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Formation of Fe–Mn–Si oxide and nontronite deposits in hydrothermal fields on the Valu Fa Ridge, Lau Basin

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ABSTRACT

Hydrothermal Fe–Mn–Si oxides and nontronite are pervasive in the Hine Hina, Vai Lili and Mariner hydrothermal fields along the central Valu Fa Ridge, Lau Basin. Morphometric and mineralogical analyses reveal that the iron-rich filaments are the most important constituents of these Fe–Mn–Si oxide deposits. Both the morphologies and chemical composition of the filaments indicate that neutrophilic Fe-oxidizing bacteria have played a key role in the formation of these deposits. A key process of the formation of these deposits is the creation of a complicated filamentous network in which a series of metabolic activities and passive sorption and nucleation processes occur. The precipitation of dissolved Si in unsaturated and saturated states leads to a "two-generation" growth model in the hydrothermal vents. The precipitation of amorphous opal occurs in a relatively narrow temperature range (41.1–42.9 °C) based on oxygen isotope analyses, indicating a fast precipitation rate of opal-A when conductive cooling of the hydrothermal fluid occurrs. Patchy nontronite in the Mariner fields is a product of the direct precipitation from hydrothermal fluids at a temperature of ~87.9 °C, whereas the scattered nontronite at the Hine Hina field is the product of the replacement of hydrothermal Fe–Si oxides at a temperature of ~46.2 °C.

1. Introduction

Poorly crystallized Fe–Mn–Si-oxyhydroxide deposits (referred to as Fe–Mn–Si oxides) are widely developed in modern hydrothermal fields in various geological settings, such as mid-ocean ridges, back-arc basins and intra-plate seamounts (e.g., Alt, 1988; Puteanus et al., 1991; Binns et al., 1993; Fortin et al., 1998; Iizasa et al., 1998; Boyd and Scott, 2001; Kennedy et al., 2003a,b; Benjamin and Haymon, 2006; Hrischeva and Scott, 2007; Kato et al., 2009; Langley et al., 2009; Dekov et al., 2010; Edwards et al., 2011). Mineralogically, these hydrothermal precipitates contain a wide range of minerals with primary ferrihydrite, goethite, amorphous silica (opal-A), todorokite, birnessite and sometimes Fe-rich phyllosilicates such as nontronite (Köhler et al., 1994; Iizasa et al., 1998; Benjamin and Haymon, 2006; Hrischeva and Scott, 2007) and Fe-rich smectite present (Cole, 1983, 1985, 1988; Taitel-Goldman and Singer, 2001a,b).

In recent years, there has been considerable interest in understanding the formation of Fe–Mn–Si oxides (especially Fe-oxyhydroxides) in seafloor hydrothermal fields. An important reason for this is that mineralized bacterial micro-textures (filaments and spheres) are ubiquitous in these deposits (e.g., Taylor et al., 1999; Emerson and Moyer, 2002; Kennedy et al., 2003a,b; Little et al., 2004; Emerson et al., 2007; Kato et al., 2009; Langley et al., 2009; Dekov et al., 2010; Edwards et al., 2011). So far, several studies based on the morphologies of the filaments and molecular biological techniques have revealed the presence of neutroliphic Fe-oxidizing bacteria (i.e., *Gallionella ferruginea, Leptothrix ochracea* and *Mariprofundus ferrooxydans*) in hydrothermal vent systems (Dhillon et al., 2003; Emerson et al., 2007, 2010; Davis and Moyer, 2008; Hodges and Olson, 2009; Kato et al., 2009), suggesting that bacteria play an important role in the formation of the hydrothermal Fe–Mn–Si oxide deposits. In addition, more and more researches have shown that these deposits are probably the analogs of ancient banded iron formations (BIFs) and umbers (Boyd and Scott, 2001; Pecoits et al., 2009; Edwards et al., 2011). Similar biogenic filamentous structures have also been discovered in similar ancient deposits (Duhig et al., 1992; Boyce et al., 2003). Some recent studies have demonstrated that the unique morphologies

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of neutroliphic Fe-oxidizing bacteria can act as robust biosignatures for the investigation of the evolution of life and for geological studies (Hofmann et al., 2008; Chan et al., 2011). In order to create a closer affinity to similar ancient deposits, this demands further thorough investigations focused on the formation of Fe–Si–Mn oxide deposits in modern hydrothermal fields. However, understanding the processes of Fe–Mn–Si oxide precipitation and the role of bacteria in seafloor hydrothermal fields still remains limited at present (Kato et al., 2009; Langley et al., 2009; Emerson et al., 2010).

Furthermore, as a common authigenic clay mineral, nontronite generally occurs in modern hydrothermal deposits intermixed with the Fe–Mn–Si oxide (Severmann et al., 2004; Dekov et al., 2007) reflecting the variable redox conditions over short distances (Severmann et al., 2004). Previous studies have revealed that nontronite can form at temperatures of 3–140 °C (Benjamin and Haymon, 2006) and various formation mechanisms for this have been proposed (Cole and Shaw, 1983; Severmann et al., 2004; Benjamin and Haymon, 2006; Benjamin and Haymon, 2006; Dekov et al., 2007) including weathering/alteration of massive sulfides, metalliferous sediments and oceanic crust (McMurtry and Yeh, 1981; Haymon and Kastner, 1986; Hekinian et al., 1993) and the direct precipitation of nontronite from low-temperature hydrothermal fluids (McMurtry et al., 1983; Alt and Jiang, 1991; Percival and Ames, 1993; Severmann et al., 2004). Moreover, several studies suggest a biogenic origin for hydrothermal nontronite and have described bacterial structures associated with this mineral (Alt, 1988; Juniper and Fouquet, 1988; Hekinian et al., 1993; Köhler et al., 1994; Fortin et al., 1998; Dekov et al., 2007). However, the relationship between Fe–Mn–Si oxides and nontronite during their precipitation in hydrothermal vents is not well established (Severmann et al., 2004).

In this paper, we present a preliminary study of the mineralogy, geochemistry and morphology of Fe–Mn–Si oxide and nontronite precipitates from hydrothermal fields on the southern and central Valu Fa Ridge (VFR), Lau Basin. The main objectives of this study were to determine the mechanism of formation of these precipitates and the role of microbes in the formation of the hydrothermal Fe–Mn–Si oxides.

2. Geological setting

The Lau Basin is located at a convergent boundary between the Pacific and Indo-Australian plates and is approximately 1500 km north of New Zealand. Below 1000 m it is largely closed to the east, south and west by a remnant arc (Lau Ridge) and an active volcanic arc (Tofua volcanic arc), respectively (Fig. 1) (Fouquet et al., 1993; Keller et al., 2008). The basin is composed of three major active spreading ridges: the Central Lau Spreading Center (CLSC), the Eastern Lau Spreading Center (ELSC), and the southernmost part of the ridge (21°20′S), which is referred to as the Valu Fa Ridge (VFR) (Jenner et al., 1987). This active back-arc basin has been opening over the past 6 Ma (Hawkins, 1995) whereas the Valu Fa spreading ridge (the southern part of the Lau Basin) began opening about one Ma ago (Lécuyer et al., 1999). The VFR extends for at least 165 km and is 5–6 km wide with the ridge flanks rising about 600 m above the surrounding seafloor (Taylor et al., 1996). Geophysical studies suggest that the VFR is divided into three sections: the southern, central and northern VFR (SVFR, CVFR and NVFR) sections (Fouquet et al., 1993), which are arranged *en echelon* a few kilometers apart. The southern Valu Fa Ridge is still propagating southwards.

Since the early 1990s, several distinct hydrothermal fields have been discovered along the VFR extensional zone (Fouquet et al., 1991, 1993; Ishibashi et al., 2006; Reysenbach et al., 2006). According to Fouquet et al. (1993), two different volcanic and tectonic stages have been recognized in the SVFR and NVFR. The Hine Hina hydrothermal field on the SVFR is in the volcanic stage and is characterized by diffuse discharge at ~40 °C (Fouquet et al., 1993; Lécuyer et al., 1999; Baker et al., 2005) through highly porous volcaniclastic material which was produced during the formation of extensive Fe–Mn-oxyhydroxide crusts covering sulfide

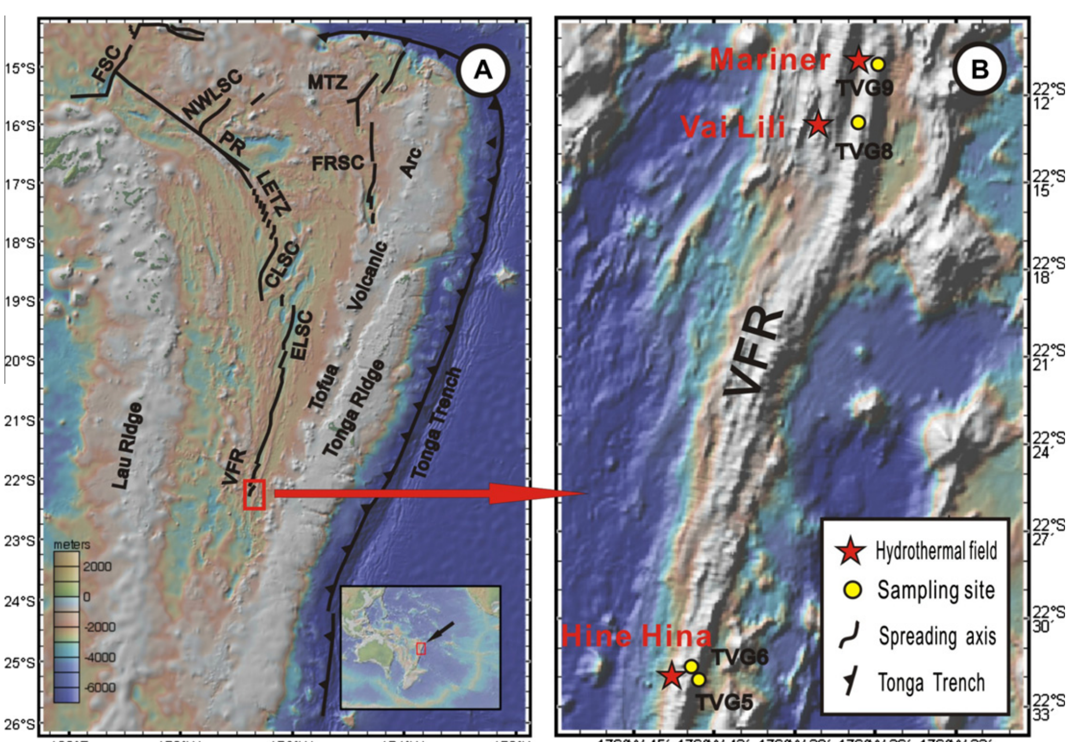

Fig. 1. Regional bathymetric map and the sample sites along the VFR, Lau Basin. Red stars = hydrothermal vent sites; yellow circles = sampling sites.