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Continental weathering fluxes during the last glacial/interglacial cycle: insights from the marine sedimentary Pb isotope record at Orphan Knoll, NW Atlantic

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ABSTRACT

Regional weathering intensity must have changed dramatically at high latitudes during the Quaternary as a consequence of repeated continental glaciation. Investigation of these glacial/interglacial changes at high temporal resolution is possible with the recent development of Pb isotopes in FeMn oxyhydroxide phases as a proxy for region-specific weathering intensity, where increases in the radiogenic component are thought to correspond to increased continental weathering fluxes. Here we present a Pb isotope record sourced from the FeMn oxyhydroxide fraction in marine sediments from IODP Sites U1302/3 on Orphan Knoll (~3500 mbsl, NW Atlantic), spanning the last 37 ka. Located at the eastern edge of the Laurentide Ice Sheet (LIS), Site U1302/3 is well-placed to monitor changes in weathering intensity associated with LIS glacial history. Overall, the data show a close correspondence to local surface water $\delta^{18}O$, with least radiogenic values during times of heavy $\delta^{18}O$ (glacial maximum) and most radiogenic values during times of light $\delta^{18}O$ (Holocene). This supports the prediction that weathering intensity in glaciated regions of the North Atlantic correlates with the exposure age of glacial debris. Superimposed on these background trends are extreme radiogenic excursions (e.g. variation in $^{206}Pb/^{204}Pb$ from ~19.2 −21.0) contemporaneous with Heinrich events and the Younger Dryas. These data are substantially more radiogenic than existing records from the NW Atlantic, and most likely represent episodes of exceptionally high inputs of pre-formed FeMn oxyhydroxides during drainage of the LIS. Due to its extreme isotope composition, at least in the NW Atlantic region, Pb would appear to be a good proxy for the fluxes of weathered continental material and perhaps, by inference, nutrients to the surface ocean.

1. Introduction

The growth and demise of Quaternary ice sheets radically increased the extent of physical erosion in glaciated regions (e.g. Bell and Laine, 1985; Dowdeswell et al., 2010), probably causing large changes in regional chemical weathering intensity, from minima during periods of maximum ice cover and lower global temperatures to enhanced rates on ice sheet retreat and exposure of highly reactive glacial debris to a warming climate (e.g. Blum and Erel, 1995; Tranter et al., 2002; Foster and Vance, 2006; Gislason et al., 2009). The precise details of the climatic feedbacks linked to chemical weathering fluxes are still debated, partly because of the erosive nature of glaciation and the lack of reliably dated archive materials. The best repositories to capture and record these changes in chemical weathering are adjacent ocean basins and the sediments accumulated therein, which can provide a near-continuous, spatially-integrated, record of processes active on the neighbouring continents.

Investigation of glacial/interglacial variation in chemically weathered solute fluxes to the oceans requires a suitable proxy. This continues to present a challenge despite various attempts to gauge weathering intensity using parameters such as oceanic Ge/Si ratios and Sr isotopes (e.g. Henderson et al., 1994; Hammond et al., 2000). Palaeoseawater records of Pb isotope composition are a more recent attempt to explore weathering intensity over these timescales (e.g. Foster and Vance, 2006; Gutjahr et al., 2009; Kurzweil et al., 2010). One of the advantages of Pb is its particle

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reactive nature and consequent short seawater residence time (e.g. ~20–30 years in the deep North Atlantic; Henderson and Maier-Reimer, 2002), which allows targeted, region-specific investigations, as opposed to proxies with long residence times that integrate global changes in seawater composition. Of course, this is also a disadvantage in cases where a global picture is sought.

Due to the near ubiquitous nature of anthropogenic Pb pollution (Settle and Patterson, 1980), understanding the processes that drive changes in the Pb isotope composition of weathered products is based mostly on laboratory experiments and soils (Erel et al., 1994; Harlavan et al., 1998, 2009; Harlavan and Erel, 2002). Both of these approaches suggest that the Pb isotopic compositions of weathering fluids is likely to be highly variable, but largely systematic, during incipient weathering, as a result of preferential release of radiogenic Pb from accessory phases (Erel et al., 1994). Further on in the weathering history, these accessory phases become depleted, and release of common Pb from major phases overwhelms the Pb isotope composition of the weathered product (Harlavan and Erel, 2002). Importantly, these systematic changes in weathered Pb isotope composition operate on a similar timescale to overall chemical weathering rates, as constrained from cation mobilisation profiles in soils of varying ages. In this latter case, a power law relationship best describes the inverse correlation between the weathering flux and soil/debris age in weathering catchments (Taylor and Blum, 1995). These observations imply that the Pb isotope composition carried by the continental weathering flux could, by proxy, be a sensitive monitor of regional variability in weathering intensity and solute flux associated with glacial/interglacial cycles (Foster and Vance, 2006).

The first hint at a link between seawater Pb isotope compositions preserved in FeMn crusts, inputs of eroded continental material and global climate (reflected in benthic foraminiferal $\delta^{18}O$ records) was noted by Christensen et al. (1997). This was followed by the recognition that glaciation of continental landmasses had a fundamental effect on the Pb isotope composition of seawater (von Blanckenburg and Nagler, 2001). This is clearly demonstrated by the rise in the radiogenic Pb isotope composition of FeMn crust records from the North Atlantic over the last ~2 Ma (Burton et al., 1997; Reynolds et al., 1999). On shorter timescales, high resolution (~10 ka/sample) FeMn crust records obtained by laser ablation from the deep North western Atlantic demonstrated that variation in the Pb isotope composition correlated well with changes in climate, and hence that the continental weathering regime varied dramatically across glacial/interglacial cycles (Foster and Vance, 2006). Specifically increases in the radiogenic component were linked to an increase in the alkalinity flux associated with increased chemical weathering of glacial debris initiated during deglaciations. More recent studies using marine sedimentary FeMn oxyhydroxides have considerably improved the temporal resolution achieved, and opened up the possibility of using the palaeo-records of seawater Pb isotope composition to investigate millennial-scale changes in continental weathering fluxes (Gutjahr et al., 2009; Kurzweil et al., 2010). To date, these high resolution records have demonstrated that rapid changes in Pb isotope composition are associated with the retreat of the LIS as well as the geographic pattern of freshwater routing during that retreat. These studies thus confirm the dominant control on marine sedimentary Pb isotope records of the continent to ocean Pb flux, in tandem with the changes that the continental weathering regime impose on the evolving Pb isotope compositions of that flux (Kurzweil et al., 2010).

The short duration of the glacial/interglacial transition (~10 ka) and the rapid sequence of oceanographic and climatic perturbations within that time period, e.g. Heinrich event 1 (H1), require archives of millennial to sub-millennial temporal resolution. In addition, studies of sites proximal to the large ice sheets have the potential to more clearly deconvolve the causes of some of the signals. Here we present Pb isotope data in the FeMn oxyhydroxide component of marine sediments from Orphan Knoll in the NW Atlantic. Through records of Pb isotope composition at this location proximal to the Laurentide Ice Sheet, we are able to investigate the detailed relationships between ice sheet advance and retreat, chemical weathering and the impact of both on the delivery of radiogenic Pb to the oceans.

2. Materials and methods

The authigenic FeMn oxyhydroxide fraction was extracted from sediments from IODP Sites U1302/3 (IODP Expedition 303/306; Fig. 1), located on Orphan Knoll in the NW Atlantic, and was analysed for its Pb isotope composition. The samples span the last 37 ka and from 0.25 to 5.85 m composite core depth (mcd). The youngest samples were taken from hole U1302D (50°10.020′N, 45°38.324′W, 3567 mbsl) and the remaining from hole U1303B (50°12.383′N, 45°41.197′W, 3524 mbsl). The coring sites are located on a ridge crest southeast of the main bulk of Orphan Knoll, which is a fragment of continental crust rising 2 km above the Labrador Sea abyssal plain (Chian et al., 2001). The canyons surrounding the core sites partially protect them from debris flows (Aksu and Hiscott, 1992). The sampled core section is Subunit IA, which consists of horizontally bedded and undisturbed sediments, mostly composed of quartz, detrital carbonate and nannofossils (Channell et al., 2006). Earlier piston cores collected from the same area demonstrate that sediments from this region record the history of the northeastern sector of the LIS, spanning the Atlantic Canadian shelf from south Labrador (~52 °N) northwards (e.g. Stoner et al., 1996; Stoner et al., 2000; Hiscott et al., 2001).

An age model was constructed using the downcore occurrence of specific climate events, as identified on the basis of magnetic susceptibility and gamma ray attenuation density by Channell et al. (2006), and their duration. Taking the mid-point core depth of each climate event occurrence (Younger Dryas, YD, and Heinrich events, HEs) and the absolute timing of these events (Hemming, 2004) as tie points, sedimentation rates and thus ages were calculated (see Table A.1 and Figs. A.1–A.3 for details). Comparison was made to the age model and $CaCO_3$ (%) record of neighbouring core MD95-2024 as verification of the age model (Fig. A.3). Although the age model we have established is approximate and will certainly be subject to revision, it serves to place the data in a temporal context that is precise enough for the purposes of interpretations presented here. Bioturbation, present at the centimetre to millimetre scale, should not lead to substantial blurring of climate signals given the sedimentation rate of ~10–18 cm/ka (Bard et al., 1987; Anderson, 2001; Fig. A.1) and millennial-scale sampling resolution.

The analytical procedures used here closely followed Gutjahr et al. (2007) and the Appendix details in full all procedures relating to the FeMn oxyhydroxide leaching technique, detrital fraction digestion, column chromatographic separation procedures for Pb and Sr, total procedural blanks, and mass spectrometry, including reproducibility of the leaching approach.

3. Results

Overall, the Pb isotope record from Orphan Knoll (Fig. 2, Table A.2) exhibits two principal features at different timescales: a slow background change across the LGM and deglaciation, and much more rapid shifts that punctuate this background trend coincident with HEs. With respect to the background changes, between 37 and ~24 ka the $^{206}Pb/^{204}Pb$ data exhibit a decrease to less radiogenic values (20.0–19.2 $^{206}Pb/^{204}Pb$) and maintain this minimum until 19.5 ka. After this, the background trend shows