Mineralogical characterization and genesis of hydrothermal Mn oxides from the flank of the Juan the Fuca Ridge

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ABSTRACT

Several sites of active hydrothermal flow have been found on the eastern flank of the Juan de Fuca Ridge. These sites are typically located along the edge of basaltic outcrops where sediment is thin. We present data on Mn-oxides formed on such outcrops (Zona Bare and Grinin Bare). These oxides are either black-layered crust or soft micro-concretions found in partially altered sediments. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses of Mn crusts indicate the presence of well-crystallized todorokite and birnessite encrusting detrital minerals and replacing siliceous fossil. Transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDX) analyses were used to identify amorphous and poorly crystallized Mn-rich phases in partially altered sediments and crusts. TEM of impregnated samples showed textural evidence suggesting that amorphous Mn oxides are incrusting cellular structures that could be bacteria. The valence state of Mn in these oxides was determined by parallel electron energy loss spectroscopy (PEELS). Results indicate that todorokite and birnessite have an average valence state of about 3.7 whereas the poorly crystallized Mn-rich phases have a lower valence state. These data suggest that the formation of hydrothermal Mn concretions occurs in several steps. The initial step is the adsorption or precipitation of Mn, Fe, and Si around cell-wall bacteria, extracellular polymers, and siliceous fossil remains. These mineralizations are poorly crystallized phyllosilicates, which progressively increase in size and crystallinity to give the final birnessite and todorokite products. All of these Mn-rich phases are the result of interactions between hydrothermal fluid and sediments and formed in areas where hydrothermal fluids discharge through the sediment.

INTRODUCTION

Mn oxy-hydroxides are ubiquitous minerals in marine sediments and form as a result of diagenetic, hydrothermal, or hydrothermal processes using reduced dissolved Mn$^{2+}$ as the precursor (Bonatti et al. 1972). These oxides, which have a +3 or +4 valence state, are largely controlled by redox and pH conditions (Burns and Burns 1979). Diagenetic or hydrothermal Mn oxy-hydroxides on abyssal plains grow slowly (1–10 mm/Ma) especially when compared to the rate at which hydrothermal Mn oxy-hydroxides form (a few millimeters per year). These hydrothermal precipitates form from either high- or low-temperature spring water. Along mid-ocean ridges where high-temperature (350 °C) springs exist, Mn in hydrothermal fluids oxidizes in the non-buoyant portion of the plume and then settles to the sea floor (e.g., Cowen et al. 1990; Klinkhammer and Hudson 1986). In contrast, low-temperature springs on ridge flanks provide Mn to the sea floor where it precipitates (Mottl et al. 1998).

Precipitation of Mn oxy-hydroxide in natural environments could result from microbial processes. Spores of a marine Bacillus bacterium SGI are able to oxidize Mn$^{2+}$ over a wide range of temperatures (0 to 80 °C; Mandernack et al. 1995) and in various environments (i.e., Takematsu et al. 1988b; Tazaki 1995). Such microbes accelerate the rate of Mn$^{2+}$ oxidation by up to five orders of magnitude compared to abiotic Mn$^{2+}$ oxidation (Takematsu et al. 1988b; Mandernack et al. 1995).

In this study, we focus on Mn deposits and partially altered sediments (enriched in Mn) that were sampled in the vicinity of the Juan de Fuca Ridge. Here, Mn-rich fluids flow up through the sediments providing a large flux of dissolved Mn relative to that from diagenetic processes alone (Wheat et al. 1997). What is the nature of these deposits and what is their mechanism of formation? To address these questions we present X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS) data to determine the mineralogy, redox state, and texture of these Mn deposits.

GEOLOGICAL SETTING

The eastern flank of the Juan de Fuca Ridge is buried by up to 700 m of sediment, which is mostly detrital in origin. About 17 km from the active portion of the ridge axis, the sea floor is relatively flat with the exception of several isolated basaltic base-