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The Geochemistry of a Relict Hydrothermal Deposit: Effects of Low Temperature Alteration

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The TAG hydrothermal mound at 26º08'N on the Mid-Atlantic Ridge is one of the largest known sulphide deposits on the modern seafloor. The episodic nature of the hydrothermal discharge exerts a cycle of mineral precipitation and dissolution, resulting in a complex assemblage of sulphides and the separation of minerals into distinct zones. A number of currently inactive mounds of similar sizes have been identified in the relict Alvin and Mir zones. During periods of hydrothermal quiescence these mounds undergo dissection by mass wasting, forming a blanket of partially oxidised sulphides and Fe-oxides. This study examines the fate of hydrothermal deposits after cessation of venting, which is crucial to our understanding of their impact on the ocean system and preservation in the geological record. A 228 cm long gravity core was recovered from the southern periphery of the Alvin zone. The metalliferous sediments were analysed for major elements (Al, Si, Fe, Mn, P, Cu, Zn, C and S), and for trace elements (V, Co, Au, Ag, Mo, Pb, U, REE). Concomitant porewater samples were analysed for metals (Fe, Mn, Cu, Zn, Mo, U) and major ions (SO_4^{2-}). Both the bulk sediment and the <2µm clay fraction were analysed for major elements and REE. At the surface the metalliferous sediments are capped by a ~50 cm thick layer of carbonate-rich sediments of dominantly pelagic origin, which grades into Fe-oxides at the base ($CaCO_3$ = 2-66%). A peak in solid phase Mn at ~30 cm marks the Mn^{2+}/Mn^{4+} redox-transition. Two distinct sulphide layers (50-70 cm and 170-228 cm), that were formed through mass-wasting from a nearby hydrothermal mound, contain dominantly pyrite and goethite with some chalcopyrite and sphalerite. The two layers are interbedded with a ~100 cm thick zone of Fe-oxysilicates, which contain up to 65% nontronite. In the upper sulphide layer the chalcopyrite has been almost completely re-mineralised to atacamite, a secondary Cu-chloride mineral. The atacamite occurs at the top of the upper sulphide layer and is interpreted to mark the extent to which oxygenated seawater has diffused into the sediments. Zn and Pb have been released from primary sulphide minerals in the upper sulphide layer and re-precipitated particularly in the intermediate layer. The effective separation of secondary Cu- and Zn-minerals into distinct zones is analogous to the zone-refining that has been described for the active TAG mound (Edmond *et al.* 1995). Co and Ag are not affected by diagenetic re-mineralisation, whilst some post-depositional uptake from seawater is evident for U, V and P. The dissolution of primary sulphide minerals may be the result of the acidic conditions that are generated *in situ* during the oxidation of pyrite, similar to the acid mine drainage that is commonly observed in mining and ore processing. Alternatively, re-mineralisation may have been driven by horizontally advected, reactive, low-temperature fluids during the later stage of hydrothermal activity in this zone. Mass balance calculations indicate that the diagenetic porewater flux of Mn from below the carbonate cap is insufficient to explain the observed peak in Mn-oxide. Low-temperature hydrothermal fluids might have acted as an additional source of Mn in the surface sediments. Nontronites are observed in the intermediate layer form by direct precipitation from hydrothermal fluids as they percolate through reducing sediments (Dymond *et al.*, 1980). Comparison of REE data for bulk sediments and clay phases indicates that the nontronite has gained Ce (Figure 1a) and is relatively enriched in heavy REE (Figure 1b). The inference is that that the fluid from which nontronite formed had only a small seawater component. Similar REE patterns were observed in pore fluids from the active TAG mound (Rudnicki and Mills, 1996) and in Mn-oxide crusts from the low-temperature zone on the eastern valley wall (Wells, 1998). Low-temperature fluids with an evolved REE signature caused post-depositional alteration of the sulphides and precipitation of hydrothermal clays in the sediments studied here. The nature of the diffused fluids is only poorly characterised, but their importance in the ore-forming process and alteration of hydrothermal deposits is increasingly being recognised (Mills *et al.*, 1996). The extent and chemistry of diffused fluids needs to be resolved in order to quantify their effects on the preservation of hydrothermal deposits and the chemical budget in the TAG hydrothermal field.

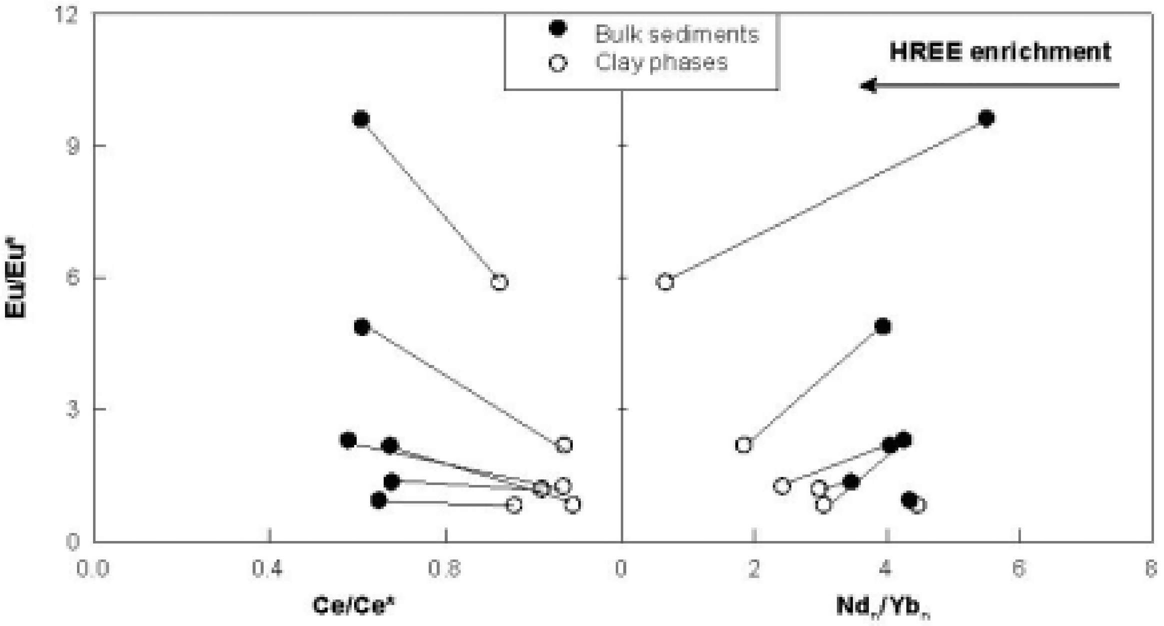

Figure 1: Comparative REE chemistry for bulk sediments and clay phases from the carbonate cap and the Fe-oxysilicate layer showing (a) the absence of significant Ce-anomalies, systematically decreased Eu-anomaly and (b) HREE enrichment in all clay phases relative to bulk compositions.

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