LETTERS

Negligible glacial–interglacial variation in continental chemical weathering rates

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Chemical weathering of the continents is central to the regulation of atmospheric carbon dioxide concentrations, and hence global climate[1,2]. On million-year timescales silicate weathering leads to the draw-down of carbon dioxide[1], and on millennial timescales chemical weathering affects the calcium carbonate saturation state of the oceans and hence their uptake of carbon dioxide[2]. However, variations in chemical weathering rates over glacial–interglacial cycles remain uncertain. During glacial periods, cold and dry conditions reduce the rate of chemical weathering[3], but intense physical weathering[3,4] and the exposure of carbonates on continental shelves due to low sea levels[5,6] may increase this rate. Here we present high-resolution records of the lead isotope composition of ferromanganese crusts from the North Atlantic Ocean that cover the past 550,000 years. Combining these records with a simple quantitative model of changes in the lead isotope composition of the deep North Atlantic Ocean in response to chemical weathering, we find that chemical weathering rates were two to three times lower in the glaciated interior of the North Atlantic Region during glacial periods than during the intervening interglacial periods. This decrease roughly balances the increase in chemical weathering caused by the exposure of continental shelves, indicating that chemical weathering rates remained relatively constant on glacial–interglacial timescales. On timescales of more than a million years, however, we suggest that enhanced weathering of silicate glacial sediments during interglacial periods results in a net draw-down of atmospheric carbon dioxide, creating a positive feedback on global climate that, once initiated, promotes cooling and further glaciation.

The oceans integrate Pb released by weathering from relatively large continental areas[7], and records of secular change in the Pb isotopic composition of seawater yield such information on long timescales. Ferromanganese crusts (hereafter simply called crusts) precipitate directly from seawater and have been shown by numerous publications to provide a faithful record of its Nd and Pb isotopic composition[8]. We focus here on three crusts that have been well dated with U-series (Supplementary Information): ALV539 2-1 (from here on termed ALV539) and BM1969.05 from the New England and adjacent San Pablo Seamounts in the northwest Atlantic (35° 36′ N 58° 47′ W, 2,665 m; 39° 00′ N 60° 57′ W, 1,800 m), and TR079 D-14 from the Desirade Seamount in the Guadeloupe Islands of the Lesser Antilles in the tropical west Atlantic (16° 55′ N 61° 10′ W, about 2,000 m). All three are currently bathed by the Deep Western Boundary Current, which is the southern extension of North Atlantic Deep Water (NADW). At present the NADW is derived from a roughly 70%/30% mixture of surface waters in the Greenland–Iceland–Norwegian Seas and in the Labrador Sea[9].

Figure 1 shows a new high-resolution Pb isotope record for these crusts, obtained with laser-ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICPMS; Supplementary Methods). Four asymmetric cycles are evident in the isotopes of Pb in the outer 550 kyr of ALV539 and BM1969.05 (Fig. 1) that clearly correlate with the O isotope record of seawater despite subtle variations (typically on timescales of the order of less than 15 kyr) relating to uncertainties in the crust age models used (principally due to small-scale variations in growth rate; Supplementary Information). The Pb isotope record shows asymmetric roughly 100-kyr cycles, with ^{207}Pb/^{206}Pb varying from 0.824 to 0.817 during the glacial stages and increasing rapidly to about 0.814 during interglacials. All other Pb isotope ratios (for example ^{206}Pb/^{204}Pb) show similar periodicities (Supplementary Information). Significantly for our interpretation, crust TR079 D-14 from 16° N has much less variability.

Secular variation in the Pb isotopic composition of the deep North Atlantic, as recorded in crusts, could reflect either variable mixing between different water masses in response to a change in the pattern of deep ocean circulation or changes in the rate and mode of weathering on the North Atlantic continents (see ref. 8 for a review). There are several lines of evidence that the latter dominates. First, Pb has a very short residence in the North Atlantic (less than 30 years (ref. 7)) and therefore Pb is not advected far by Atlantic Ocean circulation (water has a residence time of about 600 years in the Atlantic). That the Pb isotopic signal in the northern crusts is dominated by local weathering processes and is not affected by mixing of water from the south is supported by the lack of variation in the southernmost crust, TR079 D-14. Second, tracers of water mass such as Nd isotopes[10] (Fig. 1) indicate near-constant modern-NADW-like[11] isotope ratios in the crusts and show that there has been little impact of southern-derived water for the past 550 kyr (see ref. 10) (Fig. 1). Last, Fig. 2a shows that over the past 2.2 Myr the NADW has been significantly more radiogenic in Pb than its potential source areas. It has been established in numerous areas that the early stages of weathering preferentially release radiogenic Pb (for example ^{207}Pb/^{206}Pb as low as 0.680 in soils versus 0.957 in the parent rock[12]) from high-U + Th/Pb accessory phases (Fig. 2b)[12–14]. It has been suggested[15] that the radiogenic Pb at one end of the arrays in Fig. 2 is released as a consequence of this process and that it was significantly augmented after the beginning of Northern Hemisphere glaciation (2.5–3.0 Myr ago) as a result of the increased mechanical breakdown of accessory grains by glacial erosion. Although Nd isotopes are also subject to the impact of incongruent weathering, the effects are more subtle[15]. Moreover, the exotic Nd produced by incongruent weathering is released into a much larger oceanic reservoir of Nd (a consequence of its longer residence time), so that the impact on seawater is more subtle still. The data in Fig. 1 do not preclude the presence of such small excursions in seawater Nd as sampled by the crusts.

We therefore argue that the dominant process causing variation in ALV539 and BM1969.05 up and down the arrays in Fig. 2 and the glacial–interglacial variation in Pb isotope ratio is the differential release of radiogenic Pb from accessory phases during the early stages

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of weathering. Figure 2c can be interpreted to yield ages of 2.0–2.5 Gyr for the source, very similar to Nd model ages for surface seawater from the Labrador Sea over the past 1 Myr[16,17] and also to Ar–Ar ages of detrital hornblendes in North Atlantic sediments[17] and Pb isotope data (Fig. 2b, c) for leachates of Baffin Bay sediments[15]. This result could only coincidentally be a product of water mass mixing.

The lack of Pb isotopic cycles in TR079 D-14 indicates that the origin of the signal must be quite proximal to ALV539 and BM1969.05; that is, originating on the North American continent. It has been shown[12] that the radiogenic fraction of Pb released during early chemical weathering of soils is soon swamped by the release of Pb from other less radiogenic phases such that after 300 kyr the Pb isotopic composition of the soil is indistinguishable from the unweathered parent rock (Fig. 2b). Over a similar timescale (about 100 kyr) the chemical weathering rate of a soil decreases by three
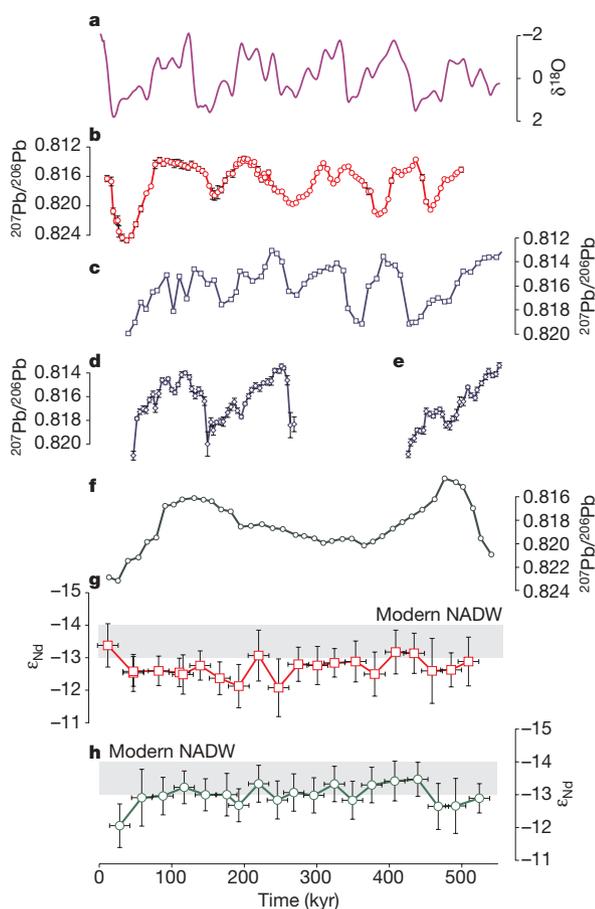

Figure 1 | High-resolution Pb and Nd isotope data for deep Atlantic ferromanganese crusts. a, The SPECMAP marine oxygen isotope record[27]. **b–h**, High-resolution LA-MC-ICPMS Pb (**b–f**) and Nd (ref. 12) (**g, h**) isotope records of BM1969.05 (**b, g**), ALV539 A (**c**), ALV539 B (**d**), ALV539 C (**e**) and TR079 D-14 (**f, h**) plotted against time from U-series isotope analysis (Supplementary Methods, and ref. 10). The ε notation used in **g** and **h** is in parts per 10,000 variation from the Chrondritic Uniform Reservoir. Nd and Pb error bars are 2 s.e. measurement uncertainties and for Pb they are typically smaller than the symbols. See Supplementary Information for the location of each Pb isotope traverse, for the tabulated data and plots of all Pb isotope ratios. For crusts BM1969 and TR079 D-14, as well as the youngest roughly 200 kyr of ALV539, age uncertainties are 10–15 kyr (Supplementary Methods). These age uncertainties do not significantly compromise the assignment of a part of the Pb isotope record to a glacial–interglacial. For the older part of the ALV539 record the age uncertainties increase and are as great as ±50 kyr. However, the similarity of the ALV539 Pb isotope record to that of the better-dated BM1969.05 significantly increases confidence in the assignment of ages to the older parts of this crust.
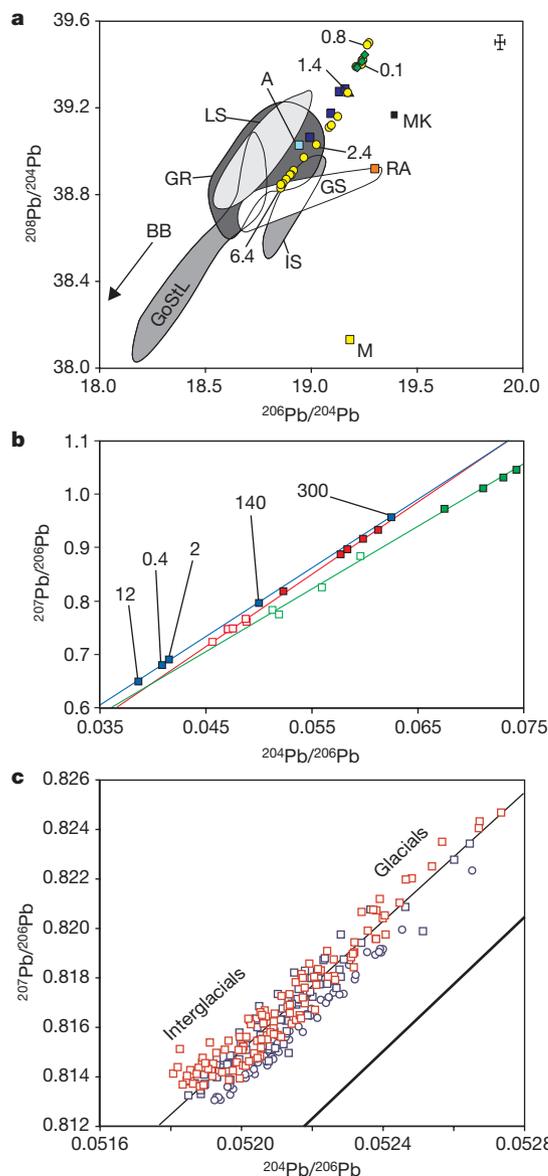

Figure 2 | Relationships between ferromanganese crust Pb isotopic data and circum-Atlantic Pb sources. a, Low-resolution[24] (labelled with ages in Myr), and some new high-resolution Pb isotope data, for ALV539 plotted with potential Pb sources (shaded fields). Source data are for either riverine suspended load[27] or geographically constrained oceanic sediments[28,29]. Data for the NADW over the past 2.2 Myr clearly extend to values more radiogenic than any known source. Error bars (top right) on the high-resolution data are the external reproducibility of NIST 612 by LA-MC-ICPMS (Supplementary Methods). A, Amazon river; LS, Labrador Rise; GR, Greenland Rise; GS, Greenland Shelf; BB, Baffin Bay; RA, Red Arctic river; MK, MacKenzie river; IS, Iceland Shelf; GoStL, Gulf of St Lawrence; M, Mississippi river. Blue squares, ALV539 glacials (0–450 kyr; LA-MC-ICPMS); green diamonds, ALV539 interglacials (0–450 kyr; LA-MC-ICPMS); yellow circles, ALV539 (0–6 Myr; ref. 24). **b**, ^{207}Pb/^{206}Pb data for soils (Wind river[12]) labelled with soil age in kyr (blue), Baffin Bay (red) and Greenland river (green) sediments[15] (leached (open red and blue symbols) and bulk (filled red and blue symbols) dissolutions). The Pb released by leaching of sediments is as enriched in radiogenic Pb as it is in young soils. **c**, Plot of ^{207}Pb/^{206}Pb against ^{204}Pb/^{206}Pb for BM1969.05 (red squares), ALV539 A (blue circles) and ALV539 B and C (blue squares). The ^{207}Pb/^{206}Pb versus ^{204}Pb/^{206}Pb data for both samples fall on statistically reasonable lines ($R^2 > 0.9$) whose intercepts give ages from 2.0 to 2.5 Gyr, in approximate agreement with model ages for large parts of the Canadian, Greenland and Scandinavian Shields. Also shown is the best-fit line (thick line) for leached Baffin Bay sediments (1.7 ± 0.4 Gyr)[15]. The similarity in the generated age provides support for the suggestion that crust arrays are produced by differential weathering (leaching) during soil formation.

orders of magnitude[4], predominantly as a result of the decline in availability of fresh and easily weatherable mineral surfaces[18]. The isotopic contrast between the labile Pb and its parent rock Pb is therefore inversely proportional to the age of the soil; the isotopic contrast is negligible for soil more than 300 kyr old and is proportional to the rate of chemical weathering of the soil. It has been strongly argued[18] that the processes observed in soils that developed in both old shield rocks in Wyoming and Mesozoic granitoids in the Sierra Nevada[12] are representative of glaciated silicate shield terrains. The glaciated terrains of the North American continent are dominated by such lithologies.

The extensive availability of fresh soil-parent material left behind by retreating continental ice sheets, in addition to the large amounts of melt water and warmer temperatures, would have caused chemical weathering rates to be highest during the early stages of interglacials[18]. This fresh soil-parent material, whether truly freshly generated or only freshly exposed to the agents of chemical weathering, would have yielded Pb with a relatively radiogenic isotopic composition[12]. As the soils aged over the interglacial the amount of weathering would have decreased[4], and there would have been a gradual decline in the radiogenic nature of the Pb released[12]. The output of a simple quantitative model (see Methods), showing the changes in the Pb isotope composition of the deep ocean that would have resulted from such a process, is compared with the measured data in Fig. 3.

This model, which successfully describes our Pb data (Fig. 3), also predicts the average age of soils in the glaciated regions of the North American continent and can therefore give some insights into the variability in chemical weathering rate by using a published relationship between soil age and cationic weathering flux[4]. The average weathering rate the model predicts for marine isotope stage 1 (0–11 kyr ago) is 32 mequiv m^{-2} yr^{-1}, which, for example, is similar to the modern average rate of about 37 mequiv m^{-2} yr^{-1} of the Slave province of Canada (calculated from ref. 19). The model allows us to estimate that, on average (excluding stage 1), 2.5 ± 0.6-fold more weathering occurs during warm interglacial periods than during glacial periods. This factor applies only to those regions that are glaciated or covered in periglacial sediment, which has been estimated to be about 25% of the continental landmass[20]. Scaled according to land area, our data indicate that globally, as a result of the abundance of

fresh soil-parent material, the average chemical weathering rate during interglacials may be about 20–50% higher than during glacials. Much higher rates are indicated during the very early stages of an interglacial (see Fig. 3). This estimate of the change in average chemical weathering rate is similar in magnitude to that permissible by the Sr isotope composition of marine carbonates[21]. Such a decrease in the flux of cations from the continents to the oceans during glacial times will be partly balanced by the exposure, by a fall in the sea level, of easily weatherable shelf carbonates, which is thought to enhance the cation weathering flux by about 25%[5,6]. The similar magnitude of these perturbations may serve to maintain a balance in the flux of cations to the oceans on short to intermediate timescales (10^3–10^6 years), providing an explanation for the lack of significant change in the calcium carbonate compensation depth in the world's oceans during glacial times[22] despite changes in the nature and location of chemical weathering[20] and calcium carbonate production[22]. However, the rapid increase in weathering rate and consequent flux of cations to the oceans after deglaciation may not be adequately balanced and provides a plausible explanation for the ocean-wide carbonate preservation event (a result of increased ocean alkalinity) centred on 9 kyr (ref. 23).

On longer timescales, and in the context of our model of oceanic Pb isotopes, the gradual shift to more radiogenic Pb values that occurred in both ALV539 and BM1969.05 about 2.5 Myr ago[24] (Fig. 2a) probably relates to an overall decrease in the average soil age in the glaciated regions of North America as glacial erosion gradually removed the preglacial regolith[25]. Preliminary *in situ* Pb data from these same crusts for the period before that highlighted here indicate that short-term high-amplitude changes in Pb isotopes are lacking before the mid-Pleistocene epoch. The gradual replacement of weathered Jurassic saprolites that previously blanketed the North American continent[25] by fresher material would have led to greater short-term variability in marine Pb isotopes and an overall increase in weathering rates[18].

It has been suggested that weathering rates approach a steady-state value of 1–5 mequiv m^{-2} yr^{-1} for soils older than about 150 kyr, a value that may be representative of rates before the onset of the Northern Hemisphere glaciation. The average weathering rate predicted by our model for the past 550 kyr is about 9 mequiv m^{-2} yr^{-1}, or about three times this value. As silicates predominantly underlie the Laurentide ice sheet[5] and the chemical weathering of silicates results in a net draw-down of CO_2, this enhanced silicate weathering, which occurs predominantly during warm interglacial periods, would increase the long-term draw-down of CO_2 and contribute to global cooling, acting as a strong positive feedback serving to promote further glaciation.

METHODS

Quantitative model of Pb isotopes in the deep North Atlantic. In the following the 'glaciated region' refers to those parts of the North American continent that, in the 550-kyr period modelled, are at some stage covered by ice. 'Non-glaciated' regions are those parts of the North American continent that have never been covered by ice. The proportion of the glaciated region covered by ice was assumed to vary linearly with $\delta^{18}O$ (ref. 26) between values of 0 (none of the glaciated region covered in ice) and 1 (all of it covered in ice) and the retreat and advance of ice sheets was simulated at 1-kyr resolution for the past 550 kyr. A linear relationship between $\delta^{18}O$ (which is predominantly ice volume) and the area covered by an ice cap is clearly an oversimplification but such a consideration is of only minor importance here. For each 1-kyr interval, the total area of glaciated region in front of the ice sheet at that time is split into age bins spaced at 1 kyr, corresponding to the time elapsed since it was last covered by ice.

The $^{207}Pb/^{206}Pb$ isotope ratio of pre-Quaternary Pb in the deep North Atlantic is about 0.825 (ref. 24). This presumably reflects the Pb released from the weathering of very old preglacial saprolites and thus the average isotopic composition of bulk rock Pb in the North Atlantic region. We have used this value of $^{207}Pb/^{206}Pb$ for 300-kyr-old soils, a value of 0.807 for the isotopic composition of the Pb released by zero-age soils[12] and a linear relationship between soil age and the $^{207}Pb/^{206}Pb$ ratio of weathered Pb between these two extremes[12]. The integrated isotopic composition of the entire area of the glaciated region in front
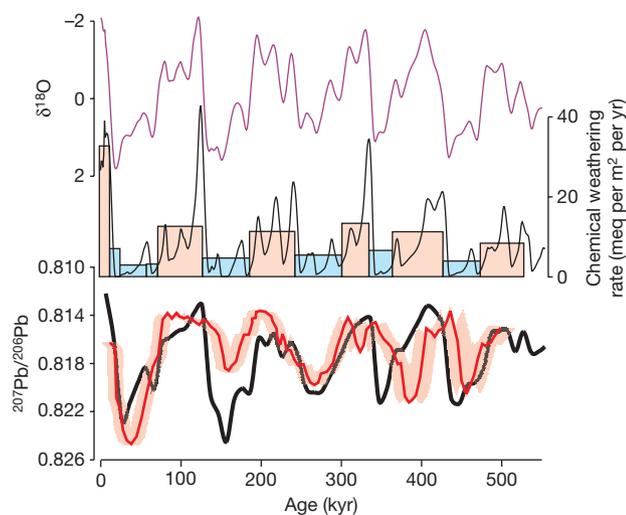

Figure 3 | Comparison between Pb isotopic data and output from a model based on variable glacial–interglacial weathering rates. Model Pb output (bottom, black line) and measured $^{207}Pb/^{206}Pb$ of BM1969.05 (red line) over the past 550 kyr with an error envelope relating to the uncertainty in the associated age model (Supplementary Methods). For the model weathering rate output (middle), bars are averages of the weathering rate during glacial (blue) and interglacial (red) marine isotope stages. The SPECMAP oxygen isotope stack is shown at the top[26]. See Methods for a more detailed description of the model.

of the ice sheet was then calculated for each 1 kyr interval. No variation in the amount of Pb released as a function of soil age was modelled, because this is not merited by the amounts of leachable Pb in soils of various ages[12]. The total flux of Pb, then, from the glaciated regions at any one time is purely a function of the fraction of the glaciated region exposed.

The processes described in ref. 18 and modelled above, operating on their own, result in much larger model glacial–interglacial swings in Pb than those observed, so we added a damping background Pb flux to the model. In the real world this is represented by the flux of Pb from non-glaciated regions to the deep North Atlantic. The quality of fit of the model to the real data is relatively insensitive to the magnitude of this flux, but the best fit is obtained when the flux from this source is about 0.3 times the flux from the glaciated region during an interglacial. The quality of fit of the model to the real data is much more sensitive to the isotopic composition of the background Pb flux and we gain some confidence from the fact that the best fit between model and data is obtained when its $^{207}Pb/^{206}Pb$ is the same as pre-Quaternary Pb in the deep North Atlantic, as recorded in long-term Fe–Mn crust records[24].

Although the fit of the resultant model output to the data is not perfect (for example, the depth of the Pb isotopic minima for marine isotope stage 6 and the less than 40-kyr discrepancy at stage 10/11), it does reproduce the major features of the data well and simulates the lows in $^{207}Pb/^{206}Pb$ associated with higher weathering rates and release of radiogenic Pb during interglacials.

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