## Paper 121

# **Exploration for VMS Mineralization in Submarine Arcs**

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### ABSTRACT

The Kermadec intra-oceanic arc is a 1,220 km long system formed by the subduction of the Pacific Plate beneath the Australian Plate. Attention has only recently been given to arc systems as locations of hydrothermal activity and formation of significant seafloor volcanogenic massive sulfide (VMS) mineralization, when compared to the mid-ocean ridges. The Kermadec arc is the most systematically explored submarine arc in the world for hydrothermal activity. Exploration over the last 9 years has shown that the majority of the volcanoes and calderas along the arc are hydrothermally active, ranging from diffuse low-temperature venting to robust black-smoker style venting with associated VMS mineralization. The primary exploration tool has been by mapping hydrothermal plumes in the water column overlying submarine volcanoes, utilizing a number of sensor to detect both physical (e.g., light-scattering) and chemical (e.g., <sup>3</sup>He) anomalies. Subsequent vectoring of these plumes back to their sources has revealed significant mineralization on several of the volcanoes along the Kermadec arc. Significantly, these systems are Au-rich, with concentrations considerably elevated compared to ridge settings.

#### **INTRODUCTION**

Since the discovery of hydrothermal venting on the Galapagos Spreading Center in 1977, considerable attention has been given to mid-ocean ridge hydrothermal systems as analogues to ancient volcanogenic massive sulfide (VMS) deposits (Herzig



**Figure 1.** The Tonga-Kermadec subduction system; the Pacific Plate is being subducted westward underneath the Australian Plate. A) The active arc is denoted by triangles. B) Expanded view of the southern portion of the Kermadec arc, showing the location of important submarine hydrothermally active volcanoes and calderas. After Massoth and de Ronde (2006).

1999). Much less attention has traditionally been given to submarine arcs (de Ronde *et al.* 2001), despite evidence for significant geothermal systems on subaerial arc volcanoes (e.g., White Island (Hedenquist *et al.* 1993; Giggenbach *et al.* 2003). Over the last 10 years or so, submarine arcs have started to

receive greater attention, with the result that many submarine arcs have been found to be hydrothermally active, with the Kermadec arc offshore of New Zealand having received the most intense and systematic exploration and research (de Ronde *et al.* 2003; de Ronde *et al.* 2005; Stoffers *et al.* 2006).

Although useful as analogs of ancient VMS ore deposition, mid-ocean ridge settings are difficult targets in terms of exploitation owing to the depth (typically > 2,500 m). Furthermore, ridge settings are dominated by basaltic lava flows, whereas many large ancient VMS deposits are associated with felsic pyroclastic rocks. Arc-associated systems are typically at much shallower water depths compared to mid-ocean ridges, and the association with arc-volcanoes means that they may be longer-lived, potentially producing much larger deposits than are typically along the mid-ocean ridges. Compared to mid-ocean ridge hydrothermal deposits, those on arcs also tend to have higher  $f_{O2}$ , lower Fe and higher Au (Wright et al. 1998; de Ronde et al. 2007). This elevated gold (Table 1) also makes such deposits more attractive for exploration and potential exploitation (Herzig 1999). This paper describes the methods used to explore and map arc



**Figure 2.** Hydrothermal plumes are mapped and sampled using a CTD (conductivitytemperature-depth) system with 19 sample bottles for discrete samples. The package either profiles the water column or is towed in tow-yo fashion to detect hydrothermal plumes. After Massoth and de Ronde (2006).

submarine hydrothermal systems and summarizes some of the styles of venting and mineralization that have been observed to date.

number of chemical and physical parameters to capture the

1998). Subsequently, a series of research cruises using New Zealand, German, Japanese and American research vessels: 1) dredged sulfide Brothers mineralization at and Rumble II West calderas (Wright et al. 1998); 2) initiated systematic mapping of hydrothermal plumes along the entire Kermadec arc (de Ronde et al. 2001; Massoth et al. 2003; de Ronde et al. 2007); and, 3) undertook detailed investigation of using fields vent manned submersibles (de Ronde et al. 2005).

The principle method of detecting and locating sites of hydrothermal venting is by mapping plumes that are formed in the water column (Figure 2); these provide a much broader and more widely dispersed exploration target. Hydrothermal plumes occur in both dissolved and particulate forms. Thus, exploration for plumes has relied on a

#### THE KERMADEC ARC

The Kermadec arc represents the southern half of the ~2,500 km long Kermadec-Tonga Arc. formed by the subduction of the Pacific Plate underneath the Australia Plate (Figure 1). Although there are about 57 submarine volcanic centers along the entire arc, the majority (33) occur within the 1,220 km-long Kermadec arc portion (de Ronde et al. 2005). The Kermadec arc represents the northeastward extension of the Taupo Volcanic Zone of the North Island of New Zealand, from continental crust into oceanic crust. This variation in crust, combined with subduction of sediments and overthickened oceanic crust of the Hikurangi Plateau, results in a variety of magma source compositions reflected in the elemental and isotopic composition of erupted products along the arc, and likely reflects in the variability in the hydrothermal fluids and mineralization (de Ronde et al., 2001; 2005; 2007; Massoth et al., 2003).

## EXPLORING FOR SUBMARINE ARC HYDROTHERMAL ACTIVITY

Prior to 1996, active hydrothermal activity along the submarine portion of the Kermadec was unknown (Wright *et al.* 



**Figure 3.** Longitudinal profile of the southern-most part of the Kermadec arc, showing contoured results for light scattering (a) and helium isotopes (b). Volcano names are: W = Whakatane, Ck = Clark, T = Tangaroa, L = Lillie, R5 = Rumble V, R3 = Rumble III, R2 = Rumble II East, S2 = Silent II, Ct = Cotton, H = Healy, B = Brothers. After de Ronde et al. (2001).

different styles of venting. Hydrothermal plumes along the Kermadec arc have been most successfully mapped in real-time using light-scattering detection ( $\Delta$ NTU), based on the presence of venting-associated particulates (primarily Fe- and Mnoxyhydroxides), and later in shore-based laboratories using He isotopes (Figure 3), although pH, and Eh anomalies are also commonly observed (de Ronde et al. 2001). During plume mapping exercises, discrete water samples are collected (Fig. 2A), permitting more detailed geochemical and isotopic characterization, including dissolved Fe and Mn, H<sub>2</sub>S, and the He isotopes. Results for the Kermadec arc show that hydrothermal plumes originate from venting (both focused high temperature and more diffuse low temperature) from simple volcanic cones and more complex caldera systems (de Ronde et al. 2001). Given that submarine arc volcanoes have depths to their summits ranging between > 1800 m and  $\sim 100$ m, plumes occur predominantly shallow and mid-water in the water column (Figure 3). The chemical composition of out at the Brothers caldera volcano (de Ronde *et al.* 2005). Brothers is host to two distinct styles of active venting; 1) gasrich, low-temperature (typically  $<70^{\circ}$ C) emanations from the young cone in the southern part of the caldera, and 2) high-temperature (max 302°C) metal-rich emanations from the NW caldera site (Figure 4). Here, sulfides crop out over a  $\sim200 \times 600$  m zone (de Ronde *et al.* 2005) that includes numerous sulfide chimney spires between 1 and 5 m tall (Figure 4). Numerous active chimneys occur around a depth centered at  $\sim1,650$  m. The walls of the NW caldera site are steep, with the active chimneys commonly perched on intervening benches and are typically aligned orthogonal to the slope of the walls.

Microscopy and X-ray diffraction studies of sulfide samples recovered from Brothers indicates that mineralization is dominated by pyrite, marcasite, chalcopyrite, and sphalerite, hematite, goethite, and barite (de Ronde *et al.* 2005). Less abundant minerals include epidote, titanite, albite, quartz, cristobalite, anhydrite, natroalunite, pyrrhotite, arsenopyrite,

 TABLE 1

 Geochemical composition of select mineralised sample from the Brothers NW caldera site (from de Ronde et al, 2005).

Sample type	Fe (wt%)	Au (ppb)	As (ppm)	Sb (ppm)	Ag (ppm)	Ba (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Single intact chimney	v									
Low	0.7	17	215	23	38	6650	8	230	220	72 100
High	15.0	1430	4390	579	1180	108 000	700	3580	85 200	380 000
Average <sup>†</sup>	4.1	467	1080	189	340	40 081	276	1081	25 207	169 541
$\pm 1\sigma$	4.4	479	1051	121	305	23 044	194	949	28 535	91 996
n	27	17	27	27	27	27	27	27	27	27
Breccia/stockwork										
Low	4.2	58	6	0.4	0.4	170	0.2	26	9	12
High	42.9	1850	1630	169	2.8	11 600	1.8	26 500	180	420
Average	24	532	605	22	1.3	3488	1.1	2905	75	127
$\pm 1\sigma$	14	596	587	52	0.8	4102	0.7	7901	53	138
n	11	9	10	10	11	11	6	11	11	10
Hydrothermally alter	red rock with di	isseminated s	ulfides							
Low	3.8	4	13	0.7	0.1	640	0.3	25	11	12
High	8.9	190	143	16.2	5.0	8240	32.0	370	490	14 400
Average	6.0	77	63	4.1	1.3	2494	6.5	107	109	2049
$\pm 1\sigma$	1.9	74	44	5.0	1.7	2471	12.5	118	151	4672
n	9	7	9	9	8	9	6	8	9	9
Fe-Si crusts/sedimen	ts									
Low	1.0	5	21	0.5	0.2	34	0.2	11	18	15
High	30.5	97	2620	88.4	1.4	2410	2.6	180	3720	1350
Average	11.0	37	646	15	0.6	831	1.0	65	789	308
±1σ	11.3	33	825	25	0.5	773	0.8	67	1147	389
n	14	6	14	13	13	14	10	13	14	14
Detection limit	0.01	2	0.5	0.1	0.1	2	0.2	10	2	5

Average calculated from those samples that had concentrations above the detection limit. Analysed by ICP-MS and ICP-ES at the Geological Survey of Canada laboratories; Au, As and Sb analysed by INAA by Activation Laboratories, Ontario.

hydrothermal plumes along the Kermadec arc are very different to those at mid-ocean ridges and commonly have elevated concentrations of Fe,  $H_2S$  and  $CO_2$ , with Fe/Mn values up to 18 significantly greater than typically found at ridges (Massoth and de Ronde 2006).

#### **MINERALIZATION**

Following the initial dredging of sulfide samples from Brothers and Rumble II West calderas in 1996 (Wright *et al.* 1998), samples of vent fluids and sulfide chimneys have been recovered from a number of vents sites along the Kermadec Arc. The most extensive exploration to date has been carried enargite, bornite, intermediate solid solution, chalcocite, covellite, galena, rutile, birnessite, and native sulfur (de Ronde *et al.* 2005).

Mineralization at Brothers is characterized by two dominant types: Cu-Fe-rich and Zn-Ba  $\pm$  Pbrich. In addition, mineralization at Brothers is relatively enriched in Au (especially with the Cu-rich mineralization), Ag, Tl, Ga, As, Sb, and Cd (Table 1) (de Ronde *et al.* 2005).

### CHALLENGES AND FUTURE DIRECTIONS

More recently, other submarine volcanic have been arcs investigated for hydrothermal activity, in particular the Mariana Arc (e.g., Embley et al. 2006), but none have been explored as systematically as the Kermadec Arc. There are currently three exploration companies dedicated to exploring for seafloor massive sulfides; Nautilus Minerals offshore of Papua New Guinea

(www.nautilus.com), Neptune Minerals along the Kermadec arc (www.neptuneminerals.com) and Blue Water Minerals, Inc. Challenges include difficulties of mining in an active arc setting, in particular the environmental impact on vent-associated communities. Future exploration will likely involve development of geochemical and geophysical techniques to explore in older, inactive portions of arc systems (e.g., Colville Ridge; Figure 1)

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**Figure 4.** *A)* Black smoker from NW caldera site, Brothers, venting at 274°C. B) Inactive chimneys from Brothers. C) Interior of massive sulfide chimney from Brothers, dominated by pyrite, chalcopyrite, sphalerite and barite. D) Diffuse venting (68°C) at Cone site, Brothers. The pale yellow/white material is dominantly elemental sulfur forming a crust over sediment.

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