

Mineralogical and geochemical hydrothermal evidences on sediments from the serpentinite-hosted Saldanha hydrothermal field

Ágata S.C.M.A. Dias¹, Fernando J.A.S. Barriga^{1,2}

¹CREMINER, Faculdade de Ciências, Universidade de Lisboa, Portugal

²Dep. Geologia, Faculdade de Ciências, Universidade de Lisboa, Portugal

Abstract. Mineralogical and geochemical data of hydrothermal sediments collected from the Saldanha site are presented. The Saldanha hydrothermal field is located at the top of a serpentinized massif Mount Saldanha (MS), at a non-transform offset (NTO5) along the Mid-Atlantic Ridge (MAR), south of the Azores. It is one of the rare known sites where direct evidence of low-temperature hydrothermal activity has been provided by direct observation of hydrothermal fluid venting through small orifices in the ocean floor sedimentary cover. This study reveals that these hydrothermal sediments are highly “diluted” within dominant foraminiferal nanofossiliferous ooze and that the mineral assemblage of the hydrothermal component is characterized by sulphides, poorly crystallized Mn oxihydroxides, Mn brucite and hydrothermal clays. Sediments with a stronger hydrothermal component are located at the top of the mount, where hydrothermal activity was observed. Here the sediments are enriched in Cu, Zn and Fe sulphides, Mn-Mg oxy-hydroxides and putative mangano-brucite. Total geochemical analyses show that all sediments are enriched in elements such as Mn, Fe, Cu and Zn, derived from hydrothermal fluids, Mg, P and V, scavenged from seawater, and Ni, Cr and Co derived from ultramafic rocks. Sediments collected next to the vents are particularly enriched in Mn. The geochemical data together with the observed mineral assemblage and the geological setting suggest that the hydrothermal fluids have much higher temperature than those measured at the escape orifices (max. 9°C), and a strong enrichment in Mg, mainly at the top of the mount, agrees with extensive mixing of the hydrothermal fluid with unmodified seawater.

Keywords. Hydrothermal sediments, low temperature vents, ultramafic-hosted hydrothermal field, Mount Saldanha

1 Introduction

Mount Saldanha (MS) is a modern seafloor hydrothermal field located at the Mid Atlantic Ridge (MAR), south of Portugal's Azores Archipelago (N36°34'; W33°26'), between the Pico Fracture Zone (PFZ), 38°N, and the Oceanographer Fracture Zone (OFZ), 35°40'N (Fig. 1A). This region of the MAR is composed of six left-lateral non-transform offsets (NTOs) characterised by peridotite massifs detached from their segment flanks and are commonly associated with hydrothermal vents (e.g. German et al. 1996). The exposure of ultramafic rocks is consistent with low magma budgets, relatively thin crust and irregular faulting patterns (Gràcia et al. 2000).

Mount Saldanha (MS) is located on NTO5, between the FAMOUS and AMAR second-order segments (Fig. 1B),

and consists of a faulted massif detached from its segment flanks, almost parallel to the ridge segment. It is composed mainly of ultramafic and gabbroic rocks and a strong methane anomaly within the overlying water column (Charlou et al. 1997). At the summit of MS, hydrothermal fluid was directly observed to be venting through centimetric orifices in the ocean floor sedimentary cover over an area of approximately 400 m² and at depths between 2200 and 2220 m.

Peridotites, serpentinites and steatites were identified. *In situ* temperature measurements of the discharge fluid at the hydrothermal orifices revealed maximum fluid temperatures of 9°C, whereas the adjacent seawater at the seafloor was at around 2°C (Barriga et al. 2003). The source of the heat at the MS hydrothermal field has been suggested to be derived from the exothermic serpentinization process (Barriga et al. 1998).

Heat balance models by Lowell and Rona (2002) suggest that heat released upon serpentinization of peridotites can explain hydrothermal venting only at temperatures ranging from a few degrees to a few tens of degrees Celsius, as happens at MS. Bach et al. (2002) reached the same conclusion after calculating that the serpentinization process can heat circulating water to 25–150 °C.

Unlike many other systems sampled so far along the MAR, at MS the hydrothermal discharge takes place through the sediments. Here the hydrothermal fluids react not only with the underlying crystalline rocks but also with the sedimentary cover.

2 Sampling and analytical methods

Hydrothermal sediments were collected at MS, during the Saldanha (Barriga et al. 1998), Seahma (Barriga et al., 2008) and CD167 (Sinha et al., 2005) missions by push- and gravitic-cores. Cores were on average 15cm long and were collected between 2200 and 3000m depth. The samples were examined by several different analytical techniques: mineralogy by optical microscopy, X-ray diffraction (XRD) and electron microprobe; bulk analysis by ICP, ICP-MS and INAA. Mn oxy-hydroxides were also examined by scanning electron microscopy (SEM).

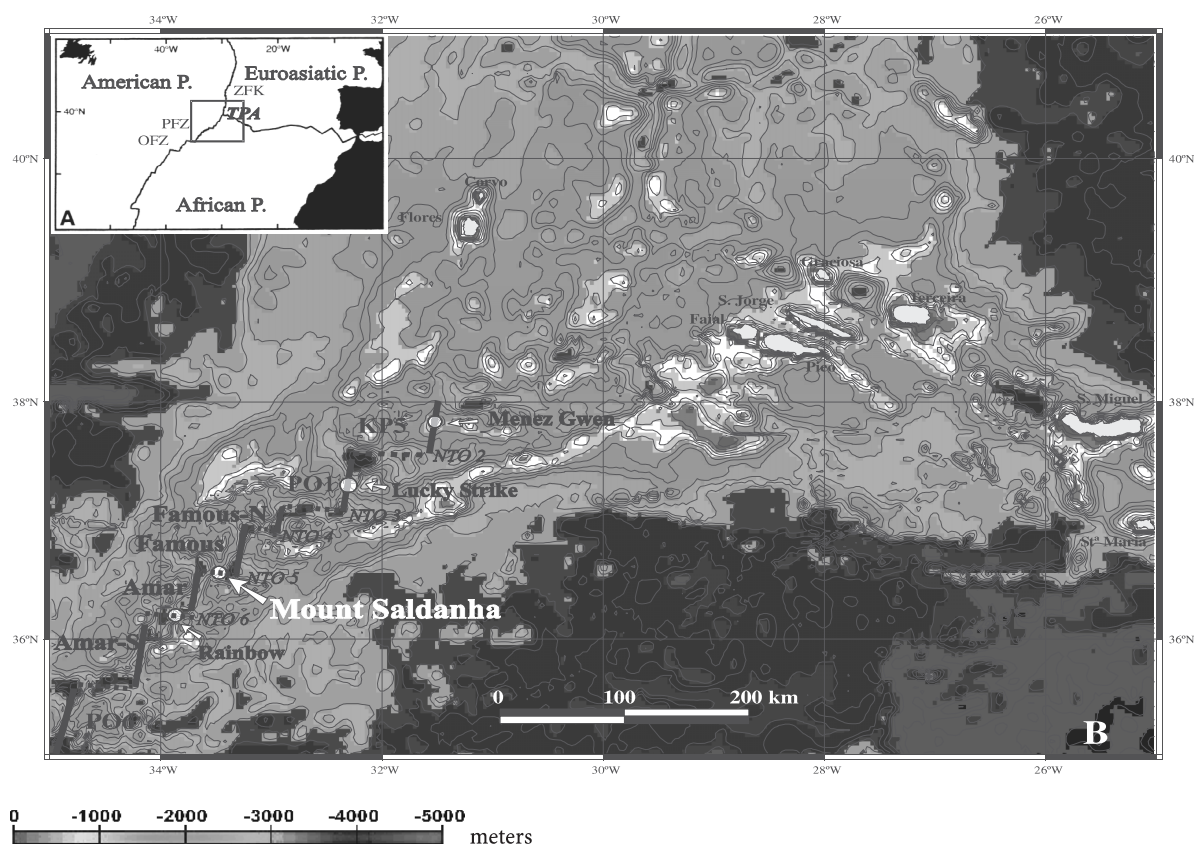


Figure 1: (A) Area between Pico Fracture Zone (PFZ) and Oceanographer Fracture Zone (OFZ) along the Mid-Atlantic Ridge, south of Azores Triple Junction (TPA); (B) relief map showing the location of Mount Saldanha at a non-transform offset (NTO5) between FAMOUS-S and AMAR segments

3 Results

3.1 Mineralogy

At the top of MS the sediments are covered by a Mn-oxides crust (Fig. 2A) that forms a millimetric cap poked by millimetric holes interpreted as micro-chimneys. XRD and SEM analyses of these crusts revealed that the interior layers consist of todorokite (tk) and/or birnesite (br) and that columnar vernardite (vr) grows in the outer massive layers, exhibiting elongated structures (Fig. 2B) formed by spheroids with honeycomb textures.

Microprobe analyses of Mn oxy-hydroxides display a low content in minor elements, a typical feature of hydrothermal origin, a large variation of MnO_2 , MgO and FeO wt% and a strong substitution of Mn by Mg in the oxides structure. More reflective minerals of these oxy-hydroxides show compositions similar to tk and/or br while less reflective minerals show a vr composition. In close association with these oxides, at the top of the mount, an uncommon and transparent mineral was identified (Fig. 2B and 3A). Chemical analyses of these crystals show an average of MnO and MgO of 22.6 and 41.6 wt%, respectively, and low totals (range:

58.8–71.7%). The small size and scarcity of the crystals precluded an XRD investigation. The mineral is most probably manganobrucite, an extremely rare, poorly known variety of brucite with $(\text{Mg}, \text{Mn}) (\text{OH})_2$ as its ideal formula.

MS sediments are mainly foraminiferal nanofossiliferous ooze (>80%) with hydrothermal precipitates and small fragments of lithoclasts and minerals from the underlying rocks (serpentinites, steatites and basic rocks). Ore microscopy and microprobe studies confirm the presence of fine-grained pyrite and isocubanite disseminated within sediments collected near the vent area. Sphalerite was only found in sediments collected at the top of the mount. Here tubular millimetric structures formed by isocubanite surrounded by sphalerite interpreted to be micro-chimneys were found (Fig. 3B) X-ray diffraction also suggests the presence of smectite-chlorite and nontronite. Putative nontronite (Al-poor Fe-smectite) is particularly abundant in samples collected near the hydrothermal orifices. Experimental data on nontronite synthesis (Harder, 1976) suggests that the solution from which this mineral forms has a low temperature (3 to 29°C), nearly neutral pH (7 to 9) and is slightly reduced ($E_h = -0.2$ to -0.8). At MS the presence of sulphide minerals and nontronite suggest that the hydrothermal fluids

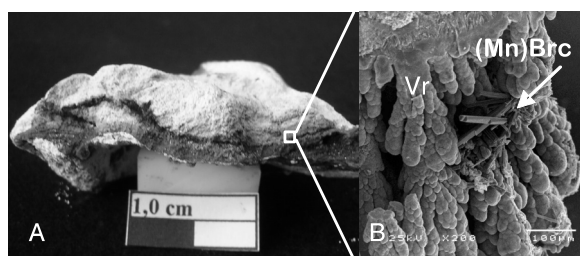


Figure 2: (A) Black-layered Mn-rich crust; (B) SEM image of Mn oxy-hydroxides elongated structures and Mn-brucite (Mn-brc).

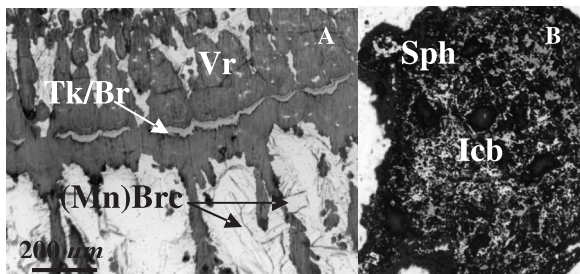


Figure 3: Photomicrographs of polished sections of: (A) poorly crystalline Mn-oxides minerals. High reflectance bands are formed by Todorokite/Birnessite (Tk/Br) and elongated structures, comprise the poorly crystalline phase identified as vernadite (Vr). Transparent fine crystals of Mn-brucite (Mn-brc) grow into open spaces at poorly crystalline Mn-oxides; (B) isocubanite surrounded by sphalerite.

have much higher temperatures than those measured at the vents (max. = 9°C). The low measured temperatures of the hydrothermal fluids are probably a consequence of cooling effects during conductive circulation and of extensive mixing with seawater in the discharge areas.

3.2 Bulk analyses

Bulk geochemical analyses show that MS sediments have high Ca and C concentrations that are in agreement with the carbonate content (average Ca = 37.6% and C=11.6%). The lowest concentration of Ca was found in a hydrothermal sediment collected at a venting orifice (Ca = 28.7% and C = 9.1%). The concentration of Mn and Mg was also higher in sediments collected near the hydrothermal vents (Mn = 3.2%; Mg=4.2%) in comparison with the remaining MS samples (average Mn = 0.3% and Mg = 0.7%). The higher Mg enrichment at the top of the mount suggests a more intense mixing of seawater with hydrothermal fluids in this area. In contrast, the Mn enrichment is derived from the hydrothermal fluids and was most visible in the hydrothermal orifice samples.

When MS sediments were normalized to pelagic sediments, enrichments in P, V, Mn, Fe, Cu and Zn were observed, revealing a clear hydrothermal signature, especially in samples from the top of the mount where Mn is particularly high. A correlation between Fe+Cu+Zn and

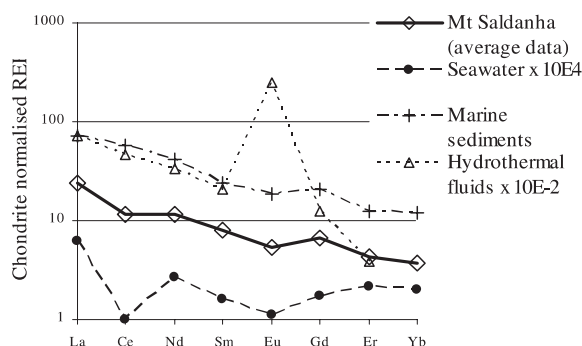


Figure 4: Chondrite-normalized REE patterns

S concentration ($r = 0.66$; $N = 14$; $p < 0.01$) confirms that these metals are present as sulphides.

High abundances of Co, Cr and Ni are likely to be due to the presence of ultramafic rocks in the sediments. Indeed, the Cr/Al and Ni/Al ratios are higher at sediments where larger amounts of ultramafic rocks were found, reflecting the presence of an ultramafic component.

Chondrite normalized REE show similar patterns (Fig. 4). They exhibit a depletion of HREE and negative Eu and Ce-anomaly (averages $Ce/Ce^* = 0.61$ and $Eu/Eu^* = 0.73$). Comparing our REE data with seawater, pelagic sediments and hydrothermal fluids from Rainbow, it is clear that MS sediments have a negative Ce anomaly, less pronounced than seawater, and lack the positive Eu anomaly of the hydrothermal fluids, presenting instead a slightly negative Eu anomaly as in seawater and pelagic sediments. Michard (1989) shows that hydrothermal fluids below 250°C are characterized by negative Eu anomalies, in agreement with MS fluids. However, the possibility remains that at greater depths the fluids are warmer and are cooled when mixed with unmodified seawater nearer the surface. The REE patterns of MS sediments clearly show that seawater and the dominant pelagic fraction overprint the REE hydrothermal signature.

4 Summary and conclusions

The hydrothermal component is strongly “diluted” in a pelagic carbonate ooze and is dominated by sulphides, Mn oxides, Mn-brucite and clay minerals. The strongest hydrothermal evidence was registered at the top of the mount where hydrothermal activity was observed.

The Mg enrichment, together with the occurrence of Cu, Zn and Fe sulphide minerals, may be explained by the interaction between seawater percolating down into the sediments with the upwelling modified seawater. Metal enrichment in sediments is either directly hydrothermally sourced (e.g., Fe, Mn, Cu and Zn) or scavenged from the seawater (e.g., V and P). Some samples also show a Co, Ni and Cr enrichment derived from ultramafic fragments. The REE pattern shows that seawater is the dominant fluid in the

sediments which is consistent with the dominant pelagic ooze fraction.

The mineralogical and geochemical data from MS sediments suggest an environment of deposition with percolation of low temperature hydrothermal fluids through pelagic sediments. However, these fluids seem to have a much higher temperature than those measured at the escape orifices, and a strong enrichment in Mg, mainly at the top of the mount, agrees with extensive mixing of the hydrothermal fluid with unmodified seawater.

Precipitation of hydrothermal minerals is likely to occur mainly inside sediments where a Mn-Mg oxidized cap prevents direct contact of the evolved hydrothermal fluid with the oxidizing unmodified seawater. Similar caps were postulated for the formation of sub-seafloor massive sulphide mineralization, both modern and fossil.

These data, together with the lack of a magmatic heat source, the presence of peridotite altered to serpentinites and steatites, and the occurrence of a strong methane anomaly within the overlying water column, agree with the system being driven mainly by heat released during the serpentinization process. Additional geophysical and geochemical data are needed to understand the heat sources of these systems.

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