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Oxygen and carbon isotopes of detrital carbonate in North Atlantic Heinrich Events

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Abstract

We report oxygen and carbon isotope results of bulk and detrital carbonate grains from the last glaciation at IODP Site U1308 (re-occupation of DSDP Site 609). Oxygen isotopic values of individual detrital carbonate grains from Heinrich events average -5.4‰±1.3‰, presumably reflecting values of limestone and dolomite derived from lower Paleozoic basins in northern Canada and northwestern Greenland. The $\delta^{18}O$ of bulk carbonate records the proportion of detrital to biogenic carbonate and $\delta^{18}O$ values decrease to -5 ‰ during Heinrich (H) events 1, 2, 4 and 5 relative to a background value of ~1 to 2‰ for biogenic carbonate. Bulk $\delta^{18}O$ values also decrease during H3 and H6 but only attain values of -1‰, indicating a greater proportion of biogenic-to-detrital carbonate. Carbon isotope values of detrital carbonate in Heinrich events average 0.2 ±1.2‰, and are not significantly different from biogenic carbonate. We suggest that oxygen isotope ratios of bulk carbonate are a sensitive proxy for recognizing detrital carbonate layers and should have widespread application for tracing Heinrich events throughout the North Atlantic ice-rafted-detritus (IRD) belt between ~40 and 55 °N.

Keywords: Heinrich events, oxygen isotopes, detrital carbonate

1. Introduction

Heinrich (1988) first described the occurrence of layers rich in ice-rafted detritus (IRD) and poor in foraminifera in sediment cores from the area of the Dreizack seamount in the eastern North Atlantic. Six Heinrich events were originally recognized and labeled "H1" through "H6" and are believed to have formed by massive discharges of ice bergs during surging of the Laurentide Ice Sheet in the region off Hudson Strait in northern Canada. The icebergs produced by these events traveled across the North Atlantic between ~40 and 55 ^{o}N, melted, and dropped their sediment load onto the seafloor. The diagnostic feature of Heinrich events is they contain detrital carbonate (limestone and dolomite) derived from large Paleozoic basins of northern Canada and northwest Greenland (Broecker et al., 1992; Andrews, 1998; Bond et al., 1999; Hemming, 2004 and references therein).

Many studies have focused on the silicate fraction of ice-rafted detritus (IRD) in Heinrich events to determine provenance (see Hemming, 2004 and references therein), but the detrital carbonate grains on which Heinrich (H) events are defined have received less attention (Parnell et al., 2007). The carbonate fraction of glacial North Atlantic sediments within the IRD belt (~40 to 55^{o}N) consists of a two component mixture of autochthonous biogenic carbonate (coccoliths and foraminifera) and allochthonous detrital carbonate (limestone and dolomite) (Balsam and Williams, 1993). Heinrich layers are rich in detrital carbonate and poor in biogenic carbonate and are characterized, therefore, by a high lithic-to-foraminifer ratio. We measured oxygen and carbon isotopic ratios of bulk sediments, foraminifera, and detrital carbonate grains from Heinrich events at IODP Site 1308 (re-occupation of DSDP Site 609) to determine if biogenic and detrital carbonate have distinct isotopic signatures that can be used to recognize detrital carbonate layers (i.e., Heinrich events) in sediment cores from the North Atlantic IRD belt.

2. Regional Setting

IODP Site U1308 represents a re-occupation of DSDP Site 609 (Fig. 1), which has played a prominent role in defining Heinrich events and correlating them to the Greenland ice cores (Broecker et al., 1992; Bond et al., 1992, 1993). It is located in the area of greatest accumulation of IRD in the North Atlantic during the last glacial period (Ruddiman, 1977). A high-resolution data set (1-cm sample spacing) was produced at DSDP Site 609 by counting foraminifera and lithics in the >150 μm fraction (Bond et al., 1992) and petrologic tracers (volcanic glass, hematite-stained grains, detrital carbonate) in the 63 to 150 μm fraction (Bond et al., 1999). DSDP Site 609 and IODP Site U1308 were precisely correlated to one another by matching gray scale signals obtained from core photographs in the upper 5 mcd (Fig. 2). Using this correlation, lithic data from Site 609 can be transferred to the composite depth scale of Site U1308.

3. Methods

For bulk stable isotope and weight percent carbonate analysis, ~1-cc of sediment was dried in an oven at 50^{o}C and the sample was ground to a homogenous powder. Bulk samples were reacted in a VG Isocarb carbonate preparation device with H_3PO_4 at 90^{o}C for 15 minutes which is sufficient to react both calcite and dolomite completely. Oxygen and carbon isotopes of evolved CO_2 gas were measured using a Micromass PRISM Series II mass spectrometer. All results are reported in parts per thousand (‰) relative to

PDB. Analytical precision (1-standard deviation) was estimated to be ±0.06‰ for $\delta^{18}O$ and ±0.04‰ for $\delta^{13}C$ by measuring standards (NBS-19, n=85) with each set of 36 samples.

Stable isotopes were also measured on individual detrital carbonate grains from each of the Heinrich events and the planktic foraminifer *Neogloboquadrina pachyderma* (sinistral) from the >150-µm size fraction. Detrital carbonate grains were leached in a weak acid to remove any carbonate adhered to the surface. Foraminifer tests were soaked in ~15% H_2O_2 for 30 min to remove organic matter. Detrital carbonate grains and foraminifer tests were rinsed with methanol and sonically cleaned to remove fine-grained particles. The methanol was removed with a syringe, and samples were dried in an oven at 50°C for 24 hr. The detrital and foraminifer calcite were loaded into individual reaction vessels and reacted with three drops of H_3PO_4 for 15 and 10 minutes, respectively, using a Finnigan MAT Kiel III carbonate preparation device. Isotope ratios were measured online by a Finnigan MAT 252 mass spectrometer. Analytical precision was estimated to be ±0.07‰ for $\delta^{18}O$ and ±0.05‰ for $\delta^{13}C$ by measuring eight standards (NBS-19, n=63) with each set of 38 samples.

We have used the H_3PO_4–CO_2 fractionation factor for calcite to correct all isotopic results, which will introduce error because the bulk and individual grains are probably composed of a mixture of calcite and dolomite, each with different phosphoric acid fractionation factors (Sharma and Clayton, 1965). Here we are concerned only with using relative variation in the $\delta^{18}O$ of bulk carbonate to recognize detrital carbonate layers at Site U1308, and are not claiming that the reported $\delta^{18}O$ values of the detrital or bulk carbonates represent accurate absolute values.

4. Results

Between 6 and 10 grains of detrital carbonate were measured individually for oxygen and carbon isotopes from each of six Heinrich events (Table 1). The mean and standard deviation of oxygen isotope values of detrital carbonate grains from all the six Heinrich events is -5.35 ±1.26‰. The mean for any single Heinrich events is not significantly different from other Heinrich events with the exception of H3 whose mean is significantly greater than Heinrich events 2, 4, 5 and 6 at 95% confidence level (Fig. 3). The mean and standard deviation of carbon isotope values of detrital carbonate grains from all the six Heinrich events is 0.23 ±1.23‰ (Fig. 4).

All six Heinrich events are marked by decreases in bulk carbonate $\delta^{18}O$ values; however, the decrease is less for H3 and H6 than for other Heinrich events (Fig. 5). During Heinrich events 1, 2, 4 and 5, bulk $\delta^{18}O$ decrease to approximately -5‰ and values are indistinguishable from those of detrital carbonate grains. During H3 and H6, $\delta^{18}O$ values decrease to only about -2‰. The $\delta^{18}O$ of *N. pachyderma* also decreases slightly during Heinrich events 1, 3, 4 and 5. The $\delta^{18}O$ of bulk carbonate outside the Heinrich events varies from ~1 to 2‰, and is closer to those of *N. pachyderma*.

Carbon isotopes of bulk carbonate are not significantly different during Heinrich events compared to intervening periods (Fig. 5). The $\delta^{13}C$ of individual detrital carbonate grains from Heinrich events overlaps values of both bulk carbonate and *N. pachyderma*.

5. Discussion

To the best of our knowledge, oxygen and carbon isotope values of detrital carbonate in North Atlantic Heinrich events have not been reported previously. Balsam and Williams (1993) measured oxygen and carbon isotopes of the sediment fine fraction in eight cores from the western North Atlantic. Cores closest to the North American margin had $\delta^{18}O$ values of fine fraction carbonate reaching -8 ‰ during the last glaciation. They interpreted these low values to indicate a source of diagenetically altered carbonate rock derived from glacial erosion.

Oxygen isotopic values of individual detrital carbonate grains from H events at Site U1308 average -5.4‰, which are comparable to published values for the lower Paleozoic (Veizer et al., 1999, 2004). The large variability in oxygen and carbon isotope values of individual carbonate grains reflects different mineralogies, diagenetic histories and/or multiple sources of detrital carbonate. For example, Heinrich events derived from Hudson Strait are dominated by calcite whereas those from Baffin Bay are largely dolomite (Andrews, 1988; Parnell et al., 2007). Measurement of oxygen isotopes in cores from the region of Hudson Strait and Baffin Bay would be useful to determine if these source areas have distinct oxygen and carbon isotope signatures. We have made no effort to distinguish different types of detrital carbonate for isotopic analysis in this study, but clearly this approach could be worthwhile in the future.

Oxygen isotope values of detrital carbonate are significantly lower (by 6 to 7 ‰) than those of biogenic carbonate and, therefore, are useful for identify detrital carbonate in North Atlantic sediment. The oxygen isotope record of bulk carbonate at Site U1308 are compared with Ca/Sr measured by scanning XRF in the same cores (Hodell et al., submitted) and with counts of detrital carbonate and lithics from Site 609 (Bond et al., 1992, 1993). Bulk $\delta^{18}O$ values decrease as percent detrital carbonate increases during each of the Heinrich events, and the relative magnitude of the signal is consistent because

$\delta^{18}O$ values decrease less for H3 and H6 when the percent detrital carbonate is lower (Fig. 6). The width of some events differ, however, in that H3 and H6 are wider for the $\delta^{18}O$ signal than in the percent detrital carbonate record and better match the peak widths of lithic grains/g. Variations in bulk $\delta^{18}O$ also coincide with changes in magnetic susceptibility and density at Site U1308 (Fig. 7), which have been used previously to identify Heinrich events (Robinson et al., 1995; Hodell et al., submitted).

Ca/Sr increases during Heinrich events 1, 2, 4 and 5 at Site U1308 because detrital carbonate has a greater Ca/Sr ratio than biogenic carbonate (Hodell et al., submitted). However, Ca/Sr does not show a similar increase associated with Heinrich events 3 and 6, whereas bulk $\delta^{18}O$ values distinctly decrease in these layers (Fig. 6). This may indicate that the amount of detrital carbonate is too low in H3 and H6 to be detected by Ca/Sr measurements obtained by core scanning XRF. Other studies have found that the flux of IRD is lower in H3 and H6 than other Heinrich events and the silicate fraction may have a different source at least in the eastern North Atlantic (Hemming, 2004 and references therein).

Our results suggest that bulk $\delta^{18}O$ is more sensitive than Ca/Sr for detecting small variations in detrital carbonate. Bulk $\delta^{18}O$ values only reach -2‰ during H3 and H6 compared to -5‰ during H1, 2, 4 and 5, indicating a lower proportion of detrital to biogenic carbonate in H3 and H6 compared to the other Heinrich events.

Oxygen isotope measurement of sediment bulk carbonate represents a new proxy for recognizing Heinrich layers with a high ratio of detrital to biogenic carbonate and possibly aiding in narrowing the source of detrital carbonate. We believe this sensitive technique will have widespread application in sediment cores throughout the North

Atlantic IRD belt (~40-55°N; Ruddiman, 1977). For example, it may be possible to use bulk carbonate $\delta^{18}O$ to track Heinrich events in more distal cores to the east of Site 609 (Thouveny et al., 2000).

In more ice proximal cores in the western North Atlantic basin, the contribution of detrital carbonate would be greater than at Site U1308. In glacial-aged sediment, for example, the $\delta^{18}O$ of fine fraction carbonate decreases in cores from east to west in the western North Atlantic reflecting a greater proportion of detrital carbonate in cores proximal to the American margin (Balsam and Williams, 1993). In the western basin, processes other than ice rafting may also transport detrital carbonate such as debris flows, turbidity currents and melt water plumes.

One of the objectives of IODP Expedition 303/306 was to study Heinrich events during older glacial periods of the Pleistocene. Hodell et al. (submitted) used Ca/Sr, magnetic susceptibility and density to identify detrital carbonate layers beyond the last glaciation (Hodell et al., submitted), but these proxies would be greatly enhanced by the addition of bulk carbonate $\delta^{18}O$ measurements.

The very low $\delta^{18}O$ values of detrital carbonate within Heinrich events also raise a cautionary note regarding proper cleaning of fine-grained carbonate from the tests of planktic and benthic foraminifera for stable isotope analysis. Any fine-grained detrital carbonate not removed from the inner chambers would lower $\delta^{18}O$ results, and could lead to an overestimation or erroneous interpretation of melt water during Heinrich events.

6. Conclusions

Heinrich events are marked by increases in detrital carbonate and decreases in biogenic carbonate. Because the $\delta^{18}O$ values of detrital carbonate in Heinrich events are ~6 to 7‰ lower than ambient biogenic carbonate, the $\delta^{18}O$ of bulk carbonate is a very sensitive indicator of the proportion of detrital to biogenic carbonate in north Atlantic sediments. This new proxy may have widespread application for tracing Heinrich events throughout the North Atlantic IRD belt and for recognizing detrital carbonate layers in older glacial periods of the Pleistocene.

7. Acknowledgments

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Figure Captions

Fig. 1. Location of Site U1308 (re-occupation of DSDP Site 609) in the central North Atlantic IRD belt.

Fig. 2. Gray scale records of Sites U1308 and DSDP 609 derived from core photographs. Data are plotted on the equivalent U1308 mcd scale after correlating Site 609 to U1308. Site 609 gray scale data from Bond et al. (1992).

Fig. 3 Mean and standard deviation (1σ) of $\delta^{18}O$ values measured in detrital carbonate grains at Site U1308.

Fig. 4 Mean and standard deviation (1σ) of $\delta^{13}C$ values measured in detrital carbonate grains at Site U1308.

Fig. 5. Oxygen and carbon isotope results of bulk carbonate (red lines), detrital carbonate grains (purple circles), and *N. pachyderma* (black lines) at Site U1308. Shaded areas indicate position of Heinrich (H) events. Bulk $\delta^{18}O$ values decrease during each of the Heinrich events as the proportion of detrital to biogenic carbonate increases. $\delta^{18}O$ values of bulk carbonate decrease to -5‰ during H1, 2, 4, and 5, equal to $\delta^{18}O$ values of detrital carbonate mineral grains. $\delta^{18}O$ values of bulk carbonate decrease to only -2‰ during H3 and H6.

Fig. 6. Ca/Sr (blue) and $\delta^{18}O$ of bulk carbonate (red) at Site U1308 and percent detrital carbonate (black) and lithic grains per gram (>150 μm) at Site 609 based on counts by Bond et al. (1993). Gray diamonds represent $\delta^{18}O$ of *N. pachyderma* (sinistral) and purple circles the $\delta^{18}O$ of individual detrital carbonate mineral grains picked from Heinrich events. Site U1308 was drilled at the same location as DSDP Site 609, and the two records were converted to a common depth scale by matching gray scale records from core photographs (Hodell et al., submitted). Ca/Sr shows peaks associated with H1, 2, 4, and 5 but not H3 and H6. The $\delta^{18}O$ of bulk carbonate decreases during each of the H events, but less so for H3 and H6.

Fig. 7. Ca/Sr (blue), $\delta^{18}O$ of bulk carbonate (red), magnetic susceptibility (green), and density (brown) at Site U1308

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Abstract

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Figure 1

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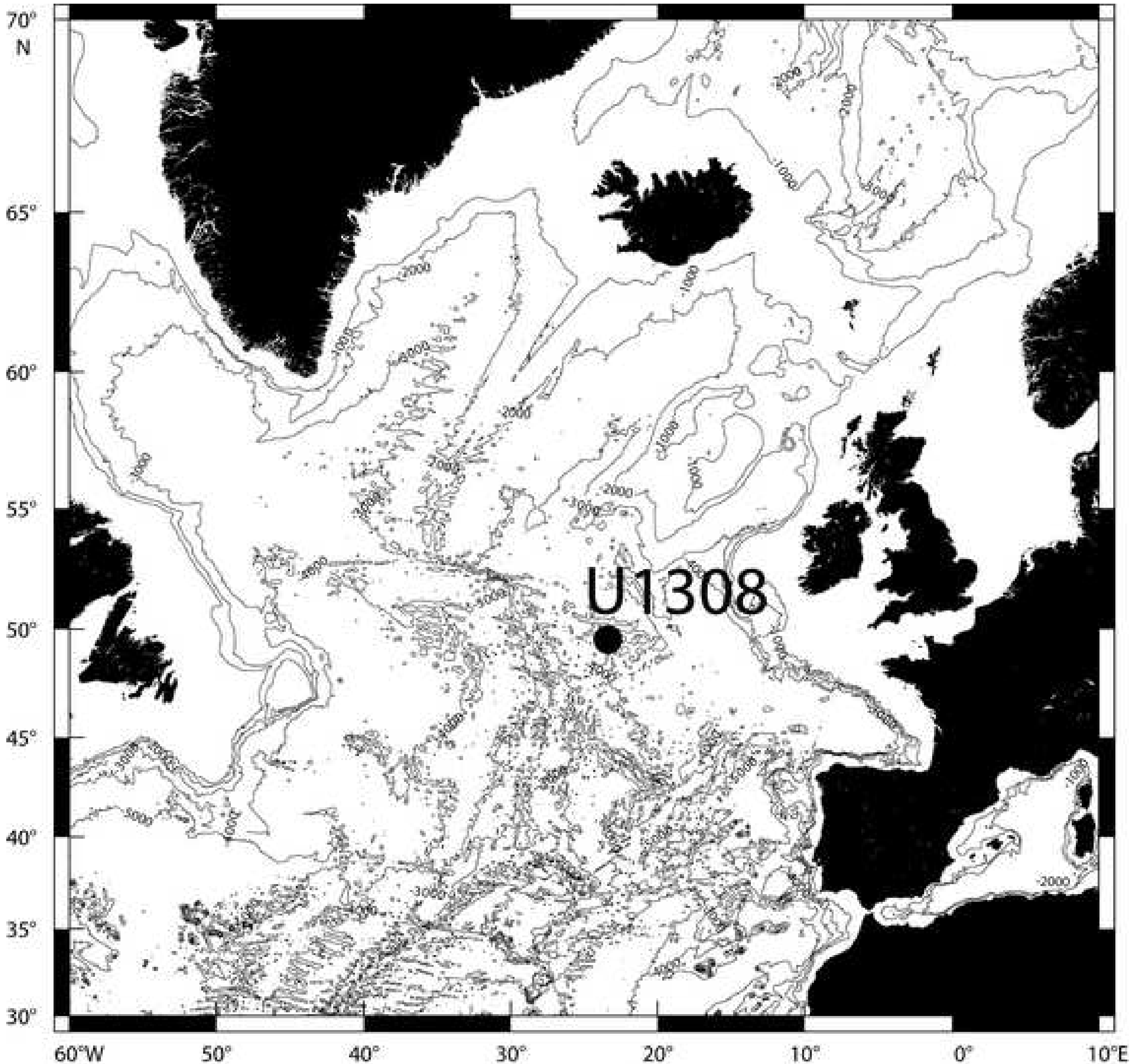

Figure 2
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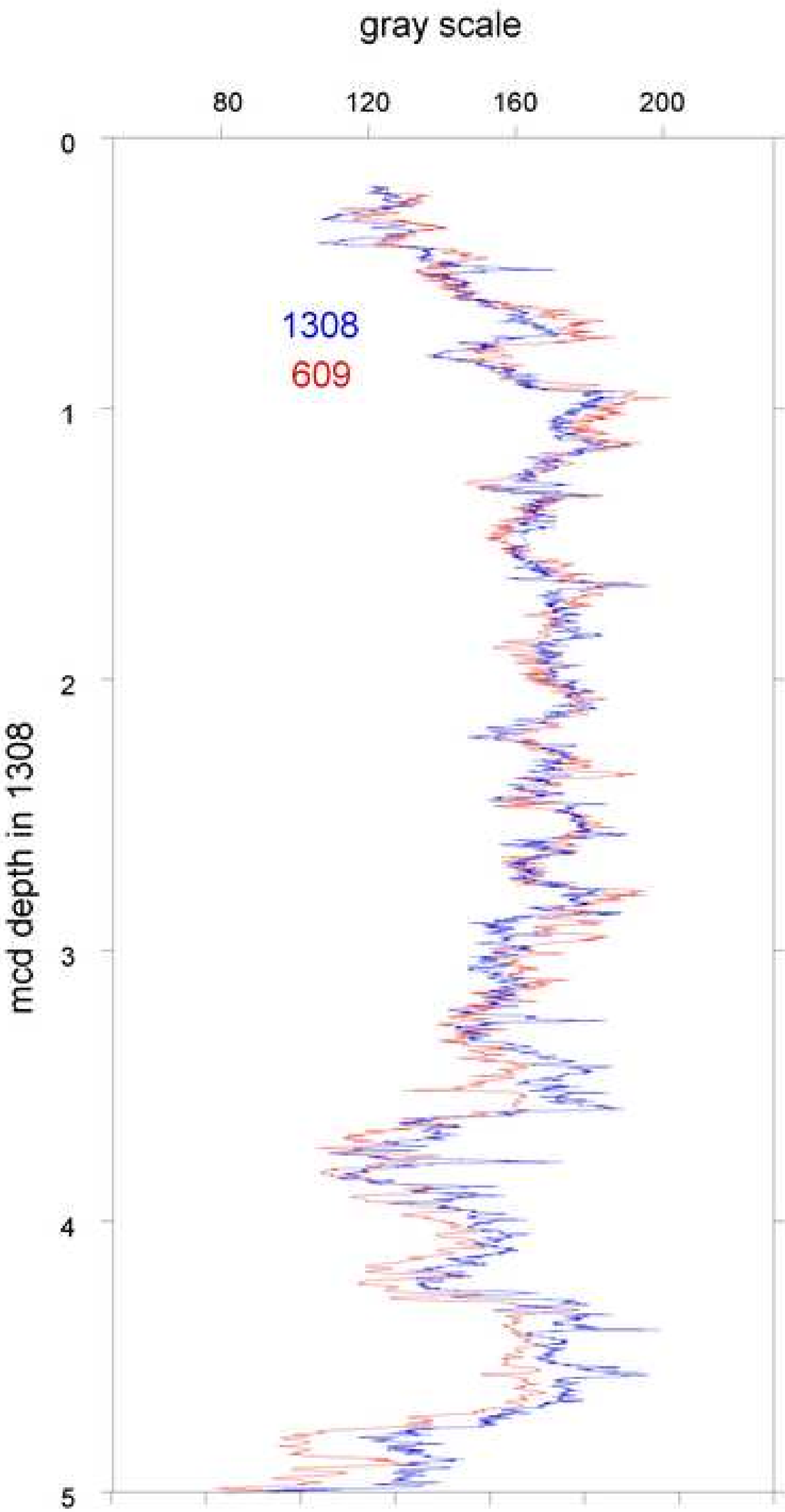

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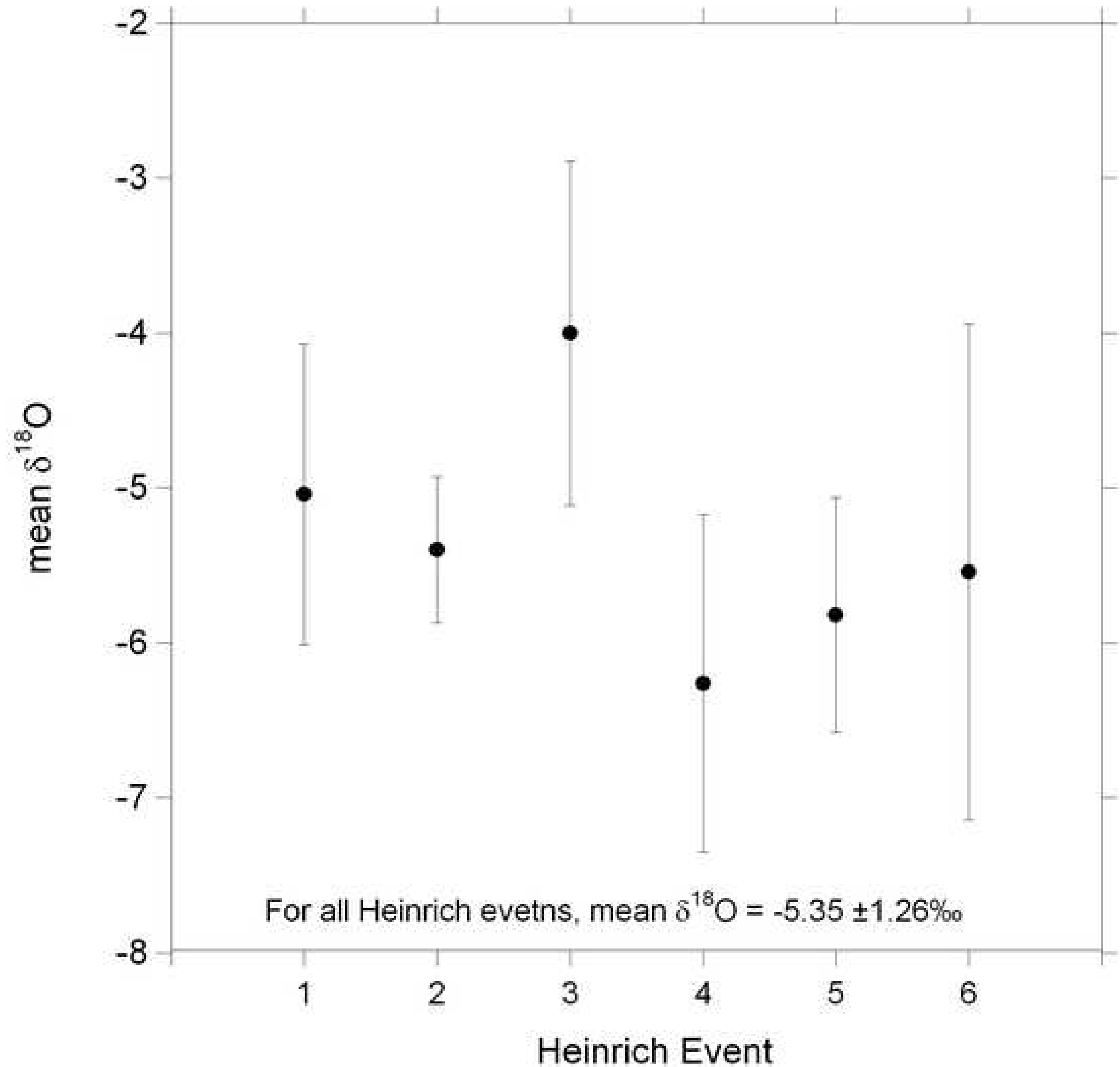

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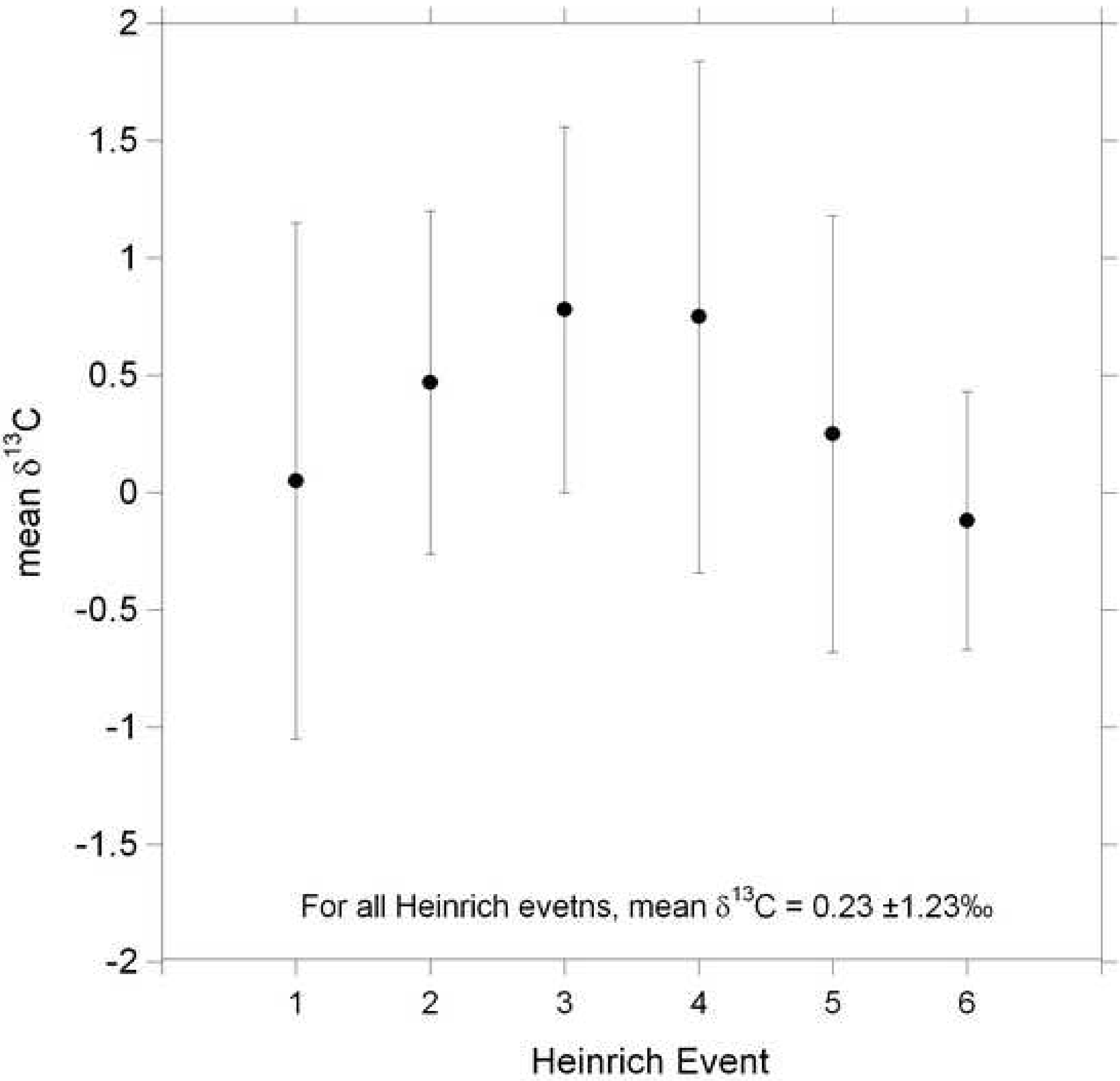

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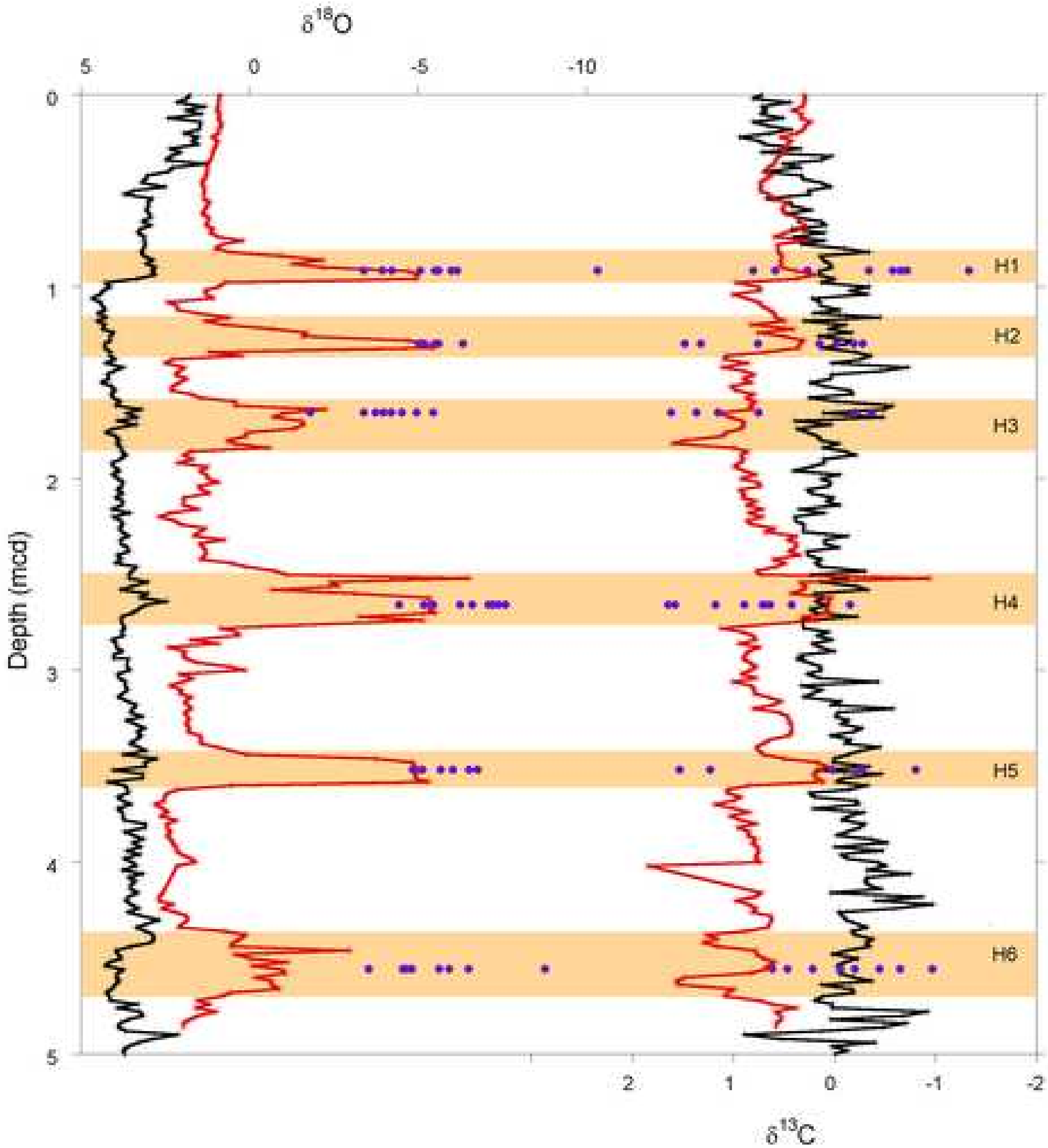

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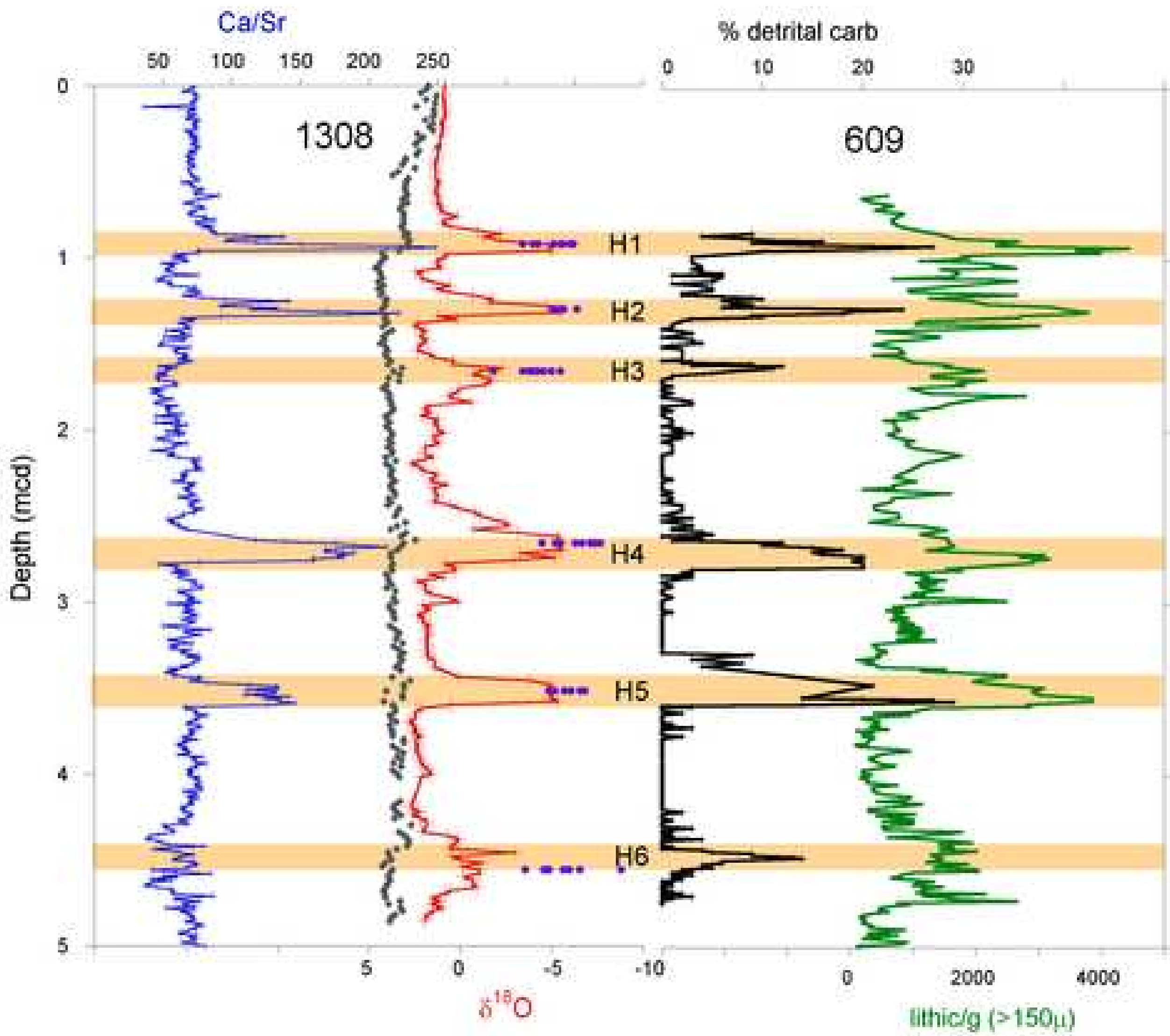

Figure 7
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