-marine epicontinental Transvaal Basin in South Africa (Fig. 2). The formation is bracketed in age by the underlying ca. 2.22 Ga Hekpoort Lava and the overlying or intruding 2.06–2.05 Ga Rooiberg Felsite Group and Bushveld Complex, respectively (Walraven, 1997; Buick et al., 2001; Dorland, 2004). Further indirect age constraints might be inferred from the ca. 2.14–2.12 Ga U–Pb ages of authigenic metamorphic monazite in metashales, metasiltstones, and quartzites of the Chuiiespoort Group and the older Central Rand Group of the Witwatersrand Supergroup reflecting recently recognized tectonic event in the Transvaal Basin (e.g. Rasmussen et al., 2007). This pre-Bushveld compressional eventfolded the upper part of the Pretoria Group including the Silverton and the overlying Magaliesberg formations in the far western part of the Transvaal Basin into open upright symmetrical folds (Hartz, 1995, 2000; Bumby et al., 1998). Furthermore, units in the upper part of the Pretoria Group, above the Magaliesberg Formation overlying the Silverton Formation, are less mature with respect to the lower part of the Pretoria Group deposited on the passive continental margin indicating change to an active tectonic regime and a sediment provenance to the north of the Kaapvaal craton (Button, 1973, 1986; Schreiber et al., 1992). These data suggest that the Silverton Formation was deposited during the 2.22–2.1 Ga Lomagundi carbon isotope excursion and most likely shortly before the 2.14–2.12 Ga tectonic event. We therefore assume a ca. 2.15 Ga age for deposition of the Silverton Formation.

In our study area, in the northwestern part of the Transvaal Basin, the Silverton Formation experienced only lower greenish facies metamorphism. The deltalic to offshore marine Silverton Formation is
sandwiched between shallow-marine tidally-influenced quartz sandstones of the Daspoort and Magaliesberg formations (Button, 1973; Fig. 1). The lower contact with the Daspoort Formation is sharp whereas the upper contact with the Magaliesberg Formation is gradational. The Silverton Formation is divided by basaltic lava into two thick units of shales and siltstones with minor chert and

Fig. 1. Correlation chart between the Transvaal Supergroup in the Bushveld Basin of southeastern Botswana and in the northwestern part of the Transvaal Basin, South Africa (modified from Key, 1983 and Bekker et al., 2004 with the Rooihoogte–Timeball Hill age from Hannah et al., 2004 and carbon isotope data from this paper). The age of the Hekpoort Formation is inferred based on the correlation with the Ongeluk Andesite of the Griqualand West Basin and its whole rock Pb–Pb age (Cornell et al., 1996) together with the age of the youngest inherited zircons reported by Dorland (2004) for the Hekpoort Formation.

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Fig. 2. Schematic map of the Late Archean and early Paleoproterozoic sedimentary successions of South Africa, showing outcrop and sub-Kalahari sand distribution of the Chuniespoort (dark grey) and Pretoria (light grey) groups in the Transvaal structural basin and Chaap (dark grey) and Postmasburg (light grey) groups in the Griqualand West structural basin of South Africa taken from the digital 1:1,000,000 geology maps of South Africa and Botswana with the additional information from the digital 1:2,500,000 map of sub-Kalahari formations (Council for Geoscience, 1997; Key and Ayres, 2000; Haddon, 2001). Similar color patterns are also used to label the correlative units in the Bushveld (B) and Kanye (K) structural basins, Botswana. All these structural basins used to belong to the same depositional basin. ‘S1’ indicates the location where carbonates in the lower part of the Silverton Formation with high carbon isotope values occur (Button, 1973; Buick et al., 1998), ‘S2’ and ‘S’ point to the locations of sampled carbonate and black shale sections in South Africa and Botswana, respectively. ‘L’ refers to the location of sequence-stratigraphically correlative Lucknow Formation in the Griqualand West Basin that also contains carbonates with high carbon isotope values.
carbonate layers. It has a thick carbonate sequence at the top in the northwestern part of the Transvaal Basin at the border between South Africa and Botswana. The Silverton Formation is known in Botswana as the Sengoma Argillite Formation (Key, 1983; Figs. 1 and 2). Our study is focused on the carbonate sequence in both South Africa and Botswana and on the immediately underlying black shales of the upper unit in the drill core Strat 2 located near Lobatse in Botswana. The formation is between 500 and 700 m thick, whereas the carbonate sequence is up to 167 m at Sengoma Hill in Botswana (Key, 1983).

Two partial (~30 and 50 m thick) sections of the carbonate sequence were sampled in South Africa 1 to 2 km from the border with Botswana (Figs. 2 and 3). Carbonates, interlayered with shales, are partially dolomitized, laminated, and rarely display the features of a shallow-water depositional environment such as wave ripples, domal stromatolites, silicified nodules, soft-sediment deformation structures, water and gas escape structures, or small-scale cross-bedding. Another partial (46 m thick) section of the carbonate sequence was sampled at Sengoma Hill, Botswana (Fig. 4). This

Fig. 3. Measured partial section of the Silverton Formation, South Africa near the border with Botswana with stratigraphic variations in carbonate and organic carbon isotope values shown as well as carbon isotope fractionation between carbonate and organic carbon (Δδ). Insets shown scatter plots for carbonate and organic carbon isotope values vs. Δδ values.
carbonate section displays wave ripple cross-laminations and flat lamination. In the lower part of this section sheet cracks (Fig. 5) are extensively developed and filled with recrystallized carbonate. These likely developed during early diagenesis as methane and CO₂ produced during remineralization of organic matter escaped from sediments.

The drillcore Strat 2 (see Key, 1983) stored at the Geological Survey of Botswana was also logged and sampled (Fig. 6). It consists of two upward-shallowing cycles with organic-rich pyriferous shales in the lower parts of the cycles deposited in a prodelta environment above wave base and hematite-rich quartz sandstones at the top of the cycles deposited in a delta plain environment. Veins

Fig. 4. Measured partial carbonate section of the Sengoma Argillite Formation, Botswana in the type section of Sengoma Hills with stratigraphic variations in carbonate and organic carbon isotope values shown as well as carbon isotope fractionation between carbonate and organic carbon (Δδ). Insets shown scatter plots for carbonate and organic carbon isotope values vs. Δδ values.
with carbonates, quartz, migrated pyrobitumen, and remobilized sulfides occur locally as, for example, in the 107–115 m depth interval.

2. Methods

The least altered (i.e. lacking veins, discoloreation, weathering rinds, and silicification) and finest-grained portions of polished thick sections of carbonates from the Silverton Formation were microdrilled with 2 mm in diameter diamond drill bits and reacted at 70 °C using a Kiel III carbonate device directly coupled to a Thermo Scientific 253 gas isotope ratio mass-spectrometer in the Saskatchewan Isotope Laboratory, University of Saskatchewan. Each set of 6 samples was bracketed by an internal calcite standard calibrated against the (NIST) NBS-19 standard. Conversion to the VPDB scale was performed using the values ±2.20% and ±1.95% for δ18O and δ13C, respectively, for (NIST) NBS-19. The external uncertainty (±1σ) based on NBS-19 analyses is 0.10% for δ18O and 0.05% for δ13C. Carbonates from the Sengoma Formation were microdrilled and reacted at 70 °C using a GasBench carbonate device connected to a Thermo Scientific 252 instrument at the Geophysical Laboratory, Carnegie Institution of Washington. Each set of 6–7 samples was bracketed by the Geological Survey of Finland dolomite standard (Tytyri dolomite; Karhu, 1993) and conversion to the VPDB scale was performed using the values ±0.78% and ±0.70% for δ18O and δ13C, respectively, for this internal standard calibrated against the (NIST) NBS-19 and NBS-20 standards. The external uncertainty (±1σ) is based on the reproducibility of the Tytyri dolomite, which is better than 0.2% for δ18O and δ13C. Major and minor element analyses for both sets of samples were performed by ICP-AES using Thermo Iris instrument. The reproducibility of the analyses is ±5% (1σ).

Samples for δ13Corg and TOC analyses were prepared by decarbonating whole rock powders with 1 N HCl, followed by a thorough rinsing in distilled water and drying in an oven at 50 °C for 24 h. δ13Corg analyses were conducted on the Thermo Scientific Delta Plus XL instrument coupled to a Carlo Erba NC2500 Elemental Analyzer at the Environmental Isotope Geochemistry Laboratory, University of Illinois at Chicago. Samples marked with an asterisk in the Supplementary materials, Table 1 were prepared and analyzed at the Geophysical Laboratory, Carnegie Institution of Washington. Aliquots of powdered samples between 1 and 15 mg in weight, depending on TOC content, were decarbonated with 6 N HCl in muffled silver boats, dried overnight in a hood and, subsequently, in an oven at 50 °C, and analyzed on the Thermo Scientific Delta Plus XL instrument coupled to a Carlo Erba NC2500 Elemental Analyzer. All stable isotope values are reported in per mil vs. VPDB and USGS-40, USGS-41, caffeine UIC, and acetanilide (Costech Analytical Technologies) standards were used to monitor external and internal uncertainty that was better than 0.2‰. Total organic carbon abundances were calculated based on carbon content measured with Elemental Analyzer and loss during decarbonation.

2.1. Geochemical data and preservation of primary δ13C values

Carbonate samples analyzed are dolostones, limestones, and marls with xenotopic mosaics of anhedral, coarsely-crystalline to very coarsely-crystalline grains with pseudospar, and rarely contain quartz or carbonate veins. Carbonates have a narrow range of δ13C values between +7.6 and +11.2‰ VPDB (Supplementary materials, Table 1). δ18O values show a much larger range from ~16.7 to ~5.2‰ VPDB. A correlation between δ13Corg and δ18O values, which has often been attributed to metamorphic decarbonation reactions (e.g. Valley, 1986; Baumgartner and Valley, 2001), is not present in our sample set. The carbonates have variable TOC contents ranging from 0.01 to 0.60% and a large range in δ13Corg values from ~24.8 to ~13.9‰. There is no correlation between TOC content and δ13Corg values as would be expected from the breakdown and volatilization of organic molecules by diagenetic and metamorphic processes (Hayes et al., 1983). Carbon isotope exchange between graphite and carbonate accounts for 13C-enrichment in graphite associated with marble, however graphite forms at temperatures above 500–600 °C (Valley, 2001), well above the lower greenschist facies metamorphism experienced by carbonates of the Silverton and Sengoma Argillite formations. Δδ values are also highly variable, ranging between 23.9 and 33.6‰, although the average (30.3‰) is close to 30‰, that is typical for Phanerozoic and Precambrian unmetamorphosed carbonates (Eichmann and Schidlowski, 1975; Knoll et al., 1986; Hayes et al., 1999). Mn and Sr contents and Mn/Sr ratios are also widely used to evaluate diagenetic effects in carbonate rocks (e.g. Kaufman et al., 1993). Carbonate samples analyzed in this study have Mn contents ranging from 27 to 1505 ppm (most samples contain less than 670 ppm), Sr contents vary from 26 to 119 ppm, and Mn/Sr ratios are between 0.5 and 26.5 (Supplementary materials, Table 1). These data are consistent with calcite or dolomite as the precursor mineralogy, rather than aragonite, and indicate only a minor to moderate amount of post-depositional alteration with respect to other Paleoproterozoic carbonates worldwide (e.g. Bekker et al., 2001, 2003a,b, 2005, 2006a; Melezhik et al., 1999; Veizer et al., 1992).

The organic matter in the middle part of the Silverton Formation carbonate section, between 15 and 32 m from the base (Fig. 3), is 13C-enriched, with δ13Corg values of ~18.8 to ~13.9‰, compared to background values from ~22.5 to ~19.1‰. Although this stratigraphic interval has, on the whole, the lowest TOC contents in the section, there are some individual samples from outside of this interval with even lower TOC content that do not show a tendency towards 13C-enrichment compared to neighboring samples (see Supplementary materials, Table 1). In addition, it is difficult to interpret this interval as having been subjected to a higher degree of post-depositional alteration since the δ13Corg and

Fig. 5. Sheet cracks in carbonates of the Sengoma Argillite Formation at Sengoma Hills.
$\delta^{18}O$ values, and trace element abundances do not appear themselves to be unusual. Alternatively, the observed $^{13}C$-enrichment through this stratigraphic interval might reflect high phytoplankton growth rates in the upwelling area where nutrients were delivered from the deep ocean. A similar interpretation was offered to explain the presence of $^{13}C$-enriched organic matter in stromatolitic phosphorites and carbonates of the ca. 2.0 Ga Jhamarkotra Formation, Aravalli Supergroup, Rajasthan, India (Banerjee et al., 1986). In our case, the relatively low TOC levels in this stratigraphic interval seem to be in conflict with the high productivity model unless organic matter was reworked from the high productivity area and transported to this depositional site. Regardless of the underlying cause of the $^{13}C$-enriched organic matter in this part of the section, it is important to note that there is no correlation between $\delta^{13}C_{\text{org}}$ values and TOC contents in this section (see Supplementary materials, Table 1) and even if these data were removed from the graph of $\delta^{13}C_{\text{org}}$ vs. $\Delta\delta$ on the inset in Fig. 3, a significant correlation with a similar slope would still be evident, suggesting that data from this $^{13}C$-enriched interval most likely reflect primary values.

$\delta^{13}C$ values of carbonates in the sampled sections of the Silverton Formation are on average 1‰ more positive than carbonates sampled at Sengoma Hills (9.6 vs. 8.6‰; Figs. 3 and 4). Because these sections are relatively close to each other and are partial sections of much thicker carbonate sequence in both areas, we relate this discrepancy to a slight difference in the stratigraphic position of the sections within the carbonate sequence rather than a shelf gradient in $\delta^{13}C_{\text{DIC}}$.

The underlying shales of the Sengoma Argillite Formation have higher TOC content, ranging from 0.14 to 21.94 wt.%, and highly variable $\delta^{13}C_{\text{org}}$ values from $-33.7$ to $-20.8$‰ with the majority of

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**Fig. 6.** Partial section of the Sengoma Argillite Formation, Botswana from the drill core Strat 2 with stratigraphic variations in organic carbon isotope values in two upward-coarsening cycles shown. Inset shows scatter plot for organic carbon isotope values vs. TOC content. Two samples that were strongly altered are shown with empty circles.
values and the average value (−270‰) lower than −25‰ (Fig. 6; Supplementary materials, Table 1). The basal part of the section has the lowest δ13C values. The overlying strata become progressively 13C-enriched upsection reaching a maximum at 219 m. At this point the trend reverses with δ13C values declining to 205 m. From 205 m until to the top of the section there are no variations in δ13C values. Two shale samples at the top of the section between 107 and 115 m depth contain veins with carbonates, quartz, migrated pyrobitumen, and remobilized sulfides. Based on their 13C-carbonate values, these samples appear to be more significantly altered than the samples without veins (Fig. 6).

In summary, both the petrographic features and geochemical data suggest that carbonate and organic carbon fractions in the carbonates and shales were not significantly altered following deposition. Therefore, we conclude that 13C-carbonate values reflect the 13C value of DIC in contemporaneous seawater in the Pretoria Basin. 13C-carbonate values correspond to the composition of organic matter deposited in this basin and may also reflect contemporaneous seawater DIC 13C values, offset by some fractionation. Whether or not this was indeed the case depends on the relative contribution of organic matter sourced from primary (photosynthetic) and secondary (e.g. methanotrophic and sulfur-oxidizing) pathways that indirectly reflects redox stratification and CO2, CH4, and 5 cycling in the basin.

3. Discussion

3.1. Do high 13C-carbonate values of the Silverton–Sengoma carbonates reflect local or global conditions?

Accepting that the Silverton–Sengoma 13C-carbonate values closely approximate seawater 13C-CIC values in the Pretoria epicontinental sea, the extent to which local scale carbon cycling processes may have overprinted the global-scale signature of the surface ocean remains unclear. Processes on both scales have been inferred to interpret the Phanerozoic carbonate carbon isotope records (e.g. Kump and Arthur, 1999; Melchin and Holmden, 2006). Modern (e.g. Florida Bay, Bahama Banks, and Shark Bay) and Phanerozoic carbonates show a large range in 13C values that might reflect vital effects of carbonate-secreting organisms, local environmental conditions (e.g. hypersalinity, biological productivity, terrestrial runoff, and diagenetic mineralization of organic matter), and shelf gradients in epicontinental basins with the restricted connection to the open ocean. Local scale effects were cited by Melezhik et al. (1999) as an explanation for very positive 13C-carbonate values (> +6 to +8‰) recorded by stromatolitic carbonates that may have been deposited during the Lomagundi Event in potentially hypersaline settings. Because we are interested in comparing fractions between organic and inorganic carbon in sediments from shallow and deeper parts of the Pretoria basin, and we lack direct constraints on carbon isotope values of DIC in the deeper part of the basin, the following discussion is focused on whether the Silverton–Sengoma 13C-carbonate values reflect local or global signals. If global signals are implied, 13C-carbonate values in the shallow part of the basin can be used as a rough estimate for the carbon isotope values of seawater DIC in the deeper part of the Pretoria basin.

Several models have been proposed to explain positive 13C-carbonate excursions in modern and Phanerozoic shallow-marine carbonates that are relevant to this discussion. These include i) weathering of carbonates during sea level lowstands, and the impact of this on the 13C value of terrestrial runoff (Kump and Arthur, 1999; Melchin and Holmden, 2006); ii) enhanced productivity in restricted settings (e.g. Swart and Eberli, 2005); and iii) 13C-enrichment in evaporating brines (Stiller et al., 1985; but see Lazar and Erez, 1990 for a different view). With respect to the carbonate weathering model, the Silverton and Sengoma Argillite formations do not directly overlie an extensive carbonate platform, although the Late Archean Campbellrand–Malmanian subgroups containing carbonates with 13C-carbonate values close to 0‰ occur significantly below these units. Enhanced cyanobacterial productivity has been inferred to explain 13C-enrichment beyond background levels during the Lomagundi Event in shallow-marine settings (e.g. Melezhik et al., 1999) with the Bahama Banks and Shark Bay used as modern analogues. High productivity on the Bahama Banks is maintained by red and green calcareous algae in shallow, restricted settings that are not analogous to an open and extensive carbonate platform in the Pretoria Basin where stromatolites reflect cyanobacterial activity are rare due to the deeper-water depositional environment. Similarly, regardless of the validity of the evaporative model for the origin of extreme 13C-enrichments, there is no evidence for hypersaline conditions during the deposition of the Silverton or Sengoma Argillite formations in the Transvaal Basin. On this basis, we conclude that none of these models appears to satisfactorily explain the 13C-enrichment in the carbonates of these units, and we suggest that 13C-carbonate values in the nearshore settings mainly reflect the global, rather than local signals.

Carbon isotope values in carbonates of the Sengoma Argillite and Silverton formations are indeed similar to those previously reported from these formations in other parts of the extensive Transvaal Basin (Master et al., 1993; Buick et al., 1998; Swart, 1999; Bekker et al., 2001) and in the sequence-stratigraphically correlative Lucknow Formation in the Griqualand West Basin (Coetsee et al., 2008; see Fig. 2 for location), and broadly correlative Paleoproterozoic carbonates deposited during the Lomagundi Event worldwide (Bekker et al., 2006a). We do not imply that small-scale shelf gradients were entirely lacking in the Paleoproterozoic epicontinental basins; rather we suggest that high atmospheric CO2 levels predicted by climatic models likely caused them to be damped by the higher seawater DIC content and higher exchange rates between atmospheric CO2 and seawater DIC (cf. Panichuk et al., 2005).

3.2. Δδ in shallow-marine carbonate environment: implication for an enhanced methane cycle

Δδ is an important parameter for characterizing carbon cycling during the 2.22–2.1 Ga Lomagundi δ13C-carbonate excursion (Karhu and Holland, 1996). Whereas the δ13C-carbonate values are generally assumed to be homogeneous in open-marine settings and faithfully recorded by δ13C-carbonate values, the carbon isotope record of marine TOC can be strongly influenced by local environmental conditions such as redox state, nutrient content, and aqueous CO2 levels, in addition to the seawater δ13C-CIC value. It is therefore difficult to constrain an average organic carbon isotopic value on the global scale for any specific time interval. δ13C-carbonate values or their stratigraphic trends in environments with high TOC contents could be strongly influenced by secondary productivity occurring in the anoxic water mass of the stratified water column (e.g. methanotrophs or S-oxidizing bacteria; Hayes et al., 1999), especially in the Precambrian ocean where dissolved oxygen levels were likely much lower (Slack et al., 2007). Intense biogeochemical carbon cycling in redox-stratified water columns thus complicates the interpretation of δ13C-delta and Δδ values. Although organic-rich sediments that were strongly influenced by secondary productivity are unlikely to provide genuine records of global seafloor 13C values, sections with high TOC contents naturally attract biogeochemical studies and, therefore, bias the secular record of global average 13C values. Shallow-water marine environments are better settings to look for faithful records of seawater δ13C trends, particularly for organic carbon isotopes, because secondary productivity there is confined to anoxic porewaters below the water–sediment interface, and direct comparison with carbonate carbon isotope values is possible in carbonate successions. There is relatively little data on Δδ values from carbonates deposited during the Lomagundi Event because most of these carbonate successions appear to have been deposited in shallow-marine and relatively well-oxygenated waters and are, thus, extremely lean in organic carbon (<0.1 mg C/g sample) with 13C values of refractory organic material.
strongly affected by nearly complete loss of organic carbon (Bekker et al., 2006a). Carbonates of the Silverton Formation therefore provide a rare opportunity to measure Δδ values in shallow-marine carbonate environments during the Lomagundi Event.

Assuming that δ13C_carb values genuinely reflect seawater δ13C DIC values and that δ13C_org values represent average carbon isotope values of organic matter, fractionation between these two reservoirs on the shallow-marine carbonate platform was close to 30‰. Until now, the Lomagundi excursion has only been shown to be present in the carbonate fraction. Since older and younger Late Archean and early Paleoproterozoic carbonate successions show similar Δδ values (e.g. Eichmann and Schidlowski, 1975; Schidlowski, 1988; Des Marais et al., 1992), the secular trend of δ13C_org values from shallow-marine carbonate successions spanning the duration of the Lomagundi Event should record a positive δ13C_carb excursion and, thus, coupling between the inorganic and organic carbon isotope records. If this interpretation is found to be correct on a global scale by further studies, then the hypothesis of an enhanced microbial degradation of organic matter associated with methanogenesis below the sediment–water interface in shallow diagenetic settings, and a decoupling of organic and carbonate carbon records during the progressive build-up of molecular oxygen in the oceans and atmosphere (Hayes and Waldbauer, 2006) is not a valid explanation for the origin of high δ13C values of carbonates deposited during the Lomagundi Event. By analogy with Phanerozoic, and younger Precambrian examples, a Δδ of ~30‰ suggests that the organic matter was mostly fixed by organisms utilizing a pathway of oxygenic photosynthesis in the water column, or perhaps at the sediment–water interface. The 13C-enrichment in both inorganic and organic carbon on the shallow-marine carbonate platform during the Lomagundi Event, therefore, provides strong evidence that the whole marine DIC reservoir was affected rather than just shallow porewaters below the sediment–water interface as predicted in the model of Hayes and Waldbauer (2006).

3.3. Chemical and redox stratification in the Silverton Basin

Carbonates in the upper part of the Silverton–Sengoma Argillite formations and the underlying black shales of the same units were deposited during the 2.22–2.1 Ga Lomagundi Event based on their geochronologic constraints discussed in ‘Regional Geology and Stratigraphy’ section and positive carbon isotope values of carbonates in the lower and upper parts of the Silverton Formation bracketing the studied shales (Buick et al., 1998; this paper). Walther’s Law dictates that in offshore settings, shales, that are interlayered with carbonates in the South African section (see Fig. 3), and conformable with an overlying carbonate sequence, are deeper-water time equivalents of shallow-water carbonates found higher in the succession. As discussed above, shales from the Strat 2 drill core in Botswana contain up to 22% TOC and are more organic-rich than the contemporaneous shallow-marine carbonates of the Silverton and Sengoma Argillite formations. The shales, therefore, suggest high organic carbon burial in offshore settings and, potentially, a strong biological pump to the deeper-water settings (cf. Hotinski et al., 2004) during the Lomagundi Event. In contrast to the associated organically lean carbonates, the TOC in the offshore shales displays significantly lower δ13C values. The apparent depth gradient in δ13C_carb values between shallow-water carbonates and deeper-water shales is about 6‰, much larger than the water column gradient in the modern ocean (~2‰; Kroopnick, 1985), even though the difference in depth of deposition for these carbonates and shales in the epicontinental basin was unlikely more than 100 m. Shore-to-basin gradients of about 4‰ have been documented across several epeiric platforms during the Hirnantian carbon isotope excursion (e.g. Melchin and Holmden, 2005). Although evidence for a seawater shelf gradient in δ13C_carb has not yet been convincingly demonstrated in Paleoproterozoic basins, we recognize that it is a challenging problem to assess the necessary evidence on account of the lack of in situ carbonate production on the deeper shelf, and the potential overprinting of deeper shelf TOC records by secondary productivity, as discussed above. Furthermore, Hotinski et al. (2004) concluded based on box modeling that significant water column gradients would be unlikely to develop in high CO2 atmosphere predicted by Precambrian climatic models (cf. Kasting, 1993) as vigorous CO2 exchange between the atmosphere and ocean would limit the impact of biological pump.

Therefore, accepting that TOC of the Sengoma Argillite Formation with its low δ13C values does not reflect a global ocean water column gradient in δ13C_carb, two alternatives must be considered: i) either the DIC in offshore settings was locally affected by enhanced mineralization of organic matter, or ii) inputs from secondary productivity significantly contributed to the TOC of the offshore shales. The Black Sea is a good example for the first scenario in that it has a significant carbon isotope water column gradient in the DIC from +0.8‰ near the surface to ~1.4‰ at 100 m depth and to about ~6.3‰ at the bottom in the deep sulfidic part of the basin (Fry et al., 1991; Schouwen et al., 2004). Therefore, the carbon isotope value of the DIC reservoir can be strongly affected in stratified basins where the exchange with the ocean is restricted at depth by sills. In contrast, areas with high organic productivity associated with upwelling zones on continental margins are vertically well-mixed and at most 1‰ lower in δ13C_carb values than the global surface ocean (e.g. Peru Upwelling Zone; Bidigare et al., 1997). Although mineralization of organic matter and methane cycling may have been important in the Pretoria basin, and bearing in mind the fact that sedimentary records of offshore δ13C_carb values are lacking or compromised, there are several lines of indirect evidence suggesting that seawater δ13C_carb values in offshore settings can be approximated by the sedimentary records of carbon in nearshore settings. First, as discussed above, it seems rather odd that a large, open-marine, tidally-influenced epicontinental basin under high Paleoproterozoic atmospheric CO2 levels would develop long-term conditions above the wave base under which δ13C_carb values could be so significantly 12C-enriched offshore. Low δ13C values similar to those observed in the thick black shale section in the drill core Strat 2 also occur in shales with lower TOC (mostly less than 1 wt.%) collected from the outcrop sections in the more proximal parts of the basin (Watanabe et al., 1997; Coetzee, 2001). Second, if a carbon isotope lateral gradient occurred in the Pretoria basin, as observed now in the Black Sea, one would expect to find carbon isotope values of carbonates to be highly variable and depth-controlled, with lower δ13C values at the base of the upward-shallowing cycles immediately above shales (see Fig. 3) and increasingly higher δ13C values at their tops. In contrast, our data do not show significant variations in carbon isotope values of carbonates with sea level changes and only highly positive carbon isotope values were found in this and previous studies (Buick et al., 1998; Swart, 1999). We therefore infer that δ13C values of DIC in the Pretoria basin were not significantly affected on the basin scale by mineralization of organic matter in sediments with high TOC content and use the δ13C values of Silverton–Sengoma carbonates as a proxy for carbon isotope values of DIC in settings where Sengoma shales accumulated. It has been suggested that Δδ values larger than 32‰ in the Late Neoproterozoic interglacial time intervals might be related to the activity of methane-oxidizing or sulfide-oxidizing bacteria incorporating light carbon either from methane or mineralized organic matter (Hayes et al., 1999). Returning to the Black Sea as a potential modern analogue for the Precambrian redox-stratified ocean, significant heterotrophic (secondary) and chemotrophic (e.g. sulfide-oxidizing and thiosulfate-disproportionating bacteria) production of organic matter in the water column there contributes ~45% of the total carbon flux to the sediments; the remainder is from primary productivity in the surface ocean above the redoxcline (Karl and Knaur, 1991). Bulk δ13C_carb values for the organic carbon in the bottom sediments of the Black Sea are less than 4‰ lower in δ13C_carb value than phytoplankton
in the surface waters (Fry et al., 1991; Hayes et al., 1999). This difference is consistent with the ~6‰ on the average lowering of $\delta^{13}C_{\text{org}}$ values between nearshore and offshore settings in the Pretoria basin, suggesting that a significant portion of the organic matter in the deeper-water shales originated from heterotrophic and chemotrophic metabolism. This would also imply a stable redoxcline in this part of the basin (Fig. 7). The redoxcline with the pronounced underlying sulfidic conditions was indeed inferred independently for the Pretoria basin on the basis of Fe speciation and $\delta^{34}S$ data (Shen and Bekker, 2006; Bekker et al., 2006b; Scott et al., 2008). Sedimentary structures in the black shale section in the drill core Strat 2 (see Fig. 6), such as wave ripples with internal laminations, climbing ripples, and soft-sediment deformation structures, however, suggest that the redoxcline developed in relatively shallow waters, above wave base, in contrast to the Black Sea analogue. It is plausible that deposition of these organic-rich shales reflects intense upwelling from the deep ocean, bringing nutrients to fuel primary productivity in the basin. The dramatic difference in carbon isotope fractionation between TOC and DIC in the Pretoria basin (~36‰ on the average) and in the Black Sea (~27‰ maximum) likely reflects a shallower redoxcline, reduced amounts of seawater sulfate and other oxidants and, consequently, extensive methanogenesis in the deeper anoxic part of the Pretoria basin with methanotrophy at the redoxcline.

A related question, therefore, is whether other shallow-water environments spanning the Lomagundi Event show evidence for a pronounced redoxcline, sulfidic conditions, and significant $^{13}$C-depletion in the preserved organic matter. Evidence from the Paleoproterozoic Francavillian Series of Gabon suggests that this may have been the case. Carbonates in the transgressive sequence with $\delta^{13}C_{\text{Carb}}$ ranging from +2.6‰ to +6.3‰ are interlayered with organic-rich shales with $\delta^{13}C_{\text{org}}$ values as low as $-46.2‰$ (Gauthier-Lafaye and Weber, 1989; 2003). The overlying volcanics were recently dated at 2083 ± 6 Ma (Gauthier-Lafaye, 2006) establishing that the organic-rich shales with low $\delta^{13}C_{\text{org}}$ values were deposited during the Lomagundi Event. Based on the speciation of Fe in the black shales (Scott et al., 2008), and basin analysis by Gauthier-Lafaye and Weber (2003), the intercalated shales were likely deposited under euxinic conditions in the epicontinental basin influenced, perhaps, by upwelling from the deep ocean. If these findings from two Paleoproterozoic basins may be taken as evidence for extensive euxinia in shallow-water epicontinental seas during the Lomagundi Event, the question arises as to the redox state of the deep ocean during that time. Giant sedimentary Mn-deposits and associated minor iron formations deposited during the Lomagundi Event (e.g. Gauthier-Lafaye and Weber, 2003; Bekker et al., 2003b) strongly suggest that the deep ocean was neither oxic nor euxinic but rather suboxic to anoxic at that time.

Combining these observations, the ocean during the Lomagundi Event was likely redox-stratified, with biological activity coupled between oxic surface waters, euxinic intermediate waters, and suboxic to anoxic bottom waters (Fig. 7). Contrary to the generally held view (e.g. Melezhik et al., 2005; Hayes and Waldhauser, 2006) that the Lomagundi Event was not accompanied by the deposition of organic-rich shales consistent with a high relative burial rate of organic carbon, several basins in West and South Africa and Brazil contain organic-rich shales. Therefore, in spite of the fact that the signature of the Lomagundi excursion might be overprinted by secondary productivity in these deeper-water shales, their high TOC and low $\delta^{13}C_{\text{org}}$ values suggest that significant amounts of organic carbon with light $\delta^{13}C_{\text{org}}$ values were removed from the oceans during this time, helping to explain high $\delta^{13}C$ values recorded in shallow-water carbonates.

Assuming that our data for the Pretoria basin are typical for globally averaged $\delta^{13}C_{\text{Carb}}$ and $\delta^{13}C_{\text{org}}$ values of carbonates and organic matter, respectively, from the shallow-water environments, shales of the Sengoma Argillite Formation deposited in the deeper-water part of the basin provide some indication of the decrease in $\delta^{13}C_{\text{org}}$ values of organic carbon below the redoxcline during the Lomagundi Event. It is therefore impossible to estimate a global average fractionation between organic and inorganic carbon during the Lomagundi Event from our dataset. However, because primary producers dominate the ocean organic carbon budget now (Hedges and Keil, 1995) and were likely similarly important during the Lomagundi Event and assuming that shallow-water environments are more likely to reflect primary productivity, we can bracket this parameter between 30 and 45‰, likely closer to 30‰.

3.4. Size of DIC and DOC reservoirs during the Lomagundi Event

Our data provide a new perspective on carbon cycling during the Lomagundi Event and allow for a test of the possible effects of large DIC and DOC reservoirs on the operation of carbon cycle. It is generally accepted that except for relatively short but important time intervals in the Late Archean, Paleoproterozoic, and Neoproterozoic, the relative proportion of carbonate and organic matter burial was stable in the

![Fig. 7. Model for biogeochemical cycling of carbon in the shallow-water and deeper-water environments of the Pretoria Basin, South Africa during deposition of the Silverton and Sengoma Argillite formations (modified from Bekker and Kaufman, 2007). Note the sulfidic oxygen-minimum zone impinging on the shelf in the shallow-marine tidally-influenced epicontinental basin overlain by the oxygenated upper part of the water column and underlain by the anoxic or suboxic deeper-waters. Organic matter in the shallow oxygenated part of the water column was dominated by primary productivity whereas secondary (heterotrophic) and chemotrophic productivity at and below the redoxcline contributed significantly to TOC in the deeper-water environments (cf. Coetzee et al., 2006; Bekker and Kaufman, 2007).](image-url)
Precambrian, and similar to that observed today based on the carbon isotope records of carbonates and organic matter (e.g. Schidlowski, 1988; Des Marais et al., 1992). A slightly different treatment of the carbon cycle involving ocean floor carbonatization, suggests that the relative burial rate of organic matter could have gradually increased over time if submarine hydrothermal weathering of the ocean crust was more important on the early Earth. Nevertheless, even in this model the range of this gradual change is rather limited (Bjerrum and Canfield, 2004). While the endogenic carbon flux to surface environments, and the ratio of organic carbon to inorganic carbon burial fluxes did not change significantly since the Late Archean, DOC and DIC reservoirs could have been larger in the past due to weaker solar...
luminosity and greenhouse requirements, and less efficient burial of organic carbon (Grotzinger and Kasting, 1993; Kasting, 1993; Rothman et al., 2003; Bartley and Kah, 2004).

Under the present conditions, the residence time of DIC is on the order of 10^5 yr whereas that of DOC is at least several orders of magnitude shorter (Holland, 1984). As a result, the smaller DOC reservoir responds faster to environmental perturbations such as changes in pCO₂ or in the ocean redox state, whereas the larger DIC reservoir responds much more slowly. This relationship is illustrated schematically in Fig. 8a using a Cenozoic record that reflects a carbon cycle evolving qua-

istatically in a succession of steady states (Rothman et al., 2003). Note that for the last ca. 50 Ma average carbon isotope values of TOC consistently increased whereas those of carbonates were steady or decreasing. This results in the overall decrease in δ¹³C values through the Cenozoic (see Fig. 3 in Hayes et al., 1999). Laboratory experiments with phytoplankton show (see Hayes et al., 1999 for review) that as pCO₂ increases δ¹³C values of photosynthetically-produced organic matter become more negative due to an enhanced biological fractionation. The increased isotopic discrimination between fixed organic carbon and DIC causes a corresponding positive shift in carbon isotope values of the seawater DIC pool that is reflected in higher δ¹³C values. Based on experiments with phytoplankton cultures, this relationship conflicts with the conventional treatment of the ocean carbon isotope mass balance (e.g. Des Marais et al., 1992; Schidlowski and Aharon, 1992), that assumes δ¹³C values were invariant over geological time. This assumption allows us to directly relate secular variations in δ¹³C values to changes in the relative burial rate of organic carbon over time. The linear relationship between δ¹³C and δ¹³C values was recently emphasized in the model of Rothman et al.’s (2003) for the Neoproterozoic carbon cycling, based on large variations in the carbon isotope fractionation between organic and inorganic carbon since the Neoproterozoic (Hayes et al., 1999). The latter model assumes that carbon isotope variations in carbonates reflect changes in δ¹³C values driven by environmental factors such as pCO₂ or ocean redox changes rather than reflecting relative burial rate of organic carbon since the former changes faster than the latter. Considering that the size and residence times of DIC and DOC reservoirs could have been different in the Precambrian than today, it is useful to discuss two end-members with the surface ocean carbon cycle dominated by either large DIC or large DOC reservoirs (Fig. 8a–c). If the size and residence time of these reservoirs are dramatically different, one of them will be relatively inert to perturbations that would affect its carbon isotope value on a time scale shorter than its residence time, whereas the other with a significantly shorter residence time will respond more quickly. Over time scales that are much longer than the residence times of both reservoirs, their isotopic values will follow a curved path as has been shown for Phanerozoic seawater C and S reservoirs (Kump and Garrels, 1986). These different scenarios are depicted schematically in Fig. 8a–c showing C isotope responses to a perturbation in the carbon cycle whose duration is the intermediate between the DIC and DOC residence times. Using a similar approach, Rothman et al. (2003) interpreted δ¹³C values reconstructed from the Neoproterozoic carbonate successions recording positive carbon isotope excursions as reflecting a dynamic system with a large DOC reservoir. In this case, carbon isotope values of carbonates are highly sensitive to external forcing whereas carbon isotope values of organic matter are less so (see Fig. 8a–c). The opposite would be true in case of a large DIC reservoir. Note that the Cenozoic carbon isotope data reflect an intermediate state of the carbon cycle between these two end-member models.

The Silverton–Sengoma carbonate data (Fig. 8d–f) may be evaluated against these models. First, we agree with Rothman et al. (2003) and Bekker et al. (2003b) that the conventional steady-state model, and in particular its reliance on organic carbon burial as a way to change seawater δ¹³C values, cannot explain the extremely high δ¹³C values recorded by the Neoproterozoic and Lomagundi Events. Similarly to the Neoproterozoic carbon cycle, the carbon isotope background for the Lomagundi excursion is +6 to +8‰, but higher carbon isotope values are not uncommon and even +28‰ values were observed in a relatively thick carbonate section deposited in an open-marine setting (Bekker et al., 2003b). The Silverton–Sengoma data plot on, or slightly above, the best-fit line on a plot of δ¹³C_Carb vs. δ¹³C for Neoproterozoic carbonate successions recording positive carbon isotope excursions and, arguably, a dynamic state of carbon cycle (Rothman et al., 2003). The Silverton–Sengoma data (Fig. 8d–f) show no correlation between δ¹³C_Carb and either δ¹³C or δ¹³C, but there is a significant correlation between δ¹³C and δ¹³C. The trend is consistent with the carbon cycle dominated by a large DIC reservoir during the Lomagundi Event. Carbonates are indeed abundant in the Paleoproterozoic sedimentary successions deposited during the Lomagundi carbon isotope excursion, and the long duration of the Lomagundi Event (~100 Ma) is consistent with the expected stability of carbon isotope values in carbonates at the time when the DIC reservoir was large. The DOC reservoir may have been larger than now as well, but due to a much larger size of the DIC reservoir, its effect on the carbon cycle is not apparent. How could the carbon cycle remain in a dynamic state regardless of how large the DIC reservoir was for the ~100 Ma duration of the Lomagundi Event? We speculate that extensive intracratonic basins and epeiric seas, with restricted connections to a redox-

stratified global ocean, developed during the protracted breakup of a Paleoproterozoic supercontinent (Bekker et al., 2006a). The paleogeography of the period, similar to that in the Neoproterozoic, favored high organic carbon burial rates, and this in turn caused a global-scale shift in the carbon cycle to higher δ¹³C values. Numerical simulations of carbon cycling study the effect of a flux perturbation by applying an instantaneous change from which the system recovers from, or a persistent forcing that drives the system into a new steady state (e.g. Kump and Garrels, 1986; Kump and Arthur, 1999). It is suggested here that under conditions of high organic carbon burial, carbon cycling operates in a dynamic rather than steady state due to perturbations occurring on a time scale intermediate between the residence times of DIC and DOC reservoirs. The carbon cycle could have been shifting from one non-steady dynamic state to another, never reaching a steady state until the breakup of the Paleoproterozoic supercontinent between 2.1 and 2.0 Ga that changed the locus of organic matter deposition to continental margins (Bekker et al., 2003b).

In conclusion, our data support the existence of a large DIC reservoir in the oceans during the Lomagundi Event. The DIC reservoir likely decreased gradually as solar luminosity increased over time and, consequently, the carbon cycle shifted to one that was dominated by a large DIC reservoir sometime before the Late Neoproterozoic. At the end of the Precambrian, the DIC reservoir was drastically reduced as deep ocean oxygen levels increased (Logan et al., 1995; Rothman et al., 2003; Canfield et al., 2006; Fike et al., 2006) marking the transition to a modern-style ocean carbon cycle. The DIC reservoir likely increased episodically in the Phanerozoic at the times when the ocean was stratified and anoxic. Shelf gradients likely waxed and waned under Phanerozoic relatively low pCO₂ levels as large epeiric seas developed in association with the tectonically-driven sea level changes (e.g. Melchin and Holmden, 2006).

3.5. Implications of δ¹³C as a diagenetic filter and of δ¹³C for reconstruction of seawater composition

A number of workers have relied on carbon isotope values of TOC as a tool for evaluating the degree of post-depositional carbonate alteration and to infer seawater δ¹³C values in Precambrian siliciclastic successions where carbonates are absent (e.g. Knoll et al., 1986; Kaufman and Knoll, 1995; Calver, 2000; Karlsstrom et al., 2000; Walter et al., 2000; Kaufman and Xiao, 2003). While this approach has been generally successfully applied to Phanerozoic carbonate and siliciclastic successions, the results of this study suggest that it can lead to erroneous conclusions when applied to deeper-water deposits in the Precambrian, where the primary photosynthetic signature is
susceptible to being overprinted by heterotrophic and chemolithotrophic productivity in redox-stratified oceans. Our study suggests that carbon isotope values of TOC during the Lagomaduni Event were strongly influenced by environmental factors changing water column redox conditions and relative contribution of secondary productivity to TOC. As a result, changes in sea level and ocean circulation affecting position of the depositional site with respect to the redoxcline in the water column and upwelling currents may have influenced carbon isotope values of TOC in deeper-water settings to such an extent that they no longer behave as reliable indicators of DIC isotope trends in seawater. Since the ocean was likely redox-stratified during most of the Precambrian, these environmental controls might be equally applicable to other Precambrian successes. This situation is rather different from that in the modern oxidized ocean where $\delta^{13}C$ values of TOC are relatively homogeneous and are generally coupled with $\delta^{13}C_{DIC}$ values.

4. Conclusions

1. During the Paleoproterozoic Lagomaduni carbon isotope excursion, fractionation between carbonate and organic carbon on the shallow-marine carbonate platform was close to 30%, but in deeper-water suboxic to anoxic and, locally, sulfidic settings it was larger, consistent with redox stratification in the ocean;
2. There is increasing evidence for deposition of organic-rich shales during the Lagomaduni excursion in deeper-water settings;
3. The large magnitude of the Lagomaduni carbon isotope excursion likely reflects the large isotope fractionation between bulk organic carbon and carbonate carbon, due to contributions from secondary productivity in addition to high relative burial rates of organic carbon. It is difficult at present to separate these two variables on the global scale;
4. Carbonate and organic carbon isotope data suggest that the carbon cycle was in a dynamic state dominated by a large DIC reservoir during the Lagomaduni Event, however the DOC reservoir could have also been larger than at present, but its influence was dwarfed by a much larger DIC reservoir;
5. In redox-stratified Precambrian oceans, carbon isotope values of TOC in deeper-water facies were likely strongly influenced by contributions from heterotrophic and chemotrophic productivity and, therefore, estimates of post-depositional carbonate alteration and carbon isotope values of DIC made on basis of carbon isotope values of organic carbon should be cautioned.

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Appendix A. Supplementary data


References

Dorn, B., 1999. 1000–1100 Ma u-fierapatite, Cambrian