Two-stepping into the icehouse: East Antarctic weathering during progressive ice-sheet expansion at the Eocene–Oligocene transition

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ABSTRACT

In conjunction with increasing benthic foraminiferal δ¹⁸O values at the Eocene–Oligocene transition (EOT; ca. 34 Ma), coarse-grained ice-rafted debris (IRD; >425 μm) appears abruptly alongside fossil fish teeth with continually derived neodymium (Nd) isotope ratios (ε<sub>Nd</sub>) in Kerguelen Plateau (Southern Ocean) sediments. Increased Antarctic weathering flux, as inferred from two steps to less radiogenic ε<sub>Nd</sub> values, coincides with two steps in benthic foraminiferal δ¹⁸O values. These results indicate that two distinct surges of weathering were generated by East Antarctic ice growth during the EOT. Weathering by ice sheets during a precursor glaciation at 33.9 Ma did not produce significant IRD accumulation during the first ε<sub>Nd</sub> shift. Glacial weathering was sustained during a terrace interval between the two steps, probably by small high-elevation ice sheets. A large increase in weathering signals the rapid coalescence of small ice sheets into an ice sheet of continental proportions ca. 33.7 Ma. Rapid ice sheet expansion resulted in a suppression of weathering due to less exposed area and colder conditions. Parallel changes in Antarctic weathering flux and deep-sea carbonate accumulation suggest that ice-sheet expansion during the EOT had a direct impact on the global carbon cycle; possible mechanisms include associated changes in silicate weathering on the East Antarctic craton and enhanced fertilization of Southern Ocean waters, both of which warrant further investigation.

INTRODUCTION

The sudden appearance of ice sheets on Antarctica during the Eocene–Oligocene transition (EOT) produced a surge of erosion that carried weathering products to depocenters around the circum-Antarctic. Remnants of this weathering event are found in Early Oligocene strata as glaciomarine sequences on the continental shelves (Cooper and O’Brien, 2004) and as coarse grains of ice-rafted debris (IRD) in pelagic sediments (Zachos et al., 1992). A shift from smectite- to illite-dominated clay mineral assemblages signals the transition from a chemical weathering regime on Antarctica to one of mechanical weathering by ice sheets (Ehrmann and Mackensen, 1992). However, knowledge of the timing and magnitude of weathering and IRD deposition in the Early Oligocene is limited compared to cooling and/or ice volume increase history gleaned from deep-sea benthic foraminiferal δ¹⁸O records, which reveal a two-step transition from greenhouse to icehouse climate (Coxall et al., 2005).

Radiogenic isotopes of long-lived radioactive systems are excellent paleoceanographic proxies for continental weathering (e.g., Armstrong, 1971) because of the great isotopic disparity between mantle-derived and continental sources (e.g., Zachos et al., 1999; Dalai et al., 2006). Seawater neodymium (Nd) is almost exclusively derived from continental weathering (e.g., van de Flierdt et al., 2007) and has a short residence time (500–1000 yr) compared to the duration of the EOT (~200 k.y.). Fossil fish teeth in pelagic sediments take up large amounts of Nd during early diagenesis (Bermat, 1975). Rates of postburial Nd uptake (e.g., Kocis et al., 2010) are very low relative to early diagenetic rare earth element (REE) uptake in oxidizing pelagic sediments (e.g., Staudigel et al., 1985; C. Trueman, 2010, personal commun.), permitting retention of bottom-water ε<sub>Nd</sub> values (e.g., Martin and Haley, 2000). Thus, changes in fossil fish tooth ε<sub>Nd</sub> records from sediment cores near Antarctica are likely to preserve a signal of Nd carried with the weathering surge in the EOT interval. The objectives of this study are to determine the signal of Antarctic weathering and evaluate the timing of weathering changes relative to IRD deposition and cooling and ice volume proxies across the EOT.

The ε<sub>Nd</sub> values reflect the ¹⁴Nd/¹²Nd ratio relative to bulk Earth, where ε<sub>Nd</sub> values of continental crust become less radiogenic (i.e., negative) with older mantle extraction ages (DePaolo and Wasserburg, 1976). Low-resolution Nd isotope records reveal anomalously low ε<sub>Nd</sub> values for Southern Ocean waters at 34 Ma (Scher and Martin, 2004, 2006), indicating a source of non-radiogenic Nd (i.e., typical of ancient continental crust). Low ε<sub>Nd</sub> values at the EOT could be a signal of Antarctic glacial weathering (Scher and Martin, 2004). Precambrian basement, including Archean terranes in Prydz Bay (Fitzsimons, 2003), outcrops in East Antarctica (Fig. 1A), contributing sediment with extremely nonradiogenic Nd to Prydz Bay and areas around the Kerguelen Plateau (Fig. 1B; Roy et al., 2007; van de Flierdt et al., 2007). These terranes are the likely source of low ε<sub>Nd</sub> values measured in Late Eocene glaciomarine sediments within Prydz Bay (van de Flierdt et al., 2008).

MATERIAL AND METHODS

We developed coupled records of benthic foraminiferal δ¹⁸O, fossil fish tooth ε<sub>Nd</sub>, and IRD concentrations from the EOT interval of Ocean
Drilling Program (ODP) Site 738 (Fig. 2). ODP Hole 738B was sampled at an average interval of 11 cm between ~18.0 and 29.5 m below seafloor (total 99 samples), spanning the interval between 34.1 and 33.4 Ma on our age model. Details for analytical methods and the age model are given in the GSA Data Repository.1

RESULTS

The δ18O record for Site 738 derived from the benthic foraminifera Cibicidoides praemundulus reveals a two-step pattern (Fig. 2, left panel), similar to that found by Coxall et al. (2005) at ODP Site 1218 in the equatorial Pacific. The first step occurs ca. 33.9 Ma and the second, larger, step occurs ca. 33.7 Ma. An interval of intermediate and relatively uniform δ18O values produces a terrace between the two prominent steps (33.9–33.7 Ma).

The primary feature of the fossil fish tooth Nd isotope record is a two-step excursion to less radiogenic εNd values (Fig. 2, center). During the preexcursion interval (34.5–33.9 Ma), εNd values average ~7.3. The excursion interval (33.9–33.6 Ma) begins with a step decrease of 0.7 εNd that coincides with the first δ18O step. The first Nd isotopic step is followed by an ~150 k.y. interval of uniform εNd values, similar to the δ18O terrace interval. The εNd terrace ends abruptly with a second, larger step decrease of 2.1 εNd at 33.75 Ma that coincides with the second δ18O step. The nadir of the excursion is ~10.2 εNd at 33.7 Ma, which is followed by an ~130 k.y. recovery interval to higher values. The εNd values in the postexcursion interval (33.6–33.3 Ma) average ~8.0.

The first significant occurrence of IRD appears ~30 cm above the onset of the second step in δ18O and εNd values, in a thin stratigraphic horizon (~50 cm thick) (Fig. 2, right). IRD concentrations and mass accumulation rates reach peak values for ~75 k.y. centered ca. 33.7 Ma.

Individual fish teeth, including six samples from within the IRD horizon, show similar shale-normalized rare earth element and yttrium (REE + Y) profiles (Fig. 3). All of the patterns exhibit prominent cerium (Ce) and Y anomalies, which are diagnostic features of seawater (German and Elderfield, 1990; Nozaki et al., 1997). Furthermore, samples in this study define a relationship of Ce versus Y anomalies that is inconsistent with mixing between oxic seawater and continental crust (see the Data Repository), making postburial uptake of IRD-derived REE + Y by fossil fish teeth unlikely.

DISCUSSION

Timing of IRD Delivery to the Kerguelen Plateau

The record of IRD accumulation at Site 738 indicates that grains were delivered to the Kerguelen Plateau during a short episode of ice rafting (<75 k.y.), consistent with earlier studies (Zachos et al., 1992). The coincidence of peak IRD accumulation with the second larger δ18O step indicates rapid, large-scale ice sheet expansion. However, no significant ice rafting was associated with the first δ18O step of the EOT or with the earliest Oligocene glacial maximum (EOGM; Liu et al., 2004).

Nature of the Nd Isotope Excursion

The Nd isotope excursion begins slightly before the onset of IRD deposition (ca. 33.7 Ma), a strong indication that both are related to a single process. Variations in bottom-water εNd values reflect changes in water mass mixing and the weathering flux to the water mass source region. If late-stage diagenesis is not an issue, coherence between IRD and εNd records can be interpreted in two ways. One is a shift in ocean circulation coincident with the expansion of ice sheets during the second step of the EOT. Alternatively, the Nd isotope excursion could reflect an increase in the dissolved weathering flux entering the source area of the water mass bathing the upper Kerguelen Plateau. Here we evaluate the likelihood of each of these interpretations.

The least radiogenic water mass during the EOT was in the North Atlantic (εNd = ~11; O’Nions et al., 1998). Northern Component Water (NCW) was exported into the South Atlantic and Southern Ocean during the Oligocene (Scher and Martin, 2008; Via and Thomas, 2006). However, mass balance indicates that the unlikely mixture of 78% NCW at ~63°S in the Indian sector of the Southern Ocean would have been required to produce the observed excursion. With the same parameters, 18% of NCW is required to produce the initial, smaller εNd.

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step. However, $\varepsilon_{Nd}$ values at 42°S in the southern Atlantic (ODP Site 1090; Scher and Martin, 2006) only shift by 0.6 $\varepsilon_{Nd}$ across the first $\delta^{18}O$ step (~251 m composite depth). Thus it is more likely that the source of nonradiogenic $\varepsilon_{Nd}$ values during the first step was in closer proximity to the Kerguelen Plateau than to the Agulhas Ridge, which argues against an influx of NCW as the source of the excursion.

Mechanical erosion of Antarctic bedrock by ice sheets followed by rapid chemical breakdown of fresh mineral surfaces would have released extremely nonradiogenic Nd into the dissolved load accompanying the weathering surge during ice sheet growth. However, the delivery of Nd from Antarctic sources to bottom waters on the Kerguelen Plateau in pulses that are coeval with the benthic foraminiferal $\delta^{18}O$ step. However, $\varepsilon_{Nd}$ values (~150 k.y.) is much longer than the residence time of Nd, requiring an ongoing flux of nonradiogenic Nd. This strongly indicates that the relatively stable small- to medium-sized ice sheets nonetheless advanced and retreated on orbital time scales, thus maintaining a supply of freshly weathered mineral surfaces for chemical weathering. This finding supports the ice sheet hysteresis hypothesis related to the height–mass balance feedback modeled by Pollard and DeConto (2005); i.e., once formed, high-elevation ice sheets are stable because the ice surface is above the zone of ablation, which is strongly controlled by atmospheric $CO_2$ levels.

It is possible that Antarctic weathering during the terrace interval contributed to lower $CO_2$ through two mechanisms. The first is nutrient delivery to the Southern Ocean supplied by enhanced weathering and vertical mixing (i.e., intensification of polar easterlies) and increased primary productivity, indicated by increased opal accumulation (Salamy and Zachos, 1999). Second, enhanced silicate weathering (Berner et al., 1983) in East Antarctica during this intermediate phase of limited glaciation may have acted as a positive feedback to cooling on EOT time scales (i.e., by increasing the silicate weathering $CO_2$ sink). Estimates of surface ocean $pH$ from Tanzanian drill cores suggest that $CO_2$ was relatively low toward the end of the terrace interval (Pearson et al., 2009), supporting the argument that ice sheet weathering feedbacks helped sustain EOT climate change. Parallel changes between Antarctic weathering flux and calcite compensation depth deepening (e.g., Rea and Lyle, 2005) further indicate that weathering was an important factor for global carbon cycling in this interval.

During phase 3, a massive and abrupt increase in weathering flux occurred as the precursor ice sheets coalesced and expanded to cover the East Antarctic craton. Comparison of $\varepsilon_{Nd}$ and IRD records shows that the dissolved weathering flux carried in proglacial rivers reached the sea slightly before IRD reached the Kerguelen Plateau. During phase 4, coinciding with the EOGM, rates of mechanical and chemical weathering slowed as temperatures dropped, liquid water became scarce, and weatherable area diminished. It is likely that these factors contributed to the termination of IRD deposition at the study site during the earliest Oligocene glacial maximum.

Over the recovery interval to higher $\varepsilon_{Nd}$ values, the impact of chemical weathering on Antarctica as a sink for $CO_2$ diminished, permitting $CO_2$ to build up in the atmosphere (e.g., Pearson et al., 2009). Zachos and Kump (2005) modeled the climate response of decreasing Antarctic weatherability as a function of ice coverage and found that the $CO_2$ response could explain the warming trend that ended the earliest Oligocene glacial maximum. Results from our study provide partial support of this hypothesis, demonstrating that a decrease in weathering accompanied the final build-up and maximum extent of the East Antarctic ice sheet during the Early Oligocene.

CONCLUSIONS

A detailed weathering history of East Antarctica during the EOT has been reconstructed on the basis of IRD MAR and $\varepsilon_{Nd}$ values from fossil fish teeth at ODP Site 738 on the Kerguelen Plateau. These tracers of terrigenous input track two extremes in the size spectrum of glacially weathered products that reach the pelagic realm: mechanically weathered coarse grains transported by drifting icebergs and chemically weathered dissolved solutes transported by proglacial rivers. We show for the first time that two distinct weathering pulses occurred during the EOT, simultaneous with two benthic foraminiferal $\delta^{18}O$ steps. Ice sheets formed in the latest Eocene (33.9 Ma) were limited to elevated regions and did not reach sea level, but persisted throughout the terrace interval until the second step. The large ice sheet that formed suddenly at 33.7 Ma quickly reduced the weatherable area on Antarctica, resulting in a weathering flux decline, with effects on the progression of global climate change during the Early Oligocene.

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