



## Submarine venting of magmatic volatiles in the Eastern Manus Basin, Papua New Guinea

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### Abstract

The SuSu Knolls and DESMOS hydrothermal fields are located in the back-arc extensional transform zone of the Eastern Manus Basin. In 2006, highly acidic and  $\Sigma\text{SO}_4$ -rich vent fluids were collected at both sites and analyzed for the chemical and isotopic composition of major and trace species. Fluids exiting the seafloor have measured temperatures from 48 to 215 °C and are milky white in appearance due to precipitation of elemental S<sup>0</sup>. Vent fluid concentrations of Na, K, and Mg are depleted by as much as 30% relative to seawater, but have the same relative abundance. In contrast, the fluids are highly enriched in dissolved  $\Sigma\text{CO}_2$ , Cl,  $\text{SiO}_{2(\text{aq})}$ , Fe, and Al relative to seawater. Measured pH (25 °C) ranged from 0.95 to 1.87 and aqueous  $\Sigma\text{SO}_4$  ranged from 35 to 135 mmol/kg. The chemical and isotopic composition points to formation via subsurface mixing of seawater with a Na-, K-, Mg-, and Ca-free, volatile-rich magmatic fluid exsolved from subsurface magma bodies during a process analogous to subaerial fumarole discharge. Estimates of the magmatic end-member composition indicate a fluid phase where  $\text{H}_2\text{O} > \text{SO}_2 > \text{CO}_2 \approx \text{Cl} > \text{F}$ . The hydrogen and oxygen isotopic composition of  $\text{H}_2\text{O}$  and carbon isotopic composition of  $\Sigma\text{CO}_2$  in the vent fluids strongly suggest a contribution of slab-derived  $\text{H}_2\text{O}$  and  $\text{CO}_2$  to melts generated in the mantle beneath the Eastern Manus volcanic zone. Abundant magmatically-derived  $\text{SO}_2$  undergoes disproportionation during cooling in upflow zones and contributes abundant acidity,  $\text{SO}_4^{2-}$ , and S<sup>0</sup> to the venting fluids. Interaction of these highly acidic fluids with highly altered mineral assemblages in the upflow zone are responsible for extensive aqueous mobilization of  $\text{SiO}_{2(\text{aq})}$ , Fe, and Al. Temporal variability in the speciation and abundance of aqueous S species between 1995 and 2006 at the DESMOS vent field suggests an increase in the relative abundance of  $\text{SO}_2$  in the magmatic end-member that has mixed with seawater in the subsurface. Results of this study constrain processes responsible for the formation of hot-spring fluids in magmatically active back-arc environments and the resulting chemical exchange between the lithosphere and water column. © 2015 Elsevier Ltd. All rights reserved.

### 1. INTRODUCTION

Submarine hot-spring fluids contain abundant magmatic volatiles that can fundamentally influence fluid–rock reactions and promote chemical exchange between the

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lithosphere and overlying water column. In back-arc and submarine arc hydrothermal environments, spatial and temporal variability in crustal composition, abundance and composition of magmatic volatiles, subduction and mantle dynamics, magmatic activity, and seafloor morphology result in a broad range of hydrothermal fluid compositions. All of these factors are influenced by the subducting slab and vary systematically with increasing distance from the arc as the depth of subduction increases (Sinton et al., 2003; Pearce and Stern, 2006; Martinez et al., 2006; Bezos et al., 2009; Escrig et al., 2009; Mottl et al., 2011; Reeves et al., 2011). In the Manus back-arc basin, for example, the Vienna Woods hydrothermal system is hosted in basaltic crust where back-arc rifting and crustal generation is fully developed along the Manus spreading center located 250 km from the New Britain arc. At this location, magmatic volatiles in seawater-derived vent fluids are dominated by CO<sub>2</sub> with no evidence for significant H<sub>2</sub>O or SO<sub>2</sub> contributions (Reeves et al., 2011), similar to mid-ocean ridge settings characterized by basaltic magmatism (Lilley et al., 2003; Shanks et al., 1995). Further to the east at the PACMANUS, DESMOS, and SuSu Knolls hydrothermal areas, hot-springs are hosted in more felsic crust within an extensional transform zone that lacks a clearly-defined spreading center. Located ≤100 km from the active New Britain arc, the influence of the subducting slab on hydrothermal fluid chemistry is readily apparent in the composition of dissolved volatiles. In addition to CO<sub>2</sub>, magmatic degassing is thought to contribute significant quantities of H<sub>2</sub>O, SO<sub>2</sub>, and HF to PACMANUS and DESMOS vent fluids (Gamo et al., 1997; Gena et al., 2006; Reeves et al., 2011). Because SO<sub>2</sub> disproportionation to sulfuric acid (Iwasaki and Ozawa, 1960; Holland, 1965; Kusakabe et al., 2000) and direct addition of other acidic magmatic volatiles such as HCl represent abundant sources of strong acids, magmatic degassing in these environments significantly influences the mineralogy and composition of crustal alteration assemblages and the transport of metals in solution.

The contribution of magmatic fluids to hydrothermal fluid chemistry has received much attention in the context of ore-deposit formation (e.g., Hedenquist and Lowenstern, 1994; de Ronde, 1995; Heinrich, 2005; Yang and Scott, 2006). It has been suggested that magmatic fluids may contain levels of magma-derived ore-forming metals that are sufficient to account for the quantities of metals observed in seafloor mineral deposits and may represent the source of metals in hydrothermal fluids responsible for ore formation (Yang and Scott, 1996, 2002). Magmatic fluids have also been invoked as a source of acidity and complexing ligands to hydrothermal fluids that may efficiently leach ore-forming metals from surrounding crustal rocks prior to concentration at the site of deposition (Hedenquist and Lowenstern, 1994). Recent studies have suggested that acidic magmatic volatiles may contribute to metal mobilization in seawater-derived metal-rich black-smoker fluids venting in arc and back-arc environments (de Ronde et al., 2005; Embley et al., 2006; Resing et al., 2007; Takai et al., 2008; de Ronde et al., 2011; Mottl et al., 2011; Reeves et al., 2011). Although these

fluids show a clear magmatic contribution, the composition of the magmatic fluid prior to mixing with the convectively circulating seawater-derived component and its role during metal mobilization is obscured by subsequent fluid–rock interaction and phase separation processes.

Magmatic volatiles have been identified in highly acidic SO<sub>4</sub>-rich low temperature white smoker fluids venting from the back-arc DESMOS vent field and the NW Rota-1 and Brothers intraoceanic arc volcanos (Gamo et al., 1997; Gena et al., 2006; Resing et al., 2007; Butterfield et al., 2011; de Ronde et al., 2011). These acid-sulfate fluids represent a very different style of hydrothermal activity compared to high temperature black-smoker fluids that have been studied extensively at oceanic-spreading centers. In particular, they are more acidic and contain substantially higher aqueous SO<sub>4</sub> and Mg concentrations relative to black-smoker fluids, sharing similarities with the fluids responsible for high sulfidation deposits in subaerial settings (Hedenquist and Lowenstern, 1994). While numerous hydrothermal systems with this type of venting are now known to exist in back-arc and intraoceanic arc environments (Gamo et al., 1997; Butterfield et al., 2011; de Ronde et al., 2011; Leybourne et al., 2012), compositional information is limited and their temporal variability has only been observed indirectly through changes in water column plume chemistry (de Ronde et al., 2003, 2005). Because their chemistry appears to be highly influenced by the abundant presence of magmatic volatiles, they can provide new insight into the composition of magmatic fluids involved in hydrothermal activity in submarine back-arc and arc settings, and their role in hydrothermal alteration and magma dynamics.

Here we report data for the composition of acid-sulfate fluids collected in 2006 from the SuSu Knolls and DESMOS vent fields located in the back-arc environment of the Eastern Manus Basin. The compositions of fluids from the SuSu Knolls vent area have not been reported previously and greatly expand the range of observations that can be used to constrain physical and chemical processes associated with submarine acid-sulfate venting. The DESMOS area was previously sampled on several occasions between 1995 and 2000 (Gamo et al., 2006 and references therein). The data presented here augment these earlier studies by providing additional information regarding the temporal evolution of acid-sulfate venting. Information regarding the abundance of dissolved gases along with non-volatile aqueous species are used to assess the composition of magmatic fluids released from sub-seafloor magmatic bodies, processes controlling the formation and composition of acid-sulfate fluids in back-arc environments, and resulting chemical exchange between the lithosphere and water column.

## 2. GEOLOGIC SETTING

The Manus Basin (Fig. 1), located in the northeastern Bismarck Sea, is a young (ca. 3.5 Ma) back-arc basin that is rapidly opening at full rates up to 137 mm/y (Tregoning, 2002). It is bordered to the north by the presently inactive Manus Trench and to the south by the active

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