

## Constraining changes in ocean circulation modes and $^{14}\text{C}$ reservoir ages in the NW Atlantic between 35 and 15 ka BP

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The Atlantic Meridional Overturning Circulation plays a key role in the climatic system by redistributing heat and carbon throughout the ocean. Reconstructions of  $^{14}\text{C}$  concentrations revealed that large changes in the partitioning of radiocarbon among the main reservoirs on earth must have occurred in the past. Thus, significant effort went into the reconstruction of past ocean circulation and its control on the storage and release of  $\text{CO}_2$  as well as its heat supply to higher Northern latitudes.

In our study we focus on a deep sea core from the North-West Atlantic (ODP Site 1063, Bermuda Rise). This core displays very high sedimentation rates (in general  $> 20$  cm/ka), which minimizes bioturbation effects, allowing extraordinarily high time resolution. For the last glacial the  $\text{CaCO}_3$  content of this core preserved Heinrich and Dansgaard/Oeschger events. Linking the ODP Site 1063  $\text{CaCO}_3$  content to Greenland ice core  $\delta^{18}\text{O}$  allows constructing a  $^{14}\text{C}$  independent age model [1]. We compared sample ages derived from this model with the  $^{14}\text{C}$  content of monospecific planktonic foraminifers measured in 35 sub-samples between 15 and 35 ka BP.

The resulting ocean surface reservoir age (R) shows almost constant values ( $\sim 1200$  years) during the Last Glacial, while during Heinrich Events (1, 2, 3), R varied between 0 and 2500 years. Additionally, we compare the surface water reservoir age with  $^{231}\text{Pa}/^{230}\text{Th}$  and  $\epsilon_{\text{Nd}}$  values available for this core [2,3]. In this way, we provide for the first time a data set of three distinct proxies of ocean circulation co-registered from the same sediment core. Comparison of these proxies give evidence of highly variable patterns of ocean circulation during Heinrich Events, characterised by differences in circulation strength, water mass age and water mass provenance during different times of melt-water hosing in to the North Atlantic.

[1] Grützner, J. et al. (2002) *Marine Geology*, Volume 189, 2-23.

[2] Lippold, J. et al. (2009) *Geophysical Research Letters*, Volume 36, L12601.

[3] Gutjahr and Lippold (2011) *Paleoceanography*, Volume 26, PA2101.

## Behavior of REE in high-alumina alteration zones formed by weathering of felsic volcanic rocks

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Variation in mineralogy and whole rock chemistry of kaolinite deposits of the Carolina slate belt, USA, are used to study processes leading to remobilization, transport, and concentration of REE and other elements (e.g., Ti, Al, As, Se, Ga, Hf, Zr) during weathering. High-alumina alteration zones are hosted by felsic volcanic rocks of the Persimmon Fork Formation (PFF). The largest deposits (Haile and Brewer, SC) contain reserves of  $>650,000$  metric tons of clay formed by saprolitic weathering of crystal tuff (1). The 554 Ma tuffs have associated feldspar and sericitic alteration and contain epithermal, hot-springs-style deposits of Fe, Au, and other metals produced by acidic hydrothermal fluids that reacted with host volcanic rocks. Chemical weathering of the PFF since the mid-Paleozoic has strongly modified the major and trace element abundances and resulted in a high-quality white clay resource ( $\sim 35\%$  kaolinite,  $\sim 45\%$  quartz,  $\sim 20\%$  sericite) with accessory phases including reaction products of the original Ti, Al, and Fe-minerals, a distinctive trace element signature (e.g., Ga-4-36, Se-0-230, As-0-541,  $\Sigma\text{REE}\sim 30\text{-}200$  ppm) and diverse secondary minerals formed primarily by weathering of crystal tuff and siliceous-ferruginous sinter, including concretions (layered goethite-Al and kaolinite), Al-REE phosphates, gibbsite, hematite, lepidocrosite, and quartz.

Geochemical traverses across bedrock, saprolite, and clay bodies show that most of the alkali elements and Fe were removed from tuffs during weathering. In contrast, Th, Hf, and Zr contents were generally preserved. Chondrite-normalized REE patterns for variably altered volcanics fall into mineralogically distinct groups. The resultant clay rocks are LREE-enriched at  $\sim 50\text{-}100\times$  chondrite and have  $\text{Ce}/\text{Yb}_N$  of  $\sim 2.0$  to  $6.6$  and  $\text{La}/\text{Sm}_N = 1.99$  to  $5.6$ . The HREE portion of the pattern is typically flat and  $\sim 10\text{-}30\times$  chondrite with  $\text{Tb}/\text{Yb}_N$  of  $\sim 0.71\text{-}1.05$ . In general, negative  $\text{Eu}/\text{Eu}^*$  anomalies of  $0.62$  to  $0.75$  characterize the clay rocks. Fe-concretions in clay rocks are enriched by factors of  $50$  in Se and  $25$  in As ( $60\text{-}230$  ppm Se and  $11\text{-}511$  ppm As) and have  $\Sigma\text{REE}\sim 150\text{-}200$ . REE mobility did occur in the hydrothermally altered and weathered volcanic rocks; as a group the altered clay rocks and Fe-concretions (normalized to the mean value for unaltered PFF) show depletions in LREE, and slight enrichments in HREE. The changes in the bulk patterns can be explained by the presence of LREE-enriched and HREE-enriched minerals and reflect adsorption onto Fe-oxyhydroxides and secondary clay minerals, rather than precipitation of secondary phosphate. Behavior of other trace elements (As, Se, Ga), relative to the parent rock, is also predictable based on the dominant mineralogy of the residual host (clay rock, silicstone, iron oxide concretions and crusts). Elements such as Ga, Hf, and Zr are retained under a combination of acidic hydrothermal and saprolitic alteration processes that result in subtle REE mobility.

[1] Foley (2007) *23<sup>rd</sup> International Applied Geochemistry Symposium*, 50.