

## Stratigraphy and geochronology of the Tambien Group, Ethiopia: Evidence for globally synchronous carbon isotope change in the Neoproterozoic

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### Abstract

The Neoproterozoic Era was an interval characterized by profound environmental and biological transitions. Existing age models for Neoproterozoic nonglacial intervals largely have been based on correlation of carbonate carbon isotope values, but there are few tests of the assumed synchronicity of these records between basins. In contrast to the ash-poor successions typically targeted for Neoproterozoic chemostratigraphy, the Tonian to Cryogenian Tambien Group (Tigray region, Ethiopia) was deposited in an arc-proximal basin where volcanic tuffs suitable for U-Pb geochronology are preserved within the mixed carbonate-siliciclastic sedimentary succession. The Tambien Group culminates in a diamictite interpreted to correlate to the ca. 717–662 Ma Sturtian snowball Earth glaciation. New physical stratigraphic data and high-precision U-Pb dates from intercalated tuffs lead to a new stratigraphic framework for the Tambien Group that confirms identification of negative  $\delta^{13}\text{C}$  values from Assem Formation limestones with the ca. 800 Ma Bitter Springs carbon isotope stage. Integration with data from the Fifteenmile Group of northwestern Canada constitutes a positive test for the global synchronicity of the Bitter Spring Stage and constrains the stage to have started after  $811.51 \pm 0.25$  Ma and to have ended before  $788.72 \pm 0.24$  Ma. These new temporal constraints strengthen the case for interpreting Neoproterozoic carbon isotope variation as a record of large-scale changes to the carbon cycle and provide a framework for age models of paleogeographic change, geochemical cycling, and environmental evolution during the radiation of early eukaryotes.

## Introduction

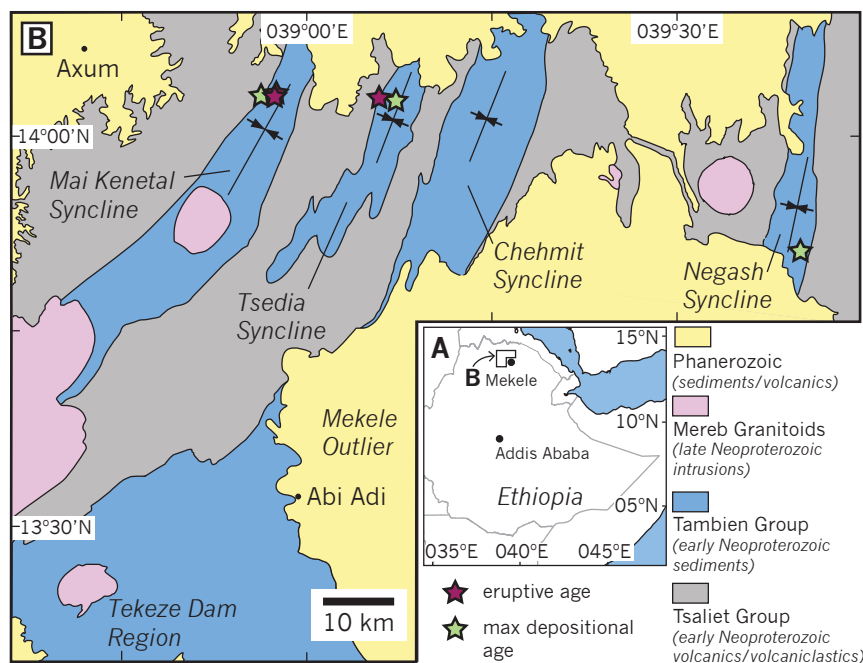
Neoproterozoic basins that developed during the rifting of the supercontinent Rodinia contain a record of the diversification of eukaryotic life (Knoll et al., 2006) contemporaneous with large-scale changes to ocean biogeochemical cycles (Halverson et al., 2010) and paleogeography (Hoffman and Li, 2009). In Neoproterozoic carbonates predating the first glaciation of the era, an interval of low carbonate  $\delta^{13}\text{C}$  values known as the Bitter Springs Stage (BSS) is followed by strata with positive  $\delta^{13}\text{C}$  values that persist until the ca. 735 Ma Islay anomaly (Rooney et al., 2014). The BSS has been interpreted to be recorded on multiple continents and is inferred to be globally synchronous based on correlation of the  $\delta^{13}\text{C}$  data and loose constraints such as subsidence models and correlation of diamictites (Halverson et al., 2010). Transient sea-level changes and shifts in paleomagnetic direction bracket the BSS in some records and could be the result of rapid true polar wander (Maloof et al., 2006; Swanson-Hysell et al., 2012). If the carbon isotope values interpreted as the BSS are globally synchronous, understanding the environmental change they represent is important for characterizing the boundary conditions that set the stage for extreme Neoproterozoic climatic fluctuations.

Much of our knowledge about global change during the Neoproterozoic has been gleaned from stratigraphic records of shallow-water carbonates that were deposited on passive margins or within intracratonic basins. While excellent for the preservation of stratigraphic archives, such environments generally have a paucity of volcanic input. The lack of volcanic tuffs in many Neoproterozoic stratigraphic sequences and the limited utility of biostratigraphy result in lower chronostratigraphic confidence than that typical of Phanerozoic successions. U-Pb dates from northwestern Canada provide some age constraints on the BSS with a date of  $717.4 \pm 0.1$  Ma from a rhyolite above the BSS and a date of  $811.5 \pm 0.3$  Ma on an ash below (Macdonald et al., 2010). At present, this  $811.5 \pm 0.3$  Ma date is the only U-Pb isotope dilution–thermal ionization mass spectrometry (ID-TIMS) zircon date from a tuff intercalated in Neoproterozoic carbonate stratigraphy prior to the ca. 717–662 Ma Sturtian glaciation (Rooney et al., 2014). Without radioisotopic age constraints on the BSS from multiple continents, (1) the global synchronicity of the BSS remains untested, and (2) the chronostratigraphic framework necessary for evaluating proposed mechanisms for marine  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  variations as well as paleogeographic change remains elusive.

## GEOLOGICAL SETTING

The Tambien Group of northern Ethiopia consists of an 5-km-thick mixed carbonate-siliciclastic succession. These sediments accumulated above volcanics and volcanoclastics of the Tsaliet Group (Figs. 1 and 2). Tsaliet Group lithologies record arc volcanism and the formation of juvenile crust that later coalesced as part of the Arabian-Nubian shield (Stern, 1994). Tsaliet Group age constraints have been interpreted through correlation with volcanics in Eritrea (Pb-Pb evaporation date of  $854 \pm 3$  Ma; Teklay, 1997). The contact between the Tsaliet and Tambien Groups is transitional, and input of volcanic ash into the basin continued during deposition of the Tambien Group (Fig. 2). Tambien Group strata are well exposed within synclinalia that formed during the East African orogeny (Fig. 1; Stern, 1994). Emplacement of granitoid plutons (Fig. 1) with U-Pb dates of ca. 610 Ma (Miller et al., 2003; Avigad et al., 2007) accompanied orogenesis; these plutons provide a minimum age constraint on the timing of

Tambien Group deposition (Fig. 1). The easternmost Negash synclinorium is cored by a diamictite with extrabasinal clasts interpreted to correlate with diamictites of the ca. 717–662 Ma Sturtian glaciation (Beyth, 2001; Hoffman and Li, 2009).



**Figure 1. A: Location of the study area within the Horn of Africa. B: Simplified geological map compiled from Alene et al. (2006) and Hailu (1975). Synclinoria containing exposed Neoproterozoic stratigraphy and the stratigraphic sections shown in Figure 2 are labeled.**

### Previous Stratigraphic Correlation

Initial carbon isotope work on Tambien Group carbonates led to identification of negative  $\delta^{13}\text{C}$  values in the Assem Formation that were suggested to be correlative to the ca. 800 Ma BSS (Alene et al., 2006). While lithostratigraphic and chemostratigraphic correlation between the Mai Kenetal, Tsedia, and Chehmit synclinoria is relatively simple (Beyth, 1972), correlation to the easternmost Negash syncline is not straightforward (Fig. 2). It was previously suggested that the Didikama Formation in the Negash syncline correlates with the Assem Formation, because they are both carbonate-rich formations overlying fine-grained siliciclastic rocks (Fig. 2; Alene et al., 2006; Miller et al., 2009). A volcanic unit below the Didikama Formation at Negash, dated and interpreted as an intrusive sill by Avigad et al. (2007), but reinterpreted as extrusive by Miller et al. (2009), has a SHRIMP (sensitive high-resolution ion microprobe) zircon  $^{238}\text{U}$ - $^{206}\text{Pb}$  weighted mean date of  $774.4 \pm 4.8$  Ma (youngest 7 of 8 dates). This date was interpreted in the context of the Didikama to Assem Formation correlation to imply that the entire Tambien Group was deposited after 775 Ma, and that correlation of the negative  $\delta^{13}\text{C}$  values from the Assem Formation with the BSS is not tenable (Miller et al., 2009, 2011).

## RESULTS AND DISCUSSION

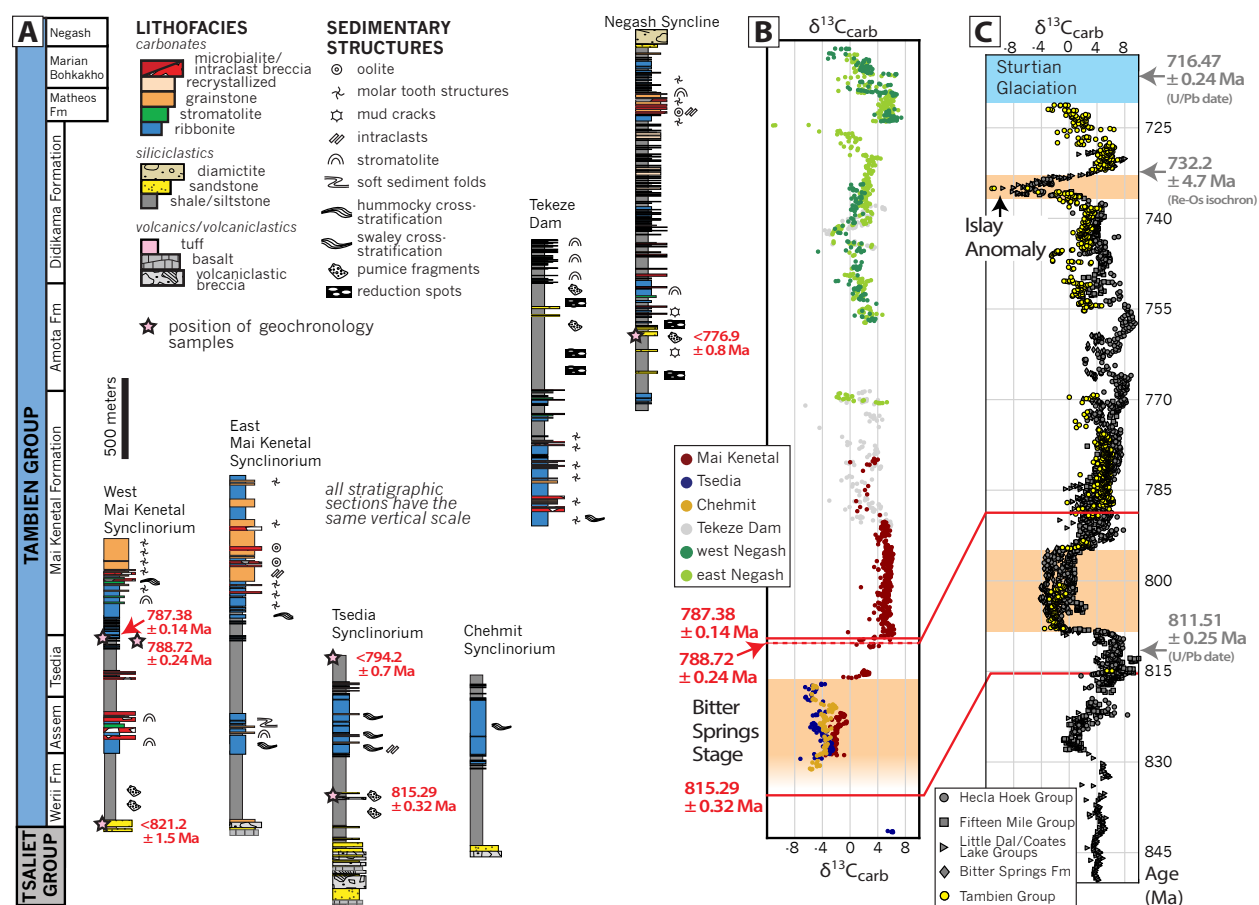
### Physical Sedimentology and Stratigraphy

In the westernmost exposure in the Mai Kenetal synclinorium, the Assem Formation contains abundant stromatolite and microbialaminite lithofacies interbedded with lenses of grainstone and intraclast breccia (Fig. 2). These lithofacies attest to deposition on a shelf environment that was transiently wave dominated. To the east, in the Tsedia and Chehmit synclinoria (Figs. 1 and 2), the Assem Formation is dominated by wavy to parallel-laminated limestone micrite. These facies suggest deposition in relatively deeper water than the stromatolitic and intraclast grainstone facies. Carbonate mud likely was transported from a shallow-water carbonate factory out to the deep shelf and upper slope to the east. Miller et al. (2009, 2011) argued that dolomitized grainstone at the base of the Assem Formation is a cap carbonate to a cryptic glaciation. While there is some dolomitization in the lower Assem Formation, the lithofacies that are dolomitized are found throughout the formation, and there are no distinctive cap carbonate sedimentary structures (cf. Hoffman, 2011). The Tsedia Formation overlying the Assem Formation comprises fine-grained siliciclastic sediment with minor carbonate beds (Fig. 2). The succeeding Mai Kenetal Formation consists of carbonate-dominated facies and contains abundant well-developed molar tooth structures. Hummocky cross-stratification of calcisiltite and carbonate grainstone in the lower portion of the formation attests to deposition under the influence of combined flow during storms without substantial reworking by fairweather currents. The formation is exposed in the Tekeze Dam region with the same distinctive lithofacies assemblage as in the northern synclinoria (Figs. 1 and 2). In the Tekeze Dam region, the formation is overlain by purple lutite of the Amota Formation. The Amota Formation is followed by siltstone to carbonate paraquences of the Didikama Formation; both formations also are found in the Negash synclinorium, leading to the lithostratigraphic correlation in Figure 2. In this correlation, the Tekeze Dam area links the Mai Kenetal and Negash stratigraphy.

### Carbon Isotope Stratigraphy

Carbonate rock samples collected during measurement of stratigraphic sections were analyzed for  $\delta^{13}\text{C}$  and  $\text{d}18\text{O}$  (methods and data tables are in the GSA Data Repository). Carbonates of the Assem Formation have negative  $\delta^{13}\text{C}$  values with an average value of  $-2\text{‰}$  in the west Mai Kenetal section and an average value of  $-4\text{‰}$ , with a transient decrease to values as low as  $-6\text{‰}$  at the top, in the deeper water Tsedia and Chehmit sections (Fig. 2; Fig. DR3 in the Data Repository). Above the Assem Formation, carbonate interbeds of the Tsedia Formation have nearly zero to positive  $\delta^{13}\text{C}$  values (to  $+3\text{‰}$ ) that are followed by values of  $+5\text{‰}$  in the Mai Kenetal Formation (Fig. 2). A prolonged interval of negative  $\delta^{13}\text{C}$  values followed by extended intervals of highly positive values characterizes the interpreted BSS in Australia (Swanson-Hysell et al., 2010), Svalbard (Halverson et al., 2010), and northwestern Canada (Macdonald et al., 2010), in contrast with more transient negative  $\delta^{13}\text{C}$  excursions (e.g., the Islay anomaly; Fig. 2).

In contrast to other formations in the Tambien Group, the Didikama Formation is extensively dolomitized and recrystallized. While some of the Didikama Formation  $\delta^{13}\text{C}$  variability may be ascribed to diagenetic alteration, coherent values of  $1\text{‰}$ – $3\text{‰}$  were obtained through much of the formation



**Figure 2. A: Simplified stratigraphic sections through the Tsaliet and Tambien Groups (Ethiopia) that are correlated on the basis of lithostratigraphy. Fm—formation. B: Correlations are supported by new U-Pb geochronology and  $\delta^{13}C$  chemostratigraphy. For detailed stratigraphic columns and their locations, see the Data Repository (see footnote 1). C: Composite of pre-Sturtian carbon isotope data that incorporates new U-Pb dates from the Tambien Group and dates from northwestern Canada (shown in gray).**

and, in one section, are followed by a negative excursion at the top of the formation (Fig. 2). In the  $\delta^{13}C$  composite (Fig. 2C), these negative values are provisionally correlated with the Islay anomaly, which predates the Sturtian glaciation by >10 m.y. (Rooney et al., 2014). In this correlation, the Didikama Formation and Matheos Formation contact is disconformable, with positive  $\delta^{13}C$  values of the Matheos Formation and the subsequent downturn within the Marian Bohkakhko Formation below the Negash diamictite being correlative with similar values in the Coppercap Formation of northwestern Canada (Fig. 2).

### U-Pb Geochronology and Chronostratigraphy

Zircons separated from 3 tuffs yield U-Pb ID-TIMS  $^{206}Pb$ - $^{238}U$  dates that we interpret as eruptive ages (for methods and data tables, see the Data Repository):  $815.29 \pm 0.32$  Ma from a tuff in the Werii

Formation (TS22),  $788.72 \pm 0.24$  Ma from a tuff in the upper Tsedia Formation (T2), and  $787.38 \pm 0.14$  Ma from another tuff in the upper Tsedia Formation (T1–1202; Fig. 2). The T1–1202 tuff is within the measured section from which  $\delta^{13}\text{C}$  data were developed and the T2 tuff was collected along strike (Fig. 2). In addition to these eruptive ages, maximum depositional ages interpreted from youngest single-grain concordant ID-TIMS dates provide further constraints (Fig. 2). These ages, along with the  $774.4 \pm 4.8$  Ma date from Negash (Avigad et al., 2007), confirm that previously published stratigraphic correlation schemes incorrectly correlated the younger Didikama Formation with the older Assem Formation. The ages support the revised lithostratigraphic correlation and demonstrate that Tambien Group deposition initiated ca. 820 Ma and spanned a significant portion of the early Neoproterozoic leading up to the Sturtian glaciation (Fig. 2).

### Age, Synchronicity, and Maximum Duration of the Bitter Springs Stage

As with other Neoproterozoic carbon isotope fluctuations, a lack of radiometric ages in successions interpreted to contain the BSS has resulted in global correlations being based solely on rough age constraints and broad similarities in isotope fluctuation amplitude and morphology. A date of  $811.51 \pm 0.25$  Ma (ID-TIMS  $^{206}\text{Pb}$ - $^{238}\text{U}$  zircon) for a tuff just preceding an interval interpreted as the BSS in the Fifteenmile Group of northwestern Canada can be compared to the new Tambien Group dates (Macdonald et al., 2010). The Werii Formation date of  $815.29 \pm 0.32$  Ma also precedes stratigraphy interpreted to record the BSS and corresponds closely with the Fifteenmile Group date, and the Tsedia Formation dates of  $788.72 \pm 0.24$  Ma and  $787.38 \pm 0.14$  Ma postdate the BSS. These dates constrain the age of the BSS to ca. 800 Ma and constitute a positive test of its global synchronicity. This result represents the second positive test of global synchronicity of a Neoproterozoic  $\delta^{13}\text{C}$  anomaly, with the other being the negative  $\delta^{13}\text{C}$  values in cap carbonates associated with the 635 Ma Marinoan deglaciation (Condon et al., 2005; Calver et al., 2013).

The synchronicity of the BSS between the Tambien and Fifteenmile Groups supports interpretations of this isotopic stage as a global, rather than local, phenomenon. Combined with covariation between carbonate and organic carbon isotopes across the BSS in central Australia (Swanson-Hysell et al., 2010), this result is consistent with interpretations of the changing  $\delta^{13}\text{C}$  values that call upon global change to the isotopic composition of dissolved inorganic carbon. Classic carbon cycle models explaining such a change invoke a decrease in the relative removal of carbon through  $^{12}\text{C}$ -enriched sinks, such as organic carbon burial, during the low  $\delta^{13}\text{C}$  values of the BSS and a high proportion of such burial before and after the stage (Halverson et al., 2010). Interpreting the interval of high  $\delta^{13}\text{C}$  values between the BSS and the Islay anomaly, that is now constrained to be  $>40$  m.y. (Fig. 2), as resulting from increased organic carbon burial requires high accompanying fluxes of oxygen to the atmosphere. Such high oxygen fluxes may be inconsistent with interpretations of proxy redox records, and increased burial of  $^{12}\text{C}$ -enriched authigenic carbonate has been invoked as an alternative mechanism for intervals of high  $\delta^{13}\text{C}$  values (Schrag et al., 2013). It is interesting to consider if elevated organic carbon burial, with associated increases in atmospheric  $\text{O}_2$  concentration, explains a portion of the elevated  $\delta^{13}\text{C}$  signal given evidence for diversification of eukaryotes in the form of armored protists, complex acritarchs, and testate amoebae between the BSS and the Islay anomaly (Strauss et al., 2014).

The  $788.72 \pm 0.24$  Ma age from the Tsedia Formation above the BSS, combined with the Fifteenmile Group pre-BSS age of  $811.51 \pm 0.25$  Ma, constrains the maximum duration of the stage to be  $22.8 \pm 0.3$

m.y. A Monte Carlo approach for extrapolating between the Tambien Group dates (for details, see the Data Repository) gives an estimate of  $794.6 \pm 0.1$  Ma for the age of the lowermost positive  $\delta^{13}\text{C}$  carbonate above the BSS (in the Tsedia Formation). This estimate constrains the duration of the BSS to be  $<16.9 \pm 0.3$  m.y. The carbonates of the Assem Formation have negative  $\delta^{13}\text{C}$  values throughout, leading to the interpretation that the BSS started before and ended after its deposition. Interpolation gives estimates of  $807.9 \pm 0.2$  and  $800.6 \pm 0.2$  Ma for the base and top of the Assem Formation, constraining the BSS duration to be  $>7.3 \pm 0.6$  m.y. These interpolated duration estimates are less certain than the  $<23$  m.y. constraint from the dates themselves, as the age model utilizes the crude assumption of a constant sedimentation rate.

The true polar wander (TPW) hypothesis for the BSS explains differences in paleomagnetic pole positions as the result of oscillatory TPW (Maloof et al., 2006; Swanson-Hysell et al., 2012). If observed shifts are the result of TPW (there and back resulting in  $83^\circ$  of total rotation in data from Svalbard carbonates), the  $<23$  m.y. duration for the BSS requires plate velocities of  $>40$  cm/yr ( $>54$  cm/yr for the  $<17$  m.y. estimate). This velocity is very high compared to rates of TPW and plate tectonics over the past 500 m.y. (Torsvik et al., 2012). However, rates this high are consistent with recent numerically modeled oscillatory TPW if lower mantle viscosity is at the low range of modeled values ( $3 \times 10^{21}$  Pa·s; Creveling et al., 2012). The TPW hypothesis currently hinges on interpretations of the magnetizations of carbonate rocks from Svalbard and Australia during the BSS as having a primary origin. The new chronological framework for the BSS presented here will enable the TPW hypothesis to be tested in noncarbonate-bearing lithologies, such as successions of extrusive volcanics.

## CONCLUSION

New physical stratigraphy, chemostratigraphy, and U-Pb zircon dates on tuffs from the Tambien Group reveal that the BSS was globally synchronous and lasted  $<23$  m.y. (likely  $<17$  m.y. and  $>7$  m.y.). Evidence of synchronous isotopic change has been difficult to establish for the Neoproterozoic, and in this case supports the hypothesis that the BSS resulted from global changes to the carbon cycle.

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