The Tambien Group, Ethiopia: An early Cryogenian (ca. 800–735 Ma) Neoproterozoic sequence in the Arabian–Nubian Shield

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Abstract

The Tambien Group in Tigrai, Ethiopia, comprises a number of inliers each containing 2–3 km thickness of interbedded carbonate and clastic sediments, capped in one inlier by a glaciogenic diamictite. A range of geochemical indices suggest near-pristine C- and Sr-isotope values are preserved and these, together with lithological variations, allow local correlation between these inliers and correlation with the global Neoproterozoic isotope stratigraphy. A composite section of the Tambien Group shows 13C in carbonate of ∼+6‰ at its base, decreasing upwards to twin lows of ∼–4‰ separated by a brief excursion back to positive values, then rises again to a plateau of ∼–6‰ before finally decreasing sharply to ∼–2‰ beneath the Negash diamictite at its top. No glaciogenic sediments are observed associated with the lower twinned negative anomalies. The 87Sr/86Sr values in carbonates change from ∼0.7063 in the lower units to ∼0.7067 in the upper units. The 13C of organic matter changes little through the sequence (−24.2 ± 1.3‰), with the result that the C-isotope fractionation between carbonate and organic matter decreases from +26 to +21‰ up through the second low in carbonate before increasing to ∼+29.5‰ in the rest of the sequence. Together with existing radiometric age constraints, the Sr-isotope data indicate that the Negash diamictite is Sturtian in age, and the lower negative C-isotope anomalies appear to correlate with the non-glaciogenic Bitter Springs Stage recognised in Australia and Svalbard. According to this correlation the Tambien Group was deposited in the interval ca. 800–735 Ma. Our data reinforce the emerging view that not all Neoproterozoic negative C-isotope anomalies are associated with glaciation. The variations in C-isotope fractionations within our sequence contrast with those from Australia and are attributed to differences in local environmental variables, probably temperature. These differences are consistent with the recent proposal that the Bitter Springs Stage anomaly is the result of a pair of inertial interchange true polar wander events [Halverson, G.P., Maloof, A., Schrag, D., Dudas, F., Hutten, M., in press. Stratigraphy and geochemistry of a ca 800 Ma negative carbon isotope stage in northeastern Svalbard: Chem. Geol.] [Maloof, A.C., Halverson, G.P., Kirschvink, J.L., Schrag, D.P., Weiss, B.P., Hoffman, P.F., in press. Combined paleomagnetic, isotopic and stratigraphic evidence for true polar wander from the Neoproterozoic Akademikerbreen Group, Svalbard. GSA Bull.], and further high-resolution dating and palaeomagnetic studies of the Tambien Group should allow testing of this hypothesis.

Keywords: Carbonate; Carbon; Oxygen; Strontium; Isotopes; Sturtian glaciation; Bitter Springs Stage; True Polar Wander

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1. Introduction

The Neoproterozoic was a critical phase in Earth evolution marking the transition from an oxygen deficient (possibly sulphidic) ocean to an oxygenated ocean more similar to the present day (Anbar and Knoll, 2002; Hurttgen et al., 2005). This was accompanied by drastic climate change, possibly including at least two ‘Snowball Earth’ global glaciations each followed by extreme greenhouse conditions (Hoffman et al., 1998b; Hoffman and Schrag, 2002). While recent dating has shown a significant time gap between the last inferred global glacia-
tion and the development of multicellular organisms and the ensuing Cambrian radiation (Hoffmann et al., 2004; Carroll, 1999). However, there is still controversy as to the exact number and intensity of glaciations in the Neoproterozoic, let alone their causes and effects. The inferred global glaciations are temporally associated with large negative carbon isotope anomalies in the sedimentary record, with the anomaly either starting at the top of the glacial deposits, or just beneath them. Interpretations of these carbon isotope anomalies vary, and they may well be the result of more than one process. (Hoffman and Schrag, 2002; Schrag et al., 2002; Pavlov et al., 2005; Kennedy et al., 2001; Jiang et al., 2003; Higgins and Schrag, 2003). Irrespective of their origin, the combination of these anomalies with the worldwide deposition of glacial deposits provides the potential for global chemostratigraphic correlation in the Neoproterozoic. (Knoll et al., 1998; Jacobsen and Kaufman, 1999; Walter et al., 2000; Melezhik et al., 2001b; Halverson et al., 2005). However, it is increasingly being recognised that some Neoproterozoic sequences contain negative carbon isotope anomalies that are not associated with glaciogenic rocks (e.g. Hill and Walter, 2000; Corsetti and Kaufman, 2003; Zhang et al., 2005; Condon et al., 2005; Melezhik et al., 2005; Halverson et al., 2005). These anomalies complicate chemostratigraphic correlations and demand alternative explanations for their origin.

Part of the Neoproterozoic Tambien Group in northern Ethiopia was recently remapped by Alene (Alene, 1998; Alene and Sacchi, 2000; Alene et al., 2000). This Neoproterozoic sequence is one of the least studied in Africa, yet lies at a critical geotectonic boundary between the Arabian–Nubian Shield (mostly juvenile crust) to the north and Mozambique belt (mostly reworked older crust) to the south. Existing data (Miller et al., 2003) suggest the Tambien Group could represent a rare sequence extending deep below the Sturtian glacial, perhaps only recorded elsewhere in Svalbard/East Greenland, Australia and Canada (Hill and Walter, 2000). We present new C- and Sr-isotope data that define a more complete isotope stratigraphy for these rocks, including at the base of the sequence a pronounced negative C-isotope anomaly that is not associated with glaciogenic rocks. These data allow us to make an improved correlation with the global isotope stratigraphy, extending this Neoproterozoic sequence downwards to at least 800 Ma in age, and provide support for a new model for non-glacial carbon isotope anomalies in the Neoproterozoic.

2. Regional setting

The Neoproterozoic basement of central Tigrai, northern Ethiopia (Fig. 1a), is composed of low-grade metavolcanics, slate, carbonates and plutonics (Arkin et al., 1971; Beyth, 1971; Garland, 1972; Alene, 1998). It is in the south (Nafka terrane) of the Arabian–Nubian Shield (ANS) that developed during the Neoproterozoic by rifting, arc accretion and terrane amalgamation processes in the East African Orogen (Stern, 1994; Meert, 2003; Johnson and Woldehaimanot, 2003). The basement is overlain by flat-lying Phanerzoic sediments and volcanics.

Two major sequences are recognised in the basement (Beyth, 1971): the Tsaliet Group, an older mainly metavolcanic/metavolcanoclastic sequence and the Tambien Group, a younger metasedimentary slate and carbonate succession. Beyth (1971) described the boundary between the two sequences as ‘probably unconformable’. However, Alene (1998) has described a grabational contact between the Tsaliet Group and basal part of the Tambien Group, although higher units of the Tambien Group onlap the Tsaliet Group indicating tilting of depocentres located on the present inliers during Tambien Group deposition. Both sequences have been subjected to two major phases of folding as a result of N–S and E–W regional compression, respectively (Alene, 1998; Alene and Sacchi, 2000). D1; folded bedding and produced tight minor folds (wavelength of mm to dm), elongation lineation and pervasive regional foliation. D2; caused long wavelength (up to 8 km), upright, open parallel folds without producing a significant cleavage. D3; is considered to be due to E–W directed shortening associated with the end-phase collision between East and West Gondwanaland, and correlates with post-accretion structures described elsewhere in the ANS (Abdelsalam and Stern, 1996).

Mineral assemblages in the Tsaliet metavol-
canics indicate that peak regional metamorphism
Fig. 1. (a) Geological map of the Mai Kenetal–Negash study area in central Tigray modified after Alene (1998). Inset map shows the location of the study area in northern Ethiopia. The Phyllite Unit is thought to be a lateral equivalent of the Tambien Group. In some literature the granites are named as the Mareb granite suite, but we prefer not to use this nomenclature as it implies a post-tectonic timing, whereas the granites here are pre-D2. Age dates are shown on pre-D2 granites; sources: Negash and Hauzien — Miller et al. (2003), single-zircon Pb/Pb evaporation method; Mai Kenetal — Beyth (1972), K–Ar age. (b) Detailed geology of the Mai Kenetal–Tsedia area and sample locations (open square in (a)), based on 1:50,000 mapping by Alene (1998). Way-up criteria include stromatolitic lamination, channel-fill and slump structures in the carbonates.
at pumpellyite–actinolite to lower greenschist facies (\(\sim 245\)–\(375^\circ\)C by chlorite thermometry) was attained coeval with D1 (Alene, 1998; Alene and Sacchi, 2000). We believe that maximum temperatures experienced by the Tambien Group are at the low end of this range <250\(^\circ\)C, on the basis of (a) \(\delta\)D–\(\delta\)18O isotope fractionations between calcite and dolomite (Alene et al., 1999), (b) close to depositional calcite-organic matter C-isotope fractionations (reported below), and (c) the black colour of palynomorphs preserved in some samples (Mullins, University of Leicester, personal communication).

Radiometric ages of the granites (Fig. 1a), locally intruded between D1 and D2 (Alene, 1998; Alene and Sacchi, 2000), constrain deposition and early metamorphism of the Tambien Group to >613 Ma. The age of the Tsaliet Group, and hence a maximum depositional age of the Tambien Group, is less well constrained, with no local radiometric data available. A metavolcanic sequence similar to the Tsaliet Group in Eritrea to the north gave a single-zircon \(\mathtt{Pb/Pb}\) evaporation method age of 854 \(\pm\) 3 Ma on low-grade metavolcanics (Teklay, 1997). A similar sequence to the Tsaliet Group to the NW in Axum yielded ages of 756–806 Ma on syntectonic granites (Sm–Nd and chemical Th–U–Pb zircon isochron methods; Tadesse et al., 2000) suggesting Tsaliet Group deposition before that time.

3. The Tambien Group

The Tambien Group is exposed in four inliers formed by D2 synclinoria, from west to east: Mai Kenetal, Tse dia, Chehmit and Negash (Beyth, 1971; Fig. 1a). Each sequence contains \(\sim 2–3\) km true thickness of sediment after dips from D2 folds are removed (Fig. 2). D2 folds cause only local repetitions of stratigraphy. In the Mai Kenetal section (Figs. 1b and 2) the lithologic sequence comprises (from bottom to top): Lower Slate (Werii Slate), Lower Limestone (Assem Limestone), Upper Slate (Tsedia Slate) and Upper Limestone (Mai Kenetal Limestone) — names in brackets are those

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**Fig. 2.** Stratigraphic sequence of the Tambien Group metasediments in the Mai Kenetal, Tsedia and Negash sections, northern Ethiopia. Unit names given in parentheses are those used by Beyth (1971). The range of thickness of units in each inlier is given; the thicknesses plotted are those in the area in which samples were taken.
used by Beyth (1971). In the Tseedia and Chehmit sections, the lower three units are represented but the Upper Limestone is not present. Although the correlation of the Lower Limestone is not straightforward, the relative stratigraphic position and lithologic (composition, grain size) and textural features (degree of deformation and fabric development) suggest that it is the same unit. In all three sections, the Lower Limestone is found between the Upper and Lower Slates.

In the Negash section (Fig. 2) the sequence is different and it includes (from bottom to top) Negash Slate, Dolomite and Slate, limestone (Negash Limestone), Slate/Pebbly slate (Diamictite Slate). The composition and grain size with only weak fabric development suggest that the Negash Limestone would be best correlated with the Upper Limestone in the Mai Kenetal section and we provide isotope data to support this below. Garland (1972) grouped the two lowermost units of the Negash sequence as the Didikama Formation and the three top units as the Matheos Formation and described both formations as units younger than the Tambien Group. However, Beyth (1971), Alene (1998) and Beyth et al. (2003) all consider the Negash section as part of the Tambien Group.

3.1. Lower Slate (Werii Slate)

A black, brown or greenish grey, well-laminated and strongly foliated slate in the Mai Kenetal and Tseedia sections (Fig. 1b). It contains greywacke and graphitic beds. The basal contact with the underlying Tsaliet Group is gradational with no major discontinuity between the two groups. Greenish grey slate and greywacke layers occur both sides of the boundary, and there is no marked deformational or metamorphic contrast across the contact.

3.2. Lower Limestone (Assem Limestone)

In the Mai Kenetal synclinorium this is exposed on the western limb as a sub-vertical layer ~700 m thick (Fig. 1b). It is grey or black limestone with stromatolitic lamination (Fig. 3a), calcite veins and dark stylolites. Stromatolitic lamination and slump structures indicate younging towards the Upper Limestone. It has fine- to medium-grained crystalline texture and is ~90% calcite; the remainder is dolomite, detrital quartz and feldspar, and minor pyrite. In cathodoluminescence (CL) it shows predominantly dull brown anhedral to subhedral calcite grains, and lesser amount of red luminescent dolomite.

In the Tseedia synclinorium the Lower Limestone is exposed in both limbs. It contains D2 folds with NNE trending sub-horizontal fold axes (Fig. 3b). The Lower Limestone here is mainly black to dark grey, commonly intercalated with slate and well bedded and laminated; in some places aplite sills intrude it. The composition is predominantly crystalline calcite (>90%), with detrital...
albite and quartz. The texture is similar to that of the Lower Limestone in the Mai Kenetal section. In CL it shows a largely dark matrix containing orange luminescent and zoned calcite having rhombic, rectangular, and less commonly sub-circular grain shapes often with dark cores (Fig. 3c). Non-luminescent, coarse-grained, sub-idiomorphic albite and quartz showing preferred orientation are also common.

3.3. Upper Slate (Tsedia Slate)

A light to dark grey, thinly bedded and well-laminated and foliated slate. At Tsedia it occurs in the core of the syncline overlying the Lower Limestone. The onlap of the Upper Slate onto the Tsaliet Group on the east side of the Mai Kenetal synclinorium (Fig. 1b) must relate to tilting of the depocentre during deposition of the Tambien Group and/or faulting of the contact.

3.4. Upper Limestone (Mai Kenetal Limestone)

This forms a sub-vertical NNE trending, massive black limestone layer in the core of the Mai Kenetal synclinorium; younging is demonstrated by slump structures. It contains minor sub-vertical fold axes, and at the base it is intercalated with the Upper Slate. Near the N-S trending fault (Fig. 1b) it is locally brecciated. It contains dark carbonaceous seams and calcareous fragments probably representing redeposited carbonate flakes. It is fine-grained and contains abundant calcite veins. It comprises mainly calcite (~95%) with detrital quartz and albite, pyrite and ±hydrated iron oxide. In CL, sample MK77 shows a micritic calcite matrix, while MK78 shows 'fragmental' calcite texture with mainly brown to dark, and to a lesser extent orange, calcite luminescence occurring in different forms including dark long fragments and circular shapes mostly speckled with black dots and having orange rims. The highly veined sample MK79 contains sporadic patches of orange luminescent calcite as well as a few fine-grained, circular calcites that exhibit bright orange luminescence; calcite veins belong to at least four generations.

3.5. Negash Slate

A dark grey and grey–green slate overlying the Tsaliet Group in the Negash synclinorium. It contains 1–2 m thick beds of spotty purple slate, well-laminated bands, graphic layers, quartzite, conglomerate and greywacke. Beyth et al. (2003) suggested a polymict conglomerate in this unit could represent a lower glacial diamictite, but we do not concur with this suggestion because it is not matrix supported and does not contain any features diagnostic of glaciogenic origin, such as striated pebbles.

3.6. Dolomite–Slate intercalation

A 1200 m thick unit comprising white to pink dolomite intercalated with dark grey, black and green slate at Negash. The dolomite is fine to coarse grained, consisting of over 90% dolomite with calcite and detrital quartz and albite. It displays tight fold and refolded structures as well as stromatolitic laminations.

3.7. Negash Limestone

This is a massive black limestone. It has gradational contacts with the underlying dolomite and overlying slate. It is fine-grained, laminated, fractured, locally stromatolitic, and contains quartz and calcite veins. In CL it shows dark to dark brown luminescent microcrystalline zones (or bands) strongly speckled with black (non-luminescent) dots alternating with zones without black dots. The presence of the black dots and the absence of well-recrystallised calcite grains are similar with that of the Upper Limestone at Mai Kenetal.

3.8. Diamictite Slate

Overlying the Negash Limestone is a light to dark grey slate that forms the core of the Negash syncline. At the base the slate is intercalated with limestone beds and towards the top it becomes diamictitic containing abundant matrix-supported pebbles and cobbles of variable size (mostly 1–15 cm diameter) and shape, sometimes with striated surfaces (Miller et al., 2003). The clasts are polymict, including black limestone, metavolcanics, greywacke, quartzites and granitic rocks. The features of the diamictite are consistent with a glacial origin.

4. Analytical methods

4.1. Sampling

Because all samples have been metamorphosed and some parts of the sequence are veined, we have sampled in order to characterise any post-D1 vein material present, identified as being coarsely crystalline (typically 1–5 mm grain size) and cross-cutting the metamorphic fabric, as well as the least altered rock away from the veins. This strategy enables us to identify the least altered samples at any horizon by monitoring the direction in which the geochemistry of samples was altered by the late vein fluids. Weathered crusts and marker pen sample
numbers were removed from all samples prior to crushing, ensuring no modern contamination. Samples for analysis of homogeneous rocks were obtained by crushing small volumes, whereas veined or laminated rocks were sampled on unweathered cut or broken surfaces with a diamond-tipped drill to obtain ~200 mg samples of vein and host rock material, and any different coloured laminae. These samples were then split for chemical, and C-, O- and Sr-isotope analysis.

4.2. Calcite chemistry

Powdered samples (~100 mg) were weighed and then treated with 1 M acetic acid for 2 h — this is believed to quantitatively dissolve calcite, but leave dolomite unreacted. Solutions were quantitatively pipetted off for analysis and residues were dried and weighed to calculate the weight of sample dissolved. This weight was then used to calculate concentrations in the dissolved calcite. Acetic acid solutions were dried down and redissolved in 10% HCl for analysis with a Jobin Yvon Horiba Ultima 2 optical emission ICP. Precision and accuracy are estimated for analysis with a Jobin Yvon Horiba Ultima 2 opti-

4.3. Calcite $^{87}$Sr/$^{86}$Sr

Approximately 20 mg of powdered sample were treated with Romil® ultrapure 1 M acetic acid. After centrifuging, leachates were dried down and the residue dissolved in 2.5 M HCl. Strontium was separated by conventional cation exchange techniques using Biorad® AG 50W-X8 ion exchange resin. Strontium was loaded onto rhenium (Re) filaments together with a tantalum oxide (TaO) activator following the method of Birck (1986). Isotope ratios were measured on a Finnegan MAT Triton multicollector mass spectrometer operated in static mode. Nineteen analyses of NBS 987 measured during the period of study yielded a mean $^{87}$Sr/$^{86}$Sr of 0.7071753 ± 0.0000062 (2σ). For consistency all the measured ratios are normalised relative to the accepted value of 0.710248 for NBS 987. Replicate determinations (n = 11) of the North Atlantic seawater standard yielded 0.7072542 ± 0.0000092 (2σ). This problem applies to all Neoproterozoic samples but is often perceived to be more acute for samples that have been metamorphosed. However, this may not necessarily be the case because, once they have recrystallised during the earliest stages of metamorphism, it is widely agreed that limestones and marbles exhibit some of the lowest permeabilities of any metamorphic rocks (Holness and Graham, 1995) and are often metamorphosed as closed systems. Even when infiltrated by fluids along veins the degree of fluid–rock interaction and exchange may be small and localised so that isotope systems in the rock are relatively resistant to exchange. Decarbonation reactions between silicates and carbonates are known to cause decreases in $\delta^{13}$C and $\delta^{18}$O in higher grade metamorphic rocks (Schidlowski, 1987; Nabelek, 1991), but provided that limestones contain low concentrations of silicate material and/or have not been heated to temperatures at which decarbonation take place, then they are likely to retain isotope signatures from the diageneric

4.5. Organic matter $\delta^{13}$C

Carbonate was removed from samples by reaction of between 19 and ~100 g of powdered rock with 5% HCl overnight. The residue containing the organic matter was washed and dried. In some samples a tiny amount of organic scum was released on dissolution and this was decanted off. Loss of this, probably insignificant amount of material, which is likely to have had lower $\delta^{13}$C than the bulk sample, means that measured $\delta^{13}$C values on the residue could represent maximum values for the total organic matter. $\delta^{13}$C analyses were performed by combustion in a Carlo Erba NA1500 on-line to a VG TripleTrap and Optima dual-inlet mass spectrometer, with $\delta^{18}$O values calculated to the V-PDB scale using a within-run laboratory standards calibrated against NBS-19 and -22. Replicate analysis of well-mixed samples indicated a precision of ± 0.1% (1 S.D.).

5. Preservation of primary isotope signatures

Because our samples have experienced deformation and low-grade metamorphism it is imperative that we demonstrate we are recording depositional isotope signatures rather than altered values imposed post-deposition. This problem applies to all Neoproterozoic samples but is often perceived to be more acute for samples that have been metamorphosed. However, this may not necessarily be the case because, once they have recrystallised during the earliest stages of metamorphism, it is widely agreed that limestones and marbles exhibit some of the lowest permeabilities of any metamorphic rocks (Holness and Graham, 1995) and are often metamorphosed as closed systems. Even when infiltrated by fluids along veins the degree of fluid–rock interaction and exchange may be small and localised so that isotope systems in the rock are relatively resistant to exchange. Decarbonation reactions between silicates and carbonates are known to cause decreases in $\delta^{13}$C and $\delta^{18}$O in higher grade metamorphic rocks (Schidlowski, 1987; Nabelek, 1991), but provided that limestones contain low concentrations of silicate material and/or have not been heated to temperatures at which decarbonation take place, then they are likely to retain isotope signatures from the diageneric...
realm. Indeed, Melezhik et al. (2001a) detailed examples of amphibolite grade marbles that have retained close to pristine C- and Sr-isotope signatures. Therefore, the end result may be that most of the processes that could have altered the isotope compositions in our rocks probably occur during diagenesis — in common with all Neoproterozoic carbonates. Many of the variables controlling the degree of alteration of isotope ratios, such as effective fluid/rock ratios, are the same whether in the metamorphic or diagenetic realms, and monitors of alteration that are proxies for these variables, such as Mn/Sr, should be expected to identify altered isotope values irrespective of their timings. Theoretical overviews of the relative robustness of carbonate isotope systems during fluid–rock interaction (Banner and Hanson, 1990; Jacobsen and Kaufman, 1999) show that, on the basis of typical concentrations of C, O and Sr in rocks and fluids, it is to be expected that δC should be more robust than δ18O. Thus if δ18O can be shown to be pristine, then it is likely that Sr and C isotopes will also be, etcetera; therefore, we deal with δ18O values first and then proceed to Sr and C isotopes.

5.1. δ18Ocarb

Rock δ18Ocarb values vary between −4.7 and −13.9‰ with an average of −9.6‰ (Table 1). Vein δ18Ocarb values are lower on average (−12.6‰), ranging between −7.9 and −20.6‰. Rock δ18Ocarb values are distinctly lower than in modern marine limestones (−0‰), but both measurements on pristine carbonates through the Phanerzoic (Veizer et al., 1999) and modelling studies (Wallmann, 2001) are increasingly indicating that Neoproterozoic seawater was significantly 18O-depleted compared to modern seawater. It is suggested that pristine Neoproterozoic carbonates may have had δ18O as low as −8‰, with variations around this value resulting from local depositional environment, temperature and glaciation. Certainly Hoffman and Schrag (2002) and Kasemann et al. (2005) present data from carbonates around the Ghaub glacial in Namibia that show parallel secular trends in δ18O and δ13C, where the δ18O data are interpretable in terms of depositional temperature variations and thus could be primary, and the latter authors argue that this is the case. These δ18O values are in the range −2 to −11‰, similar to estimates of Mesoproterozoic primary marine calcite δ18O of −6 to −10‰ (Frank and Lyons, 2000; Kah, 2000). Thus it is possible that some of our higher δ18O values are close to primary values, but many are below typical cut-offs (e.g. >−11‰; Kaufman et al., 1999) used to distinguish pristine values. These low values are due to interaction with low δ18O meteoric or metamorphic fluids that formed post-D1 vein samples MK72v and MK79v (Table 1).

Two of the lowest δ18O samples in the Upper Limestones (MK79 and 80) are close to the prominent post-D2 N–S fault (Fig. 1b) suggesting that this was a conduit for low δ18O fluids and providing a further constraint on the timing of fluid alteration. The δ18O value of MK72v calcite of −20.6‰ V-PDB (+9.6‰ V-SMOW) would be in equilibrium with fluid of −9‰ V-SMOW at −200 °C (Zheng, 1999), but vein temperatures would have to have been as low as 100 °C for the calcite to be deposited in equilibrium with a fluid of −8‰ V-SMOW — the upper limit of Neoproterozoic meteoric water if seawater was −8‰. Thus even the fluid that formed MK72v was probably not dominated by seawater or meteoric water, but was positively shifted by fluid rock exchange; this suggests relatively low fluid/rock ratios. Note that the MK72 rock has retained a higher δ18O value than the veins in the same rock, indicating that either water/rock ratios were low (<1; Jacobsen and Kaufman, 1999), or that exchange was kinetically limited, or some combination of the two. Since Sr-isotope exchange requires similar or larger water/rock ratios compared to O-isotope exchange to become significant (Jacobsen and Kaufman, 1999), and Sr-exchange kinetics are likely to be the same rate or slower than oxygen isotope exchange, this lends support to preservation of depositional Sr-isotope signatures in these samples.

5.2. 87Sr/86Sr

Two Upper Limestone samples (~600 m apart (~225 m stratigraphically) have strontium isotope ratios that are identical (mean: 0.706732 ± 0.000002; Table 1) within analytical error. Two samples of the Lower Limestone at Mai Kenetal and Tsedia have a mean ratio of 0.7062 ± 0.0001; one vein in the Lower Limestone shows a slightly lower value (0.70603).

Several criteria have been used to assess the preservation of Sr-isotope ratios in Neoproterozoic carbonates (e.g. Asmerom et al., 1991; Kaufman et al., 1993; Kaufman and Knoll, 1995; Jacobsen and Kaufman, 1999; Fairchild et al., 2000; Melezhik et al., 2001b; Thomas et al., 2004). Low δ18Ocarb values may indicate exchange with meteoric or metamorphic water, although as discussed above, the initial starting point, and therefore what represents a ‘low’ value is still debatable. Furthermore, meteoric water will not contain significant Sr unless it has interacted with rocks earlier in its flow-path, and then its acquired 87Sr/86Sr ratio may or may not be different from the rocks that we are examining. Hence
Table 1

Isotope data and element concentrations in acetic acid soluble fraction of Tigrai Neoproterozoic carbonates

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Unit</th>
<th>Description</th>
<th>Height (m)</th>
<th>δ13Ccarb (‰)</th>
<th>δ18Ocarb (‰)</th>
<th>εTOCc (‰)</th>
<th>TOCd (%)</th>
<th>Ca (wt.%)</th>
<th>Fe (ppm)</th>
<th>Mg (ppm)</th>
<th>Mn (ppm)</th>
<th>Sr (ppm)</th>
<th>Mn/Sr</th>
<th>Mg/Ca</th>
<th>Residue (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mai Kenetal</td>
<td>MK77</td>
<td>U. Lst. Whole-rock black limestone</td>
<td>2550 +5.8 - 8.5 -23.7 +30.2 0.21</td>
<td>0.708730 ± 24</td>
<td>40.23</td>
<td>2045</td>
<td>2228</td>
<td>160</td>
<td>2450</td>
<td>0.085</td>
<td>0.006</td>
<td>7.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MK76v</td>
<td>U. Lst. Vein containing calcite and quartz</td>
<td>2325 +5.6 - 9.6 -22.1 +26.4 0.14</td>
<td>0.708730 ± 24</td>
<td>40.00</td>
<td>3621</td>
<td>2838</td>
<td>283</td>
<td>2598</td>
<td>0.094</td>
<td>0.008</td>
<td>11.7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MK78v</td>
<td>U. Lst. Vein containing calcite and quartz</td>
<td>2250 +5.2 - 9.4 -23.8 +20.7 0.06</td>
<td>40.07</td>
<td>2125</td>
<td>2099</td>
<td>529</td>
<td>2752</td>
<td>0.192</td>
<td>0.005</td>
<td>14.2</td>
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<th>/H9254 13Ccarb (‰)</th>
<th>/H9254 18Ocarb (‰)</th>
<th>/H9254 13Corg (‰)</th>
<th>εTOCc (‰)</th>
<th>TOCd (%)</th>
<th>87Sr/86Sr (wt.%)</th>
<th>Ca (ppm)</th>
<th>Mg (ppm)</th>
<th>Mn (ppm)</th>
<th>Sr (ppm)</th>
<th>Mn/Sr</th>
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a Calculated height above base of Taimen group.

b Relative to V-PDB standard.
c εTOC is the C-isotope fractionation between carbonate and organic matter = 10^3 [\(\alpha_{TOC} - 1\)]=1 03 {\[\frac{1}{H9254}13C_{carb} + 1000}{\frac{1}{H9254}13C_{org} + 1000}\] − 1 ≈ \(\frac{1}{H9254}13C_{carb} - \frac{1}{H9254}13C_{org}\) (Hayes et al., 1999).
d Total organic carbon in rock sample.
e Acetic acid insoluble residue.

Fig. 4. Crossplots of carbonate /H9254 18O vs. (a) 87Sr/86Sr, (b) /H9254 13C. Additional data (small open symbols) from Miller et al. (2003) and Alene et al. (1999).

Oxygen isotope evidence of interaction with meteoric or metamorphic water is not a priori evidence of alteration in Sr-isotope ratios. Our rock samples from Mai Kenetal and Tsedia that were measured for Sr-isotope have a limited range of /H9254 18O values, with only the Tsedia sample being <−11‰ (Fig. 4a). The highly 18O-depleted vein from Mai Kenetal (MK72v) has a higher 87Sr/86Sr ratio slightly (<0.00009) less radiogenic than MK73, the vein-free rock sample just above it in the stratigraphy, suggesting that the vein fluid could have previously interacted with the low 87Sr/86Sr volcanics of the underlying Tsaliet Group. Negash Limestone samples analysed by Miller et al. (2003) have rather higher /H9254 18O than our samples and 87Sr/86Sr values overlap with our Upper Limestone samples, but have a larger range in 87Sr/86Sr over a similar height of stratigraphy (Fig. 4a). Their dolomite sample 87Sr/86Sr falls within the range of our Lower Limestone samples.

If limestones contain high Rb/Sr detrital phases such as feldspars and phyllosilicates it is possible that these could release or exchange Sr with high 87Sr/86Sr during metamorphic recrystallisation, hence increasing the Sr-isotope ratios of the carbonate (Jenkin et al., 2001). This is unlikely to be significant at low temperatures and in any one unit 87Sr/86Sr does not correlate with the amount...
Fig. 5. Crossplots of carbonate $^{87}$Sr/$^{86}$Sr vs. (a) Silicate residue % after dissolution in acetic acid, (b) Sr concentration, (c) Mn/Sr. Arrow shows possible alteration trajectory towards vein samples in Lower Limestones. See Fig. 4 for key to symbols.

of silicate residue (Fig. 5a), suggesting that this effect is insignificant in these samples.

The Sr content of samples has been used as an indicator of alteration, although simple loss of Sr is again not a priori evidence of change in $^{87}$Sr/$^{86}$Sr ratio. Sr is high (>2000 ppm) in the Upper Limestone at Mai Kenetal and, except MK99, the Lower Limestone at Tsedia (Table 1; Fig. 5b), but the Lower Limestone samples from the Mai Kenetal section (MK71-75) show strong depletion in Sr to ≤230 ppm. The high Sr content in most of the samples suggests retention of Sr from an original high-Sr aragonite precursor. The low-Sr values in samples MK71-75 can be related to either alteration by the low $^{87}$Sr/$^{86}$Sr fluid in the veins or to an initially low-Sr calcite precursor in this inlier. Low $^{87}$Sr/$^{86}$Sr in the Lower Limestone at Mai Kenetal may correlate with low Sr when compared to the Lower Limestone sample from Tsedia (Fig. 5b). On this plot alteration trajectories would be convex-upward curves (Jacobsen and Kaufman, 1999), and it is not possible to fit all the data to one trajectory, consistent with the Lower Limestones having a distinctly lower initial $^{87}$Sr/$^{86}$Sr (~0.7063) compared to the Upper Limestones.

Mn and Mn/Sr ratio may be useful indicators of alteration because Mn generally increases with both marine and meteoric diagenesis as well as metamorphism (Tucker and Wright, 1990; Jacobsen and Kaufman, 1999) and may act as a tracer for oxidising fluids that have interacted with crustal material. Various cut-offs in Mn/Sr ratio have been specified above which Sr-isotope data are liable to be altered and these range from <2 (Kaufman and Knoll, 1995) to <0.2 (Misi and Veizer, 1998; Fairchild et al., 2000). Our samples, with the exception of the Mai Kenetal Lower Limestone sample MK73 and nearby vein, and samples of Miller et al. (2003), except the dolomite sample, all lie below the latter most stringent cut-off value (Fig. 5c). Therefore, we suggest that the $^{87}$Sr/$^{86}$Sr in MK73 is a minimum value having been decreased by interaction with a low $^{87}$Sr/$^{86}$Sr-high Mn/Sr fluid, from a value initially similar to the value in MK100 in the Tsedia Lower limestone (~0.7063), as shown by the trajectory on Fig. 5c. Such concave-upward fluid alteration trajectories on this plot can be simulated using reasonable parameters for alteration of limestone (Jacobsen and Kaufman, 1999). Minor changes in $^{87}$Sr/$^{86}$Sr of <0.0002 are insignificant in making stratigraphic correlations and we conclude that all our Sr-isotope rock data are reliable enough for isotope stratigraphy.

5.3. $^{13}$C_carb

The near-pristine Sr-isotope data suggest that carbonate C-isotope values are likely to be pristine. The $^{13}$C_carb values consistently increase upwards in the stratigraphy from the Lower Limestone in the Tsedia (~4.5 to −0.7‰) and Mai Kenetal (~2.0 to −0.8‰) sections to the Upper Limestone at Mai Kenetal (+4.5 to +6.0‰ including veins; ~+5.5 ± 0.3‰ excluding veins). Such compositional variation over hundreds of metres of stratigraphy together with homogeneity on smaller scales is indicative of primary variations, substantially unaltered by regional metamorphism. Vein samples show similar or slightly lower $^{13}$C than the host rock suggesting that C-isotopes are rock dominated and little affected by fluid movement. Relatively constant and reasonable C-isotope fractionations between carbonate and organic matter within any single unit at Mai Kenetal and Tsedia provide further support that carbonate $^{13}$C values are little affected by post-depositional effects. In samples from all three inliers there is no correlation between $^{13}$C_carb values and amount of silicate residue (Table 1), indicating that metamorphic decarbonation reactions were not important in controlling $^{13}$C_carb.
show a positive correlation that runs from /H9254 or graphite usually results in a maximum of 3‰ positive communication). observed (Mullins, University of Leicester, personal material would be readily apparent and none was sphaeromorph organic-walled microfossils; mod- shows that the organic material in MK100 and MK75 is (c) An ongoing study of the palynology of these samples be the result of contamination and correlate with the modern contamination. Further evidence that the δ13C of the organic material in our samples has not undergone large increases comes from εTOC in the Upper Limestones (Table 1). Here εTOC averages +29.5‰, only 4‰ less than the maximum value recorded in the Neopro- tozoic and later (Hayes et al., 1999). Thus, since we argue δ13Corg is robust, then the δ13C of the organic material in these samples cannot have been shifted by more than +4‰. Moreover, as discussed in the analyt- ical section, there was some loss of a tiny amount of organic scum that could also have caused positive shifts in δ13Corg. The δ13Corg are therefore maximum values, but we suggest original values can only have been lower by a maximum of 4‰. For this reason we do not use these values in making correlations (although they sup- port them), but we are able to use them to constrain εTOC and the environmental variables that control this.

6. Correlation and stratigraphic age of the Tambien Group

6.1. Local correlation

Correlation between the Mai Kenetal and Tsidia inliers is relatively straightforward (Fig. 6), with the Tsidia inlier containing a more expanded sequence that is truncated to a deeper level by the sub-Phanerozoic unconformity. The distinctive C- and Sr-isotope data in the Lower Limestones in both inliers confirm this litho- stratigraphic correlation. To the east, the even thicker Chehmit inlier (Fig. 1a) is structurally more complex and further work is required to unravel the stratigraphy. Nev- ertheless, Alene et al. (1999) measured calcite δ13C in three samples from a limestone unit in Chehmit thought to be equivalent to the Lower Limestone and their δ13C of −3 to −4.4‰ support this correlation, emphasising the continuity of stratigraphy across these inliers.

Correlation of the Mai Kenetal, Tsidia and Chehmit inliers with the Negash inlier over 35 km to the east is more difficult; we suggest the intervening Phyllite Unit (Fig. 1a) represents a deeper water clastic-rich facies. However, both the distinctive lithologic features and C- and Sr-isotope ratios of the Upper Limestone at Mai Kenetal in the west and the Negash Limestone in the east allows reliable correlation of these units (Fig. 6), with the Upper Limestone preserving a more expanded section. This correlation indicates that the Mai Kenetal and Tsidia sections are older than the diamictite at...
Fig. 6. Local and global lithostratigraphic and chemostratigraphic correlation of Tambien Group sequences, Tigrai, Ethiopia. All isotope data are plotted to the same horizontal scale. See Fig. 4 for key to symbols. Global Neoproterozoic C-isotope curve from Halverson et al. (2005). This is not time calibrated, apart from the dates shown. Note however, that Condon et al. (2005) place the anomaly correlated with the Gaskiers glaciation by Halverson et al. (2005) significantly later terminating at ∼551 Ma. The Tigrai granites intruded into the Tambien Group provide a minimum age constraint of >613 Ma for sedimentation. The global Sr-isotope curve only includes data relating to the same sequences used by Halverson et al. (2005) to construct their C-isotope curve, thus minimising the possibility of errors due to incorrect correlations. This Sr-isotope curve is not substantially different from that of Halverson et al. (submitted for publication), which also includes much previously unpublished data. Sources for Sr-isotope data are: Svalbard — Halverson et al. (2005), Derry et al. (1989); N. Namibia — Halverson et al. (2005), Yoshioka et al. (2003); Oman — Burne et al. (1994). Data sources for age dates are: Precambrian/Cambrian boundary — Amthor et al. (2003); Gaskiers glaciation — Bowring et al. (2003); Marinoan glaciation — 636 Ma, Hoffmann et al. (2004), 635 Ma, Condon et al. (2005), 760 Ma date – ash bed in Ombombo Subgroup N. Namibia – Halverson et al. (2005). Dates for the Sturtian glaciation and Bitter Springs Stage are discussed in more detail in the text.

Negash. It is tempting to lithostratigraphically correlate the Negash Dolomite–Slate Unit with the Lower Limestone to the west, but although the Sr-isotope data match well, the δ^{13}C data in the Lower Limestone are all negative, whereas values in the Dolomite–Slate unit (Alene et al., 1999; Miller et al., 2003) are positive apart from one sample indicating a negative excursion. At the base of the Tambien Group there are strong petrographic similarities between the Lower Slates in the west and the Negash Slate in the east, and assuming that the Tsaliet Group–Tambien Group boundary represents a gradational, time-equivalent, feature (our interpretation) rather than an unconformity, it seems logical to correlate the Lower Slates with the Negash Slates across the area. Thus, given that there are no major depositional breaks in our sequences, the Lower Limestone plus Upper Slate in the west must be the correlative of the Dolomite–Slate unit in the east. In this case the negative C-isotope excursion in the Dolomite–Slate unit is correlated with the negative values in the Lower Limestones, which at Tsedia do appear to show an increase downwards that can be correlated with increase to positive values towards the base of the Dolomite–Slate unit (Fig. 6). Within the Negash Slates, C-isotope values are negative (Miller et al., 2003), suggesting that within the lower Negash sequence there were two periods of negative δ^{13}C, separated by a brief excursion to slightly positive values. It should be noted however that these Negash Slate data are based on samples with only a few % of carbonate that could have had their δ^{13}C altered by exchange with the host rock. Even if these data are not reliable, the bottom half of the Tambien Group definitely shows a strong negative C-isotope anomaly. Interestingly, a single 6–8 m thick limestone bed identified in the Tsaliet Group ∼150 m below the boundary of the Tsedia inlier shows a strongly positive δ^{13}C value of +5.8‰ (Fig. 6; Alene et al., 1999), constraining the lower limit of the negative C-isotope excursion and demonstrating that the ocean had high δ^{13}C values before Tambien Group deposition.
6.2. Correlation with the global isotope stratigraphy

According to our local correlations a composite section for the Tambien Group would show initial $\delta^{13}C_{\text{carb}}$ values of $\sim -6\%$ at the very base decreasing to twin lows to $\sim -4\%$ in the Lower Slate/Lower Limestone/Dolomite–Slate units, then rising to a plateau of $\sim -6\%$ in the Upper Limestone/Negash Limestone before decreasing sharply to $\sim -2\%$, just beneath the Negash diamictite (Fig. 6). The $^{87}\text{Sr}/^{86}\text{Sr}$ data change much less from $\sim 0.7063$ in the lower units to $\sim 0.7067$ in upper units. The large C-isotope shifts are typical for Neoproterozoic sequences worldwide and provide a reliable basis for global correlation (Kaufman et al., 1997; Halverson et al., 2005). The Neoproterozoic global C-isotope stratigraphy is being continually refined, and while we use the most recent compilation available (Halverson et al., 2005), it is implicit that our correlations are liable to change with the availability of new data from other sequences and can only ultimately be confirmed by high-precision U–Pb dating of points in the sequence. Negative $\delta^{13}C$ peaks are associated with all established glacial episodes in the Neoproterozoic (Fig. 6) and the collapse in $\delta^{13}C$ from a high plateau of $\sim +6\%$ to negative values just beneath the unequivocally glaciogenic Negash diamictite is consistent with expectations. The $\sim -4\%$ negative peak(s) towards the base of the Tambien Group could be consistent with a glacial episode at this horizon, but we reiterate that there are no glaciogenic deposits or breaks in deposition in this part of the sequence and this needs to be accounted for in our correlation.

Deposition of the Tambien Group is constrained to be $\sim 613$ Ma, thus excluding the possibility that the Negash diamictite correlates with the late Neoproterozoic Gaskiers glaciation (Fig. 6). However, because of the recent redating of the Marinoan glaciation to terminate at $\sim 635$ Ma (Hoffmann et al., 2004; Condon et al., 2005), the possibility now exists that the Negash diamictite could correlate with either the Marinoan or the Sturtian-glacial. The Sr-isotope data are key in distinguishing between these possibilities because pristine pre-Sturtian carbonate Sr-isotope data are essentially $<0.707$ whereas, apart from cap carbonates immediately above the Sturtian diamictite, younger Neoproterozoic carbonates have Sr-isotope ratios of $>0.707$ (Fig. 6). All of our data, and those of Miller et al. (2003), are $<0.70673$ putting them firmly in the pre-Sturtian part of the global Sr-isotope curve. Additional features that support a pre-Sturtian age include:

1. Marinoan glaciogenic deposits are typically immediately underlain by a prolonged negative $\delta^{13}C$ anomaly (“Trezona anomaly”; Fig. 6) and this is not observed below the Negash diamictite, although it is possible it could be hidden in the lower slaty part of the Pebbley Slate unit.
2. There is no known negative C-isotope anomaly below the sub-Marinoan Trezona anomaly until the Sturtian cap carbonate is reached (Fig. 6). Our lower negative anomaly is unlikely to be Sturtian cap carbonate because it is part of a continuous sequence with argillites below, not glaciogenic sediments, and the twin negative anomaly would not be consistent with a cap carbonate.
3. A limestone band intercalated in the Negash diamictite is Fe and Mn rich (Miller et al., 2003) and, although this could be a diagenetic feature, the presence of iron enrichment and BIF is feature more typical of Sturtian diamictic than Marinoan ones (Halverson et al., 2005; Kennedy et al., 1998; Hoffman and Schrag, 2002).

Thus we assign the Negash diamictite to the Sturtian glaciation, and the rest of the Tambien Group as a pre-Sturtian sequence. This being the case, the negative $\delta^{13}C$ peaks in the lower Tambien Group must relate to a pre-Sturtian event. The next negative $\delta^{13}C$ excursion downwards in the global sequence is the Bitter Springs anomaly, identified in sequences in Svalbard (Halverson et al., 2005; Hill et al., 2000). Interestingly this is a non-glaciogenic anomaly that has twin negative $\delta^{13}C$ spikes separated by a brief excursion just into positive values (Fig. 6) — features identical to the Tambien Group sequence and it seems logical to correlate with this. Filtered Sr-isotope data for the Bitter Springs anomaly in Svalbard (Halverson et al., 2005, in press) are close to 0.7064, very close to our best estimate of $\sim 0.7063$ for Lower Limestones. Other alternative, but less likely, correlatives of the Lower Limestones negative $\delta^{13}C$ peak are a minor negative peak to about $\sim -2\%$ in the pre-Sturtian Burra Group of Australia (Hill and Walter, 2000), or a sharp pre-Sturtian spike to as low as $\sim -8\%$ in the Coates Lake Group, Mackenzie Mountains, Canada, although these rocks have rather higher $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.7064–0.7067 (Halverson et al., submitted for publication). A small pre-Sturtian negative spike at about the same level is also recorded in the Chuar Group, Grand Canyon (Dehler et al., 2005). However, it is not yet known if these anomalies are of global rather than regional extent.
7. Chronostratigraphic age and duration of the Tambien Group

The age, and indeed number, of Sturtian glacial intervals is still a matter of debate. Available high quality geochronological data that constrain the age are summarised in Fig. 7. The body of evidence is consistent with a glaciation of global extent at $\sim 745$–$735$ Ma, most closely constrained by the following dates:

1. A maximum age constraint of $746 \pm 2$ Ma from the Naawpoort Volcanics, >700 m beneath the Chaus Formation in N. Namibia (Hoffman et al., 1996).
2. Rhyolitic flows, dated at $742 \pm 2$ Ma (Fetter and Goldberg, 1995), beneath the glaciogenic Grandfather Mountain formation, Appalachians.
3. Synglacial ash, dated at $723 +16$ $-10$ Ma, from the Ghubrah diamictite in Oman (Brasier et al., 2000); the lower of two diamictites, and assumed to be a Sturtian correlative.
4. Altered volcanic pods, dated at $735 \pm 5$ Ma, lying above the Kundelungu glacial deposits in Zambia (Key et al., 2001).
5. An age of $741 \pm 6$ Ma for meta-rhyolites overlying a presumed Sturtian diamictite in SW Namibia (Frimmel et al., 1996).

The Snowball Earth model demands a minimum duration of glaciation of $\sim 4$–$10$ Ma to allow atmospheric CO$_2$ to build up to overcome ice-albedo feedback (Caldeira and Kasting, 1992; Hoffman and Schrag, 2002); these age constraints are consistent with this timescale. Significantly younger ages in Idaho between $709$ and $667$ Ma (Lund et al., 2003; Fanning and Link, 2004) have also been attributed to the Sturtian glaciation (Fig. 7), so that either this glaciation is younger than indicated above, or there was another regional-only glaciation in Laurentia at this time.

The age of the Bitter Springs Stage (BSS) is not well constrained. Hill and Walter (2000) suggest $\sim 830$ Ma if the Gardiner Dyke Swarm ($827 \pm 6$ Ma; Wingate et al., 1998) is correlated, on the basis of strong geochemical and isotopic similarities, with the Bitter Springs Volcanics present throughout the Bitter Springs Formation (Zhao et al., 1994). Preiss (2000) prefers to correlate the Bitter Springs sequence with the Curdimurka Subgroup that includes the Rook Tuff ($802 \pm 10$ Ma; Fanning et al., 1986). These ages for the base of the Tambien Group are older than previously suggested (Miller et al., 2003) but are not inconsistent with existing age constraints on deposition of the underlying Tsait Group elsewhere ($854$ Ma; Teklay, 1997), but imply that the metamorphism $\sim 786$–$806$ Ma experienced by Tsait Group rocks in the Axum area $\sim 100$ km NW (Tadesse et al., 2000) did not occur in Tigrai, where sedimentation was ongoing at that time. The age of the Tambien group is thus early Cryogenian under the most recent geologic timescale (Gradstein et al., 2004), but note that some Neoproterozoic workers (e.g. Knoll, 2000) advocate placing the base of Cryogenian at the start of the Sturtian glaciation, in which case the Tambien Group would be Tonian–Cryogenian.

Taking our best age estimates, Tambien Group deposition in Tigrai took between $\sim 60$ and $90$ Ma, corresponding to sedimentation rates of $48$–$32$ m/Ma for the complete Negash sequence, in line with typical sediment accumulation rates due to thermal subsidence (Kaufman et al., 1993; Hoffman et al., 1998a). The truncated Mai Kenetal sequence took perhaps $10$ Ma less, giving a similar value of $54$–$34$ m/Ma. If, on the other hand, the base of our sequence correlated with the Coates Lake/Burra Group negative anomaly ($\sim 755$ Ma; Hill and Walter, 2000), Tambien Group deposition could have taken as little as $20$ Ma.
Fig. 8. Carbon isotope data for a composite Mai Kenetal/Tsedia section (Table 1). Filled symbols; this study, squares — Mai Kenetal, triangles — Tsedia. Open triangles — Mai Kenetal (Alene et al., 1999). The $\delta^{13}C_{\text{org}}$ represents maximum values, whereas $\varepsilon_{\text{TOC}}$ represents minimum values — see text for further details. $\varepsilon_{\text{TOC}}$ is the C-isotope fractionation between carbonate and organic matter = 100 ($\alpha_{\text{TOC}} - 1$) = 100 ($([\delta^{13}C_{\text{carb}} + 1000] / [\delta^{13}C_{\text{org}} + 1000]) - 1$) = $\delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{org}}$ (Hayes et al., 1999).

8. $\delta^{13}C_{\text{org}}$ data and C-isotope fractionation

Fig. 8 shows profiles of C-isotope data for a composite Mai Kenetal/Tsedia section. As discussed above, considering the possible effects of diagenesis and sample preparation, the $\delta^{13}C_{\text{org}}$ represents maximum values and thus the fractionation between carbonate and organic matter = $10^5 ([\delta^{13}C_{\text{carb}} + 1000] / [\delta^{13}C_{\text{org}} + 1000]) - 1$ = $\delta^{13}C_{\text{carb}} - \delta^{13}C_{\text{org}}$ (Hayes et al., 1999).

Our data show a good 1:1 correlation between $\varepsilon_{\text{TOC}}$ and $\delta^{13}C_{\text{carb}}$ ($\delta^{13}C_{\text{carb}} = 1.176\varepsilon_{\text{TOC}} - 29.5; r^2 = 0.92$) typical of Neoproterozoic samples. This is explained by Rothman et al. (2003) as a consequence of an unusually large oceanic reservoir of organic carbon in that period. The $\varepsilon_{\text{TOC}}$ values of $+28$ to $+30\%$ in the Upper Limestones are typical for much of the Neoproterozoic and Phanerozoic record, usually associated with warm periods, anoxic bottom waters and relatively high CO$_2$. If these were increased by 4% to values of $+32$ to $+34\%$ to take into account maximum diagenetic effects on $\delta^{13}C_{\text{org}}$, then this would indicate significant inputs from sulphide-oxidising or chemosynthetic bacteria that appear to be prevalent during the Neoproterozoic (Hayes et al., 1999). In contrast, the low values of $\varepsilon_{\text{TOC}}$ in the Lower Limestones are less common and usually associated with cooler periods of Earth history — including the Sturtian and Marinoan glaciations, low levels of CO$_2$, and infrequent phytoplankton growth rates and/or high ratios of cellular volume to surface area. These low $\varepsilon_{\text{TOC}}$ values do however become less exceptional if the maximum correction is made for diagenetic effects. Whilst the Lower Limestones contain a carbon isotope signature in both the carbonate and organic material that is identical to those associated with the Sturtian and Marinoan glaciations, we reiterate that there is no evidence for glaciation at this level. Furthermore, in the marine levels of the Bitter Springs Formation in Australia, which we believe is a correlative, $\delta^{13}C_{\text{carb}}$ has relatively normal values of $\sim -28$ to $-30\%$ resulting in $\varepsilon_{\text{TOC}} = +28\%$, and evaporites in the sequence suggest a hot, arid environment (Hill et al., 2000). Thus while our $\delta^{13}C_{\text{carb}}$ data suggest an unusual state in the global carbon isotope system during Lower Limestone deposition, the low $\varepsilon_{\text{TOC}}$ in our samples compared to Australia must reflect differences in a regional factor (temperature or biologic parameters) rather than CO$_2$ which would be the same globally. One possibility is that the Lower Limestones were deposited in cooler water perhaps associated with a nearby regional glaciation and evidence for this should be sought elsewhere in the ANS. If the Bitter Springs Stage C-isotope anomaly was the result of a regional glaciation more similar to those in the Phanerozoic this would place important constraints on the conditions necessary for development of the subsequent Snowball Earth events.

9. Geotectonic context of the Tambien group

Sequences spanning the Bitter Springs Stage are recognised only in Svalbard (Lower Akademikerbreen Group; Halverson et al., 2005), Australia (Bitter Springs Stage).
As a corollary of Snowball Earth glaciation, mechanism (1) is widely regarded as being the major cause of the Sturtian and Marinoan anomalies (e.g. Hoffman and Schrag, 2002), although (3) has also been suggested to explain both the pre-glacial part of the anomaly (Schrag et al., 2002) and the post-glacial section (Kennedy et al., 2001; Jiang et al., 2003) and kinetic (Rayleigh distillation) fractionation on rapid transfer of CO₂ from a high pCO₂, post-glacial atmosphere to the oceans could also contribute to the anomaly (Hoffman et al., 1998b).

Mechanisms (4) is suggested by Melezhik et al. (2005) and deserves further consideration, although they argue that mass balance renders it unlikely to be significant, and mechanism (2) is only expected to have a minor effect that could not in isolation cause significant depletion. Thus we are left with (1) and (5), which focus on oceanographic controls, but the question remains: how, in the absence of glaciation, can the carbon cycle in the oceans suddenly change?

Recent work on the Bitter Springs anomaly in Svalbard (Halverson et al., in press; Maloof et al., in press) provides a remarkable hypothesis to explain its origin. Palaeomagnetic declination suddenly changes by ~55° at the base of the C-isotope anomaly and then changes back to the pre-anomaly value its top. These observations are interpreted as the result of a pair of Inertial

1. Decreased biological productivity and burial due to reduction or shutdown of the carbon pump.
2. Decreased δ13C of the weathering flux to the oceans.
4. Decreased δ13C of the mantle degassing flux.
5. Large oceanic organic C reservoir, perhaps in a stratified ocean that overturns.

As meromictic lake, the Bitter Springs Stage anomaly is crucial to constraining the conditions that may have resulted in global glaciations starting ~60 Ma later.

Melezhik et al. (2005) list possible causes of negative C-isotope anomalies:

- decreased biological productivity and burial due to reduction or shutdown of the carbon pump.
- decreased δ13C of the weathering flux to the oceans.
- release of 13C-depleted methane from methane hydrate reservoirs.
- decreased δ13C of the mantle degassing flux.
- large oceanic organic C reservoir, perhaps in a stratified ocean that overturns.

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Interchange True Polar Wander (IITPW) events at the top and bottom of the anomaly. An IITPW event involves the rotation of the entire silicate Earth by up to 90° relative to the spin axis and climate zones that remain fixed in the celestial reference frame (Gold, 1955; Goldreich and Toomer, 1989; Fisher, 1974; Evans, 1998, 2003).

It is argued that these paired IITPW events caused the negative C-isotope anomaly by rotating the continents from a dominantly equatorial position into higher latitudes during the anomaly and as a result decreasing carbon burial during this period (Halverson et al., in press; Maloof et al., in press). This hypothesis provides a series of testable predictions because TPW will affect every continent differently, but predictably, depending on its changing position relative to the Earth’s spin axis. Thus Svalbard moves across the equator and poleward, whereas the Bitter Springs Formation in Australia is predicted to have moved from the tropics to the subtropics and experienced an increase in aridity, in accord with the deposition of evaporites in this formation (Maloof et al., in press). Independent support for this hypothesis comes from the palaeomagnetic data of Li et al. (2004) that indicates a large jump in palaeopoles in S. China between ~800 and 750 Ma consistent with 90° of TPW in that period. The uncertain palaeogeographic position of the Tambien Group during this period does not allow us to directly test this model in terms of change of palaeolatitude, but the contrasting fTOC between our Lower Limestones and the Bitter Springs Formation perhaps provide some support for this hypothesis. Since effects of atmospheric CO2 on fTOC will affect both sequences equally, the difference in fTOC is either the result of different biologic parameters (cell volume/surface area, growth rate) or temperature (Hayes et al., 1999). The fTOC data could thus be consistent with the Tambien Group experiencing cold conditions during the anomaly, whereas Australia was hotter — as demonstrated by the lithologies in the Bitter Springs Formation. If the changes in fTOC across the boundaries of the anomaly are interpreted in terms of temperature change only (i.e. other factors remain constant), then the similar fTOC beneath the anomaly and within it in Australia (Hill et al., 2000) would support the suggestion that Australia stayed within warm climates through the anomaly, whereas in the Tambien Group the increase in fTOC from the Lower Limestones/Dolomite–Slate to the Upper Limestone/Negash Limestone could be evidence of a sudden switch from high latitude coldwater (but not glacial) conditions during the anomaly to lower latitude warmer conditions after the anomaly. This would place the Tambien Group much further from the TPW rotation axis compared to Australia. Palaeomagnetic data for the Tambien Group would thus be critical in testing the IITPW hypothesis.

11. Summary

Radiometric age constraints together with isotope stratigraphic correlations indicate that Tambien Group deposition in Tigrai commenced during the Bitter Springs Stage and continued into the Sturtian glaciation. Radiometric ages on correlated sequences suggest deposition occurred in the interval ca. 800–735 Ma. The Tambien Group represents a rare example of a pre-Sturtian sequence extending through the Bitter Springs Stage, only recognised elsewhere in Svalbard, Australia, and possibly Canada. The pronounced negative δ13C anomaly that defines this stage is, as in correlatives elsewhere, not associated with glaciogenic sediments, further emphasising that there is no simple correlation between negative C-isotope anomalies and glaciation in the Neoproterozoic. Neoproterozoic C-isotope anomalies clearly reflect major perturbations in the Earth’s environment, but not all of these result in glaciation. Contrasting C-isotope fractionations between carbonate–organic matter (fTOC) through the BSS in Ethiopia and Australia must relate to differences in local environmental variables during this interval, most probably temperature. These differences are consistent with the recent proposal that the BSS anomaly is the result of a pair of IITPW events bracketing the anomaly that rotated the Tambien Group into high latitudes during the anomaly, but kept Australia at relatively low latitudes. This makes high-resolution dating and palaeomagnetic studies on the Tambien Group a high priority in order to test the predictions of this remarkable hypothesis.

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References

Hoffman, P.F., Schrag, D.P., 2002. The snowball Earth hypothesis:
Kasemann, S.A., Hawkesworth, C.J., Prave, A.R., Fallick, A.E., Pear-
98
M. Alene et al. / Precambrian Research 147 (2006) 79–99
Jacobsen, S.B., Kaufman, A.J., 1999. The Sr, C, and O isotopic evolu-
1059–1063.
M. Alene et al. / Precambrian Research 147 (2006) 79–99
Rappbog, P., Hofmann, P.F., in press. Combined paleomagnetic, isotopic
Kaufman, A.J., Knoll, A.H., Narbonne, G.M., 1997. Isotopes, ice ages,
Kendy, M.J., Christie-Blick, N., Sohl, L.E., 2001. Are Proterozoic cap carbo-
nates and isotopic excursions a record of gas hydrate destabilization following Earth's coldest intervals? Geology 29.
Key, R.M., Littopu, A.K., Nunn, F.M., Somner, V., Banu, J., Mose-
Earth Sci. 33, 503–528.
Geol. 88, 542–565.
372.
Mazof, A.C., Halverson, G.P., Kirschvink, J.L., Schrag, D.P., Weis, B.P., Hofmann, P.F., in press. Combined palaeomagnetic, isotopic and stratigraphic evidence for true polar wander from the Neopro-
terozoic Akademikerbreen Group, Svalbard. GSA Bull.
Morn, J.G., Torsvik, T.H., 2003. The making and unmaking of a super-
Melezhik, V.A., Fallick, A.E., Pukovski, B.G., 2005. Egenmatic nature of thick sedimentary carbonates deposited in13C beyond the canon-
ical mantle value: the challenges to our understanding of the ter-
Melezhik, V.A., Gorshkov, I.M., Fallick, A.E., Gijel, S., 2001a. Stron-
tium and carbon isotope geochemistry applied to dating of car-
cations for ‘blind dating’ Terra Nova 13, 1–11.
Mio, A., Veizer, J., 1998. Neoproterozoic sequences of the Ura Group, Iréce Basin, Brazil: chemostratigraphy, age and correlations. Pre-
cambrian Res. 89, 87–100.


