International Research: **Island arc/BAB**

Submarine Hydrothermal Mineralisations and Fluids off the Lesser Antilles Island Arc – Initial Results from the CARIBFLUX Cruise SO 154

P. Halbach[1], H. Marbler[1], D.S. Cronan[2], A. Koschinsky[1], E. Rahders[1] and R. Seifert[3]

[1] *Freie University of Berlin, Department Geochemistry, Hydrogeology, Mineralogy, Berlin, Germany*
[2] *T.H. School of Environment, Earth Sci. and Eng., Imperial College of Sci., Tech. and Med., London, UK*
[3] *University of Hamburg, Institute of Biogeochemistry and Marine Chemistry, Hamburg, German*

Introduction

In comparison with other island arcs such as those in the Mediterranean Sea and SW Pacific, there have been only few studies of submarine hydrothermal mineralisations in the Caribbean island arcs. Kang (1984) described some hydrothermal manganese deposits from the region and Polyak *et al.* (1992) reported on a hydrothermal water column anomaly between Montserrat and Guadeloupe. More recently, Johnson & Cronan (2001) have reported considerable metal enrichments in hydrothermal fluids and metalliferous sediments off the central Lesser Antilles volcanic arc. The elements variably enriched in the fluids as a result of the hydrothermal activity are Fe, Mn, As, Si, B, Li and in the sediments are Fe, P, Mo, As, Sb, Hg, Cu and Pb. Variations in the concentrations of these elements in both fluids and sediments along the arc were thought to result from a number of factors, the most important of which is the stage that each island's volcano has reached in its eruptive cycle.

In order to investigate submarine hydrothermal mineralisation off the Lesser Antilles in more detail, a research cruise (CARIBFLUX) was carried out from January 15 to February 8, 2001, with the German research vessel *"R/V Sonne"* (SO 154). The main objectives of this cruise were to carry out measurements and water sampling in the water column and the near-bottom water layer as well as the study of local tectonics and the recovery of hard rock and sediment samples to look for indications of recent to subrecent submarine hydrothermal activity in the area of the Lesser Antilles island arc. The western slope of the arc was selected as the main target area since this area has many nearshore shallow water thermal springs (Johnson and Cronan, 2001).

Major target areas were the Kahouanne Basin and the Montserrat Ridge S and SW of the island of Montserrat, the area W of Dominica, St. Lucia and the Kick'em Jenny submarine volcano NW of Grenada (Fig. 1).

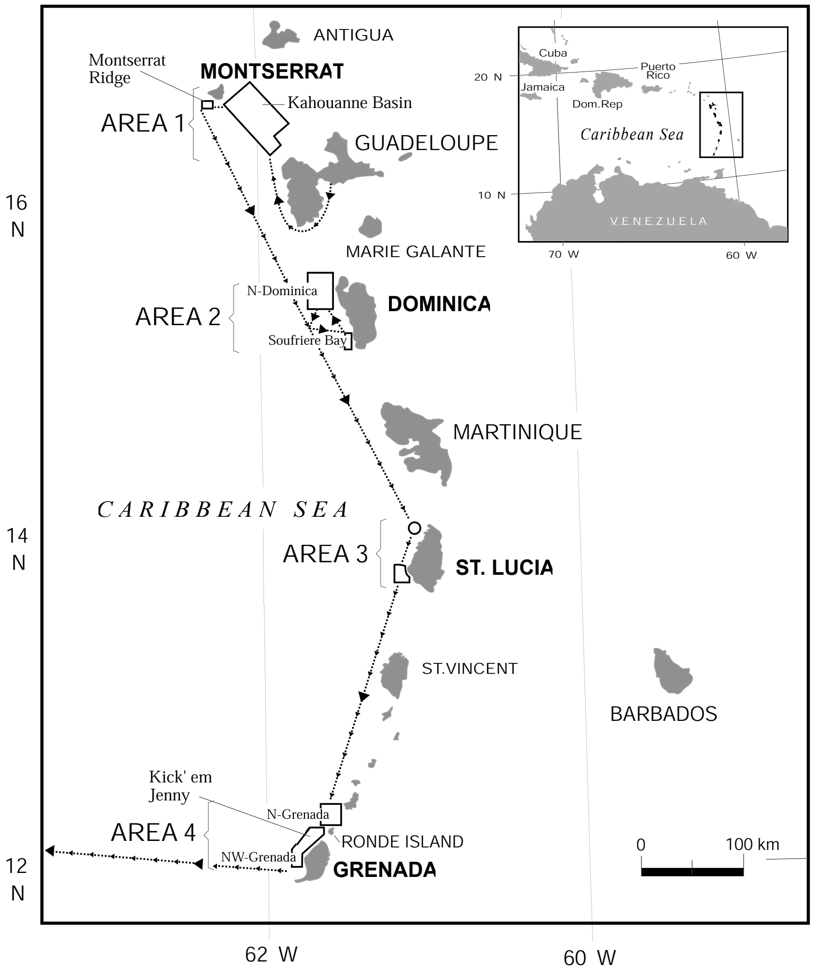

Figure 1. Map of the Lesser Antilles with cruise track and target areas.

Kahouanne Basin

Sample locations in the deepest part of the Kahouanne Basin and close to the Shoe-Rock-Spur (SRS) fault zone (western margin of the basin) were chosen. Methane concentrations in water samples in that area were generally below 3.5 nmol l^{-1}, and values exceeding 1.5 nmol l^{-1} were restricted to the upper 400 m of the water column. Anomalous Zn concentrations in the lower water column (earlier described by Polyak *et al.,* 1992) could not be confirmed.

Sediments contained a few pyrite and chalcopyrite grains, rarely nontronite was found in the southern Kahouanne Basin, and in one dredge haul Mn-crusts of thicknesses up to 6 cm were sampled. This pointed to subrecent hydrothermal activity in this region: further dredge sampling led to the discovery of an inactive hydrothermal site on a small plateau in the upper part of the SRS fault zone. These observations and samplings suggest that a young massive sulphide deposit may exist beneath the sea floor. The post-cruise detailed geochemical and mineralogical studies of the manganese crusts, the nontronite samples and the gossan fragments support this in certain respects (*e.g.* high Pb-values in certain Mn-oxide-layers of the crusts).

The nontronite fragments are of dark greenish to orange/reddish colour (in the upper oxidised part) with thicknesses up to 10 cm. Beside the predominant iron clay mineral nontronite occur llite, muscovite and small amounts of calcite. The content of total Fe (bulk) is up to 18 wt.% with depleted Mg, Ca and Al contents.

In the "gossan" fragments the values of total Fe reaches 17 wt.%. The Mn contents are up to 6.5 wt.%, which is relatively high for this type of rocks. Values of trace metals including Ni, Pb, Zn and V are relatively low and range from 160 up to 300 ppm. The mineral composition of these samples includes iron minerals such as goethite (also a small amount of hematite), nontronite, aragonite and a low content of quartz and manganese oxides. No secondary Cu or Pb minerals were determined.

Montserrat Ridge

At the Montserrat Ridge, again no clear indications of present hydrothermal activity were found in the water column. Hydrothermal Mn crusts up to 27 cm thickness were dredged, and Mn-cemented ashes are abundant along the ridge. The crusts from the Montserrat Ridge are unique and are described here for the first time from this part of the Lesser Antilles Island arc. They might have the function of a cap rock above a sulphide deposit.

Within the Mn crusts massive layers occur which show very heterogeneous mineralogic compositions. Manganese minerals including todorokite, birnessite and psilomelane occur as thin layers (up to 7 mm) alternating with layers (up to 2.5 cm) of light calcitic and aragonitic sediments and layers of sediments (up to 1.5 cm) with a manganese cement in the outer parts. Within the crusts appear metasomatic replacements of the limestone, including abundant fossil shells as well as irregular enrichments of nontronite and other clay minerals. The Mn contents for single layers can reach 55 wt.%. The Mn/Fe ratio is very high (up to 118) suggesting little or no input from normal seawater. The contents of most trace metals (Ni, Zn, Pb and Co) are very low (Table 1) and the concentrations of the rare earth elements are less than 10 ppm. The outer layers and some internal layers of the crusts with distinct petrographical and geochemical compositions indicate that the crusts precipitated from distinct hydrothermal episodes and are not a product of continuous deposition.

West of Dominica

Near-shore investigations of Soufriere Bay at the southern tip of Dominica showed that a supposed water-covered continuation of a hydrothermally active caldera, which occurs on land, does not exist. Off NW Dominica, five seamounts were investigated. The older ones are

Table 1. Chemical composition of manganese crusts

sample		18cd	52cd-a	52cd-b	83cd
W.depth	m	1144	950	950	1252
Fe	wt%	5,15	0,64	3,82	8,15
Mn	wt%	40,8	55,3	29	23,6
Al_2O_3	wt%	5,76	1,98	2,44	8,3
MgO	wt%	1,58	3,42	3,23	3,95
CaO	wt%	2,15	6,7	7,67	6,07
Cr	ppm	9	13	4	19
Cu	ppm	59	114	149	226
Ni	ppm	57	308	714	657
Zn	ppm	53	197	271	298
Ti	ppm	864	457	1140	1830
Co	ppm	21	26	345	67
Mo	ppm	53	360	317	350
Li	ppm	17	66	-	250
Pb	ppm	140	11	1420	9

Sample description. 18cd: manganese cemented sediments (Kahouanne Basin); **52cd:** massive crust, **-a:** inner Mn oxide-layer, **-b:** outer Mn oxide-layer (Montserrat Ridge); **83cd:** incrustation of volcanic rock (north of Dominica). Data from XRD and ICP-OES

International Research: **Island arc/BAB:** Halbach *et al.,* cont...

covered by Mn-oxides, and brecciated material often contained barite. Of particular interest are andesitic breccias cemented by hydrothermal manganese-oxyhydroxides. Methane concentrations in the water column were below 3.0 nmol l^{-1}, with highest concentrations in the biologically influenced upper water body, while in deeper water 1 nmol l^{-1} was not surpassed. However, further water analyses indicated local enrichments of reduced Cr species and Zn, which may indicate hydrothermal contributions. The highly sensitive determination of Cr species has been shown to be an effective means to trace hydrothermal sources (Sander and Koschinsky, 2000) because the hydrothermal Cr(III) signal is stable in the water column. However, the various measurements revealed a strong variability, probably caused by strong local variabilities in oceanographic parameters and possibly several small hydrothermal sources. As hot springs are known to exist along the coast and offshore Dominica (Johnson and Cronan, 2001), we assume that the signals we identified are derived from various fluid sources at different water depths off Dominica.

West of St. Lucia

Enhanced methane concentrations up to 13.8 nmol l^{-1} were found in the St. Lucia Bay at water depths between 50 and 100 m. Methane data correlate with a similar depth profile of Cr(III) and a maximum of Cr(III) at the same depth. This input of reducing waters can probably be related to the hydrothermal springs at the coast of the bay. No hydrothermal solid samples were recovered.

Kick'em Jenny

Enrichments of reduced Cr species and of zinc were identified in many water column profiles throughout the area; these enrichments mostly coincide with maxima of methane and can be attributed to the influence of submarine hydrothermal springs. The valley south of the volcano contains small, step-like normal faults. Fluids with methane contents about 5-fold the background concentration (about 14 nmol l^{-1} compared to 2-3 nmol l^{-1}) as well as positive anomalies of Zn (up to 120 nmol l^{-1} in unfiltered samples) were discovered in about 600 m water depth, indicating that low-temperature hydrothermal fluids are emanating from the faults. High resolutions of the CTD sensor profiles revealed small negative salinity anomalies at various depths; however, temperature anomalies could not be identified clearly.

Unfortunately, we had no permission to sample the crater of the volcano. Six water samples were taken directly at the seafloor on the flanks of the volcano with the Hydro Bottom Station (HBS) which is an instrument especially designed to sample diffuse hydrothermal fluids (Halbach *et al.,* 2001). These samples showed increased concentrations of Si (up to 33 µmol l^{-1} compared to a background of 18 µmol l^{-1}), methane (up to 22 nmol l^{-1}), and of several trace metals such as Zn, Cu and Ni. There is a significant deple-

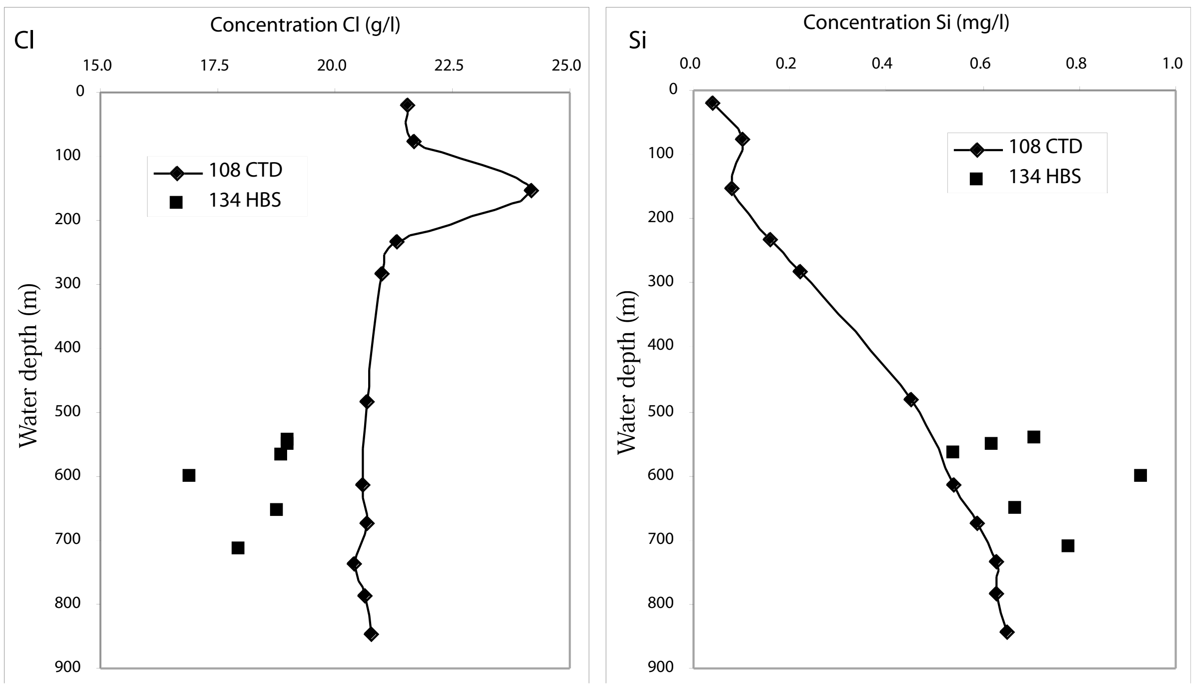

Figure 2. Chloride and silica concentrations in the water column profile of station 108 CTD and in the bottom water samples of station 134 HBS at the southern flank of the Kick'em Jenny submarine volcano.

tion in Cl (0.48 mol l^{-1} compared to the background of 0.59 mol l^{-1}), sulphate, Na, K and Mg compared to the ambient bottom water. Very small chemical signals were also visible in the water column profiles at this depth range (Fig. 2). As mixing of seawater with meteoric water can largely be excluded, the reduced chlorinity of the samples may indicate boiling and phase separation in the subseafloor. Boiling in hydrothermal systems produces a vapor phase that is enriched in gases but depleted in chloride and metal ions and a brine phase that is highly saline and metal-rich (*e.g.*, Butterfield *et al.,* 1990). Accordingly, our samples would represent a condensed vapor phase. Measurements of stable isotopes support this theory.

Discussion

Although hydrothermal mineralisation on the sea floor close to the islands is only low grade, it is hypothesised that phase separation in the hydrothermal fluids at depth could be leading to higher grade mineralisation below the vent fields or the discharge of metal rich brines on the lower flanks of the volcanic islands.

The widespread occurrence of manganese precipitates on the western side of the Lesser Antilles shows that a fractionation process producing low-temperature hydrothermal solutions enriched in manganese has taken place possibly at more or less the same geological time throughout the study area. Additional work on the manganese crusts has shown that ferromanganese precipitation took place along faults and fractures and on ridges, and was promoted by the mixing of modified sea water (in a small amount) with hydrothermal fluid. The very low trace metal concentrations lead to the conclusion, that the mineralising fluid was mainly of hydrothermal origin. In the ternary diagram after Usui *et al.,* 1992 (Fig. 3a) it is shown that due to the low concentration of Ni, Cu and Zn, most of the analysed samples plot in the hydrothermal field. The diagram Mn/Fe vs. Co demonstrates that the hydrothermal samples are characterised by high Mn/Fe ratios and low Co concentrations (Fig. 3b); the three samples with higher Co concentrations indicate enhanced hydrogenetic input.

Because of the wide distribution of the manganese mineralisation in certain areas, it is thought to have been controlled by both focussed and diffuse hydrothermal flow. An additional but less important mechanism of mineralisation is a diagenetic remobilisation and concentration of manganese by pore fluid in the unconsolidated sediment.

It is clear from the above that the two main indicators of submarine hydrothermal activity in the region as a whole are manganese crusts and water column anomalies.

Other minerals of hydrothermal origin were only recovered between Guadeloupe and Montserrat, namely nontronite and sulphides. The nontronites indicate low-temperature hydrothermal activity whereas pyrite and chalcopyrite indicate higher temperature hydrothermal-

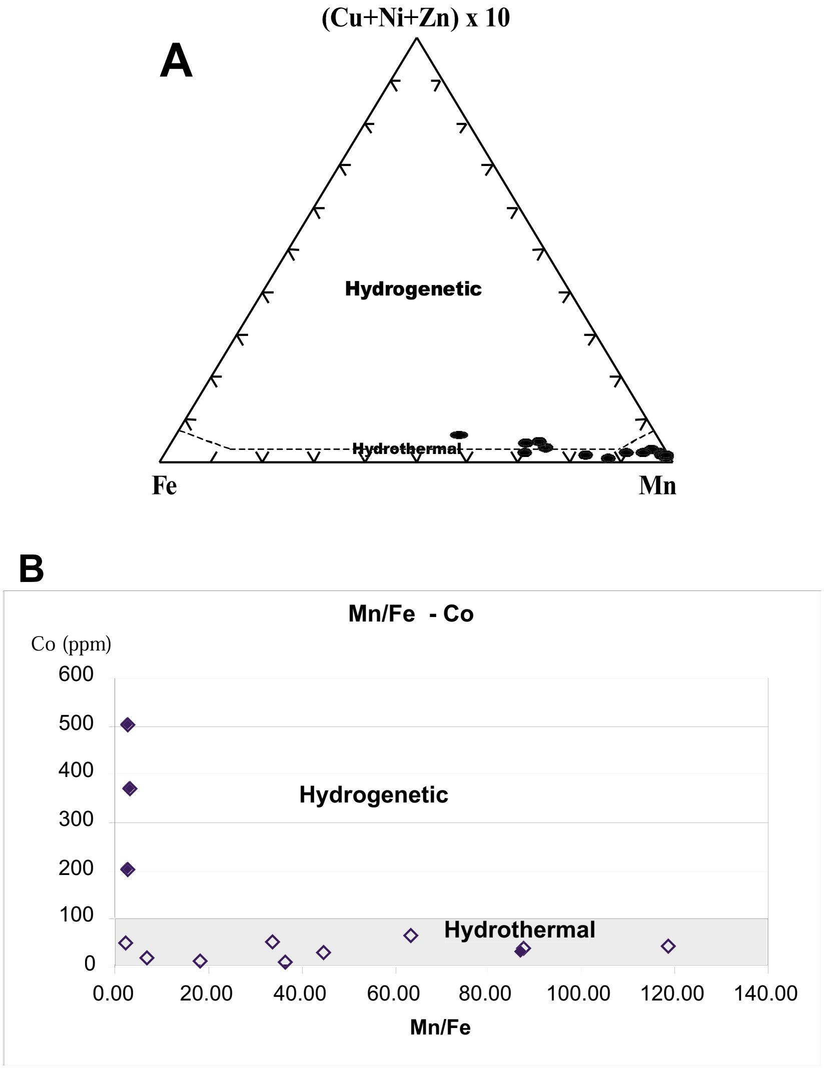

Figure 3. Elemental relationships of all Mn oxide samples recovered during cruise SO 154; **(A)** Ternary Diagram Fe– Mn (Cu+Ni+Zn) x 10 after Usui *et al.* (1992); **(B)** Co vs. Mn/Fe

ism. Detailed geochemical analyses of the sediments have confirmed the enrichments.

Although the study area off the Lesser Antilles was sampled in detail in all likely hydrothermal locations, no massive sulphides were found on the sea floor. There are indications, however, that they may be present at shallow depth under the sea floor, beneath a cover of gossan or manganese crust. Nevertheless overall hydrothermal activity in the area appears to be less than, for example, in the western Pacific arcs.

Acknowledgements

Cruise SO 154 and the project CARIBFLUX (grant no. 03 G 0154) are funded by the German Federal Ministry of Education and Research (Bundesministerium für Bildung und Forschung BMBF). We thank the captain and crew of *R/V Sonne* for the skilled support during the cruise.

References

Butterfield, D.A., Massoth, G.J., McDuff, R.E., Lupton, J.E. and Lilley, M.D. Geochemistry of hydrothermal fluids from Axial Seamount hydrothermal emissions study vent field, Juan de Fuca Ridge: Sub-seafloor boiling and subsequent fluid-rock interaction. Journal of Geophysical Research, 95(B8), 12895-12921, 1990.

Freie Universität Berlin and partners. Technical Cruise Report CARIBFLUX with RV Sonne, cruise no. SO 154, 2001.

Halbach, P., Holzbecher, E., Koschinsky, A., Michaelis, W. and Seifert, R. Deep-sea hydrothermal microplume generation - a case study from the North Fiji Basin. Geomarine Letters, 21, 94-102, 2001.

Johnson, A. & Cronan, D.S. Hydrothermal metalliferous sediments and waters off the Lesser Antilles. Marine Georesources & Geotechnology, 19, 65-83, 2001.

Kang, J.K. Les encroûtements ferromanganésifères sous-marine de l'est Caraïbe. These, Universite d'Orleans, 1984.

Polyak, B.G., Bouysse, Ph., Kononov, V.I., Butuzova, G.Y. Evidence of submarine hydrothermal discharge to the northwest of Guadeloupe Island (Lesser Antilles island arc). Journal of Volcanology & Geothermal Research, 54, 81-105, 1992.

Sander, S. and Koschinsky, A. Onboard-ship redox speciation of chromium in diffuse hydrothermal fluids from the North Fiji Basin. Marine Chemistry, 71, 83-102, 2000.

Usui, A. and Nishimura, A. Hydrothermal manganese oxide deposits from the Izu-Ogasawara (Bonin)-Mariana Arc and adjacent areas. Bulletin of the Geological Survey of Japan, vol. 43 (4), 257-284, 1992.