## Geochemical signals of diagenesis and Heinrich layers in NE Atlantic sediments of the last glacial period

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The eastern sector of the north Atlantic from 40-65°N, often termed 'the Ruddiman MacIntyre triangle', is an area where the deep-sea sedimentary record contains evidence of recent major changes in climatic conditions. Micro-palaeontological and sedimentological techniques have been used to chart the retreat of the surface-ocean polar front over the period 16-6 ky B.P., which includes the last deglaciation (Ruddiman and MacIntyre, 1981). More recently, there has been intensive study of 'Heinrich events'. These are discrete, coarse-grained, ice-rafted layers up to several cm thick found only in sediments of glacial times (i.e. oxygen isotope stages 2, 3, 4 and 6), which form at times of intense cold and may be symptomatic of global climatic changes (e.g. Bond et al. 1992, 1993; Grousset et al. 1993). Although the changing micropaleontology, sedimentology and mineralogy of the sediments in the Ruddiman-MacIntyre area has been investigated, however, relatively little attention has been paid to the geochemical consequences of the changing fluxes of sediment and sediment type in the area through time.

Kastenlot core CD63/9K (46°23.8'N, 12°32.8'W; 3849 m uncorrected), from the Armorican Seamount in the deep NE Atlantic south-west of the British Isles, exhibits enhanced concentrations of several elements at different levels in the sediments laid down at the height of the last glacial and during the subsequent deglaciation. In this core Holocene carbonate ooze/marl from 0-40 cm overlies a glacial clay which persists to the base of the core at 178 cm. A prominent feature of the core is a dark layer at 62.5-65 cm in the upper glacial sediments, identified as an Fe-enriched layer. Both pore water data gathered at the time of core collection and the onset of drab colours immediately below this layer indicated that the active oxic/post-oxic redox boundary in the sediments was located within this Fe-enriched layer. Such Fe bands are often observed in the sediments of the last glacial/ interglacial transition in several Atlantic localities.

Two types of elemental enrichment have been identified in the bulk sediment compositional data, primary Mg/Al ratio signals which mark the presence of three Heinrich events, and a diagenetic redox succession. Heinrich events are usually quantified by size separation investigations, but the bulk sediment Mg/Al ratio appears to be a good alternative geochemical method for their visualisation. Increases in the Mg/Al ratio in samples hosting the Heinrich events are caused by a contemporaneous increase in dolomite and decrease in phyllosilicates, and in this core all three events are < 6 cm thick. <sup>230</sup>Th<sub>excess</sub> profiling in and around the Heinrich layers demonstrates that accumulation rates were much higher than the glacial norm during the events. The radiocarbon ages estimated for Heinrich events (H1, 14.3 ky; H2, 21 ky; and H4, 35.5 ky; (Bond et al. 1992,1993)) also provide a chronology for the core, and indicate a considerably slower sediment accumulation rate (2.2 cm  $ky^{-1}$ ) during and after the glacial/interglacial transition than in glacial times (6.5 cm  $ky^{-1}$ ).

When expressed as elemental ratios against Al, the redox-sensitive elements Mn, Fe, As, Pb, Se, V and U in the bulk sediment all exhibit peaks in their depth profiles, at various depths and unrelated to those of the Heinrich events. The Mn peak is uppermost in core CD63/9K, above the coincident peaks for Fe, As and Pb, which in turn are above those for the near-coincident Se and V peaks, and U exhibits the deepest peak. All these diagenetic peaks are located between Heinrich events 1 and 2. These elements have been observed arranged in a similar depth sequence in previous work (Thomson et al. 1993), where the sequence was produced by a prolonged localisation of the oxic/post-oxic boundary. When the sediment accumulation rate decreased from glacial into post-glacial time in core CD93/9, the characteristic oxic depth maintained in the sediments in glacial times

would increase, and result in the development of a progressive oxidation front. The progress of this front would be a function of the amount of oxidation to be performed on organic carbon in the glacial sediments and on other reduced species such as  $Mn^{2+}$  and  $Fe^{2+}$  in the sediment pore waters. The fact that the oxic/post-oxic boundary is now located in the Fe-enriched band demonstrates that the peaks are still actively forming, and that steady state with Holocene conditions has not yet been achieved. The source of the reactive fractions of most of the elements which form these diagenetic peaks (Mn, Fe, As, Pb) is likely to be reductive dissolution from the carbonate-poor glacial sediments, although bottom waters are likely to have supplied U and V.

The Mn and Fe peaks are particularly large and well-separated in this core. Mangini et al. (1990) have proposed that Mn enrichments located in sediments of the last glacial/interglacial transition may be the result of climatic change. Their envisioned sequence of events is that precipitation of  $Mn^{2+}$  as  $MnO_2$  occurs when a glacial, sub-oxic deep ocean is reventilated at some time during the transition into interglacial times. The presence of Mn in a diagenetic sequence of redox-sensitive elements suggests that such an interpretation is not applicable here. The diagenetic Fe-enriched layer at this site also exhibits a stronger magnetic susceptibility signal than is observed for any of the Heinrich layers. Heinrich events are often most conveniently identified and correlated by their magnetic suceptibility signatures observed in whole-core magnetic profiling, so that diagenetic Fe presents an important complication for such core screening.

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