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# Sulfide mineralization in an ultramafic-rock hosted seafloor hydrothermal system: From serpentinization to the formation of Cu–Zn–(Co)-rich massive sulfides

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## Abstract

The Rainbow vent field is an ultramafic rock-hosted seafloor hydrothermal system located on the Mid-Atlantic ridge issuing high temperature, acidic, metal-rich fluids. Hydrothermal products include Cu–Zn–(Co)-rich massive sulfides with characteristics comparable to those found in mafic volcanic-hosted massive sulfide deposits. Petrography, mineralogy and geochemistry of nonmineralized and mineralized rocks sampled in the Rainbow vent field indicate that serpentinized peridotites host the hydrothermal vent system but serpentinization reactions occurred prior to and independently of the sulfide mineralization event. The onset of sulfide mineralization is reflected by extensive textural and chemical transformations in the serpentine-group minerals that show clear signs of hydrothermal corrosion. Element remobilization is a recurrent process in the Rainbow vent field rocks and, during simple peridotite serpentinization, Ni and Cr present in olivine and pyroxene are incorporated in the pseudomorphic serpentine mesh and bastite, respectively. Ni is later remobilized from pseudomorphic serpentine into the newly formed sulfides as a result of extensive hydrothermal alteration. Bulk-rock geochemistry and correlation coefficients discriminate the different processes: serpentinization, sulfide mineralization and superficial seafloor low-temperature processes related to the circulation of seawater (e.g. carbonatization, sulfide oxidation and B and U uptake).

*Keywords:* Rainbow vent field; Mid-Atlantic ridge; serpentinite; seafloor hydrothermal systems; volcanic-hosted massive sulfide deposits

## 1. Introduction

Ancient and modern volcanic-hosted massive sulfide deposits (VMS) are conventionally thought to form as a result of sub-seafloor heat-driven seawater circulation reacting with crustal or upper mantle rocks leaching metals and subsequently precipitating them as sulfides when the fluid mixes with cold, metal-depleted, ambient seawater (Scott, 1985; Large, 1992 and references therein; Ohmoto, 1996; Barrie and Hannington, 1999). The leaching process can account for accumulations of metals but mass balance calculation fails to fully explain the formation of some giant VMS deposits (Yang and Scott, 2003, 2006). The

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presence of ore metal-rich magmatic fluids may play an important role on the formation of massive sulfide deposits contributing large quantities of metals (e.g. Ni + Cu + Zn + Fe) and volatiles although the magmatic signature typically is masked by the large volumes of circulating seawater (de Ronde, 1995; Yang and Scott, 1996, 2002, 2006). The modern seafloor hydrothermal systems, with their black smokers issuing hot metal-rich vent fluids, hosted in mafic or felsic volcanic rocks, represent modern analogs for the formation of VMS ore deposits (e.g. Scott, 1985; Bischoff and Rosenbauer, 1989; Fouquet et al., 1993; Goodfellow and Franklin, 1993; Rona and Scott, 1993; Rona et al., 1993; Seyfried and Ding, 1995; Herzig and Hannington, 1995; Von Damm, 1995; Fouquet et al., 1996; Donval et al., 1997; Langmuir et al., 1997; Scott, 1997; Charlou et al., 2000; Douville et al., 2002; Von Damm et al., 2003). In particular, sediment-free basalt-hosted seafloor hydrothermal systems like TAG, MESO and Snake Pit share characteristics comparable to those of on-land mafic VMS deposits having Cu–Zn–(Co) sulfide mineralization with high Cu/Zn ratios (e.g. Kase et al., 1990; Rona et al., 1993; Herzig and Hannington, 1995; Tivey et al., 1995; Herzig et al., 1998; Münch et al., 1999; Lawrie and Miller, 2000). The recent discovery of modern seafloor hydrothermal systems hosted in ultramafic rocks, i.e. serpentinized peridotites, in slow to ultra-slow spreading ridges represents a remarkable novelty in the conceptual models of VMS ore deposit formation. In most cases, on-land ultramafic-hosted sulfide deposits, if not clearly of primary magmatic origin, are linked to serpentinization processes with element remobilization of metals (Fe, Ni and Co) from primary silicates (e.g. olivine) into hydrothermal sulfides if enough $H_2S$ is available (*e.g.* Eastern Metals, Canada — Auclair et al., 1993; Tsangli, Greece — Economou and Naldrett, 1984; Hayachine, Japan — Shiga, 1987; Limassol Forest, Cyprus — Thalhammer et al., 1986; Bou Azzer, Morocco — Wafik et al., 2001). Thus, the study of modern ultramafic-hosted seafloor hydrothermal systems may provide new insights into the formation of some ancient VMS spatially related to ultramafic rocks such as the Outokumpu Cu–Co–Au deposits of Finland (Gaál and Parkkinen, 1993; Loukola-Ruskeeniemi, 1999; Sorjonen-Ward et al., 2004) and the Kidd Creek Cu–Zn deposit of Canada (Barrie et al., 1999).

The five well known ultramafic-hosted seafloor hydrothermal sites at MAR include the low and moderately low-temperature systems of Saldanha (36°34’ N), Menez Hom (37°8′ N) and Lost City (30° N) and the high-temperature systems of Rainbow (36°14′ N) and Logatchev (14°45′ N) (Batuyev et al., 1994; German et al., 1996; Donval et al., 1997; Langmuir et al., 1997; Fouquet and IRIS Scientific Party, 2001; Kelley et al., 2001; Barriga et al., 2003). The high-temperature, ultramafic-hosted Rainbow vent field produces significant Cu–Zn–(Co) rich massive sulfide accumulations with conspicuous chemical and textural similarities to those found in modern basalt-hosted seafloor hydrothermal systems and ancient, on-land, mafic-hosted VMS deposits (Marques et al., 2006). In this paper, mineral chemistry, and major and trace element geochemistry of nonmineralized and mineralized rocks sampled from the Rainbow vent field have been investigated in order to distinguish between peridotite serpentinization processes, ubiquitous in exposed mantle outcrops, from later, overprinting, localized magmatic/hydrothermal-driven sulfide-mineralization.

## 2. Regional setting and hydrothermalism

The Rainbow hydrothermal vent field is an ultramafic rock-hosted hydrothermal field located at 36°14′ N–33°53′ W, south of the Azores archipelago and on the Mid-Atlantic Ridge at ~2300 m depth (Fig. 1A). Rainbow’s particular geological setting, within an inside corner of a non-transform offset between the AMAR and South AMAR second order segments (Fig. 1B), plays an important role in the tectonic and magmatic character of the system (Fouquet et al., 1997; Gràcia et al., 2000; Parson et al., 2000). First discovered in 1994 (German et al., 1996), the Rainbow vent field area underwent extensive surveys of its water column chemistry and plume paths that revealed the strongest thermal and chemical output recorded so far at the Mid-Atlantic ridge (German and Parson, 1998; Thurnherr and Richards, 2001; Thurnherr et al., 2002). In 1997, the first direct observations of the Rainbow hydrothermal field using the submersible Nautile (Barriga et al., 1997; Fouquet et al., 1997) revealed a vigorously venting hydrothermal system with 10 groups of active massive sulfide chimneys producing high temperature (up to 364 °C), acidic (pH = 2.8), Cl-, metal-and REE-rich fluids (Donval et al., 1997; Douville et al., 1997, 2002) with significant $H_2$ and methane concentrations (Charlou et al., 2002). The Rainbow vent fluids have the highest concentrations of Fe, Mn, Cu, Zn, Co and Ni ever reported for Mid-Atlantic ridge hydrothermal vents in both mafic and ultramafic environments. These particular properties were also imprinted within the surrounding hydrothermal sediments recording important