



# Sulfur and carbon geochemistry of the Santa Elena peridotites: Comparing oceanic and continental processes during peridotite alteration



Esther M. Schwarzenbach<sup>a,b,\*</sup>, Benjamin C. Gill<sup>a</sup>, Esteban Gazel<sup>a</sup>, Pilar Madrigal<sup>a</sup>

<sup>a</sup> Department of Geosciences, Virginia Tech, 4044 Derring Hall, Blacksburg, VA 24061, USA

<sup>b</sup> Institute of Geological Sciences, Freie Universität Berlin, 12249 Berlin, Germany

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## ABSTRACT

Ultramafic rocks exposed on the continent serve as a window into oceanic and continental processes of water–peridotite interaction, so called serpentinization. In both environments there are active carbon and sulfur cycles that contain abiogenic and biogenic processes, which are eventually imprinted in the geochemical signatures of the basement rocks and the calcite and magnesite deposits associated with fluids that issue from these systems. Here, we present the carbon and sulfur geochemistry of ultramafic rocks and carbonate deposits from the Santa Elena ophiolite in Costa Rica. The aim of this study is to leverage the geochemistry of the ultramafic sequence and associated deposits to distinguish between processes that were dominant during ocean floor alteration and those dominant during low-temperature, continental water–peridotite interaction.

The peridotites are variably serpentinized with total sulfur concentrations up to 877 ppm that is typically dominated by sulfide over sulfate. With the exception of one sample the ultramafic rocks are characterized by positive  $\delta^{34}\text{S}_{\text{sulfide}}$  (up to +23.1‰) and  $\delta^{34}\text{S}_{\text{sulfate}}$  values (up to +35.0‰). Carbon contents in the peridotites are low and are isotopically distinct from typical oceanic serpentinites. In particular,  $\delta^{13}\text{C}$  of the inorganic carbon suggests that the carbon is not derived from seawater, but rather the product of the interaction of meteoric water with the ultramafic rocks. In contrast, the sulfur isotope data from sulfide minerals in the peridotites preserve evidence for interaction with a hydrothermal fluid. Specifically, they indicate closed system abiogenic sulfate reduction suggesting that oceanic serpentinization occurred with limited input of seawater. Overall, the geochemical signatures preserve evidence for both oceanic and continental water–rock interaction with the majority of carbon (and possibly sulfate) being incorporated during continental water–rock interaction. Furthermore, there is evidence for microbial activity that was possibly stimulated by carbon sourced from water–rock interaction with adjacent sediments or fluid inclusions. This study provides detailed insight into the complex hydrothermal history of continental serpentinization systems and adds to our understanding of the carbon and sulfur cycling within peridotite-hosted hydrothermal systems.

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## 1. Introduction

Hydrothermal alteration of ultramafic rocks is a key process in many global geochemical cycles (Alt et al., 2013; Früh-Green et al., 2004) and supports microbial life through abiogenic production of hydrogen and reduced organic compounds (Lang et al., 2012; Proskurowski et al., 2008). On the ocean floor serpentinization commonly occurs where detachment faulting exposes mantle rock to seawater. In continental settings serpentinization can occur when meteoric water infiltrates and interacts with obducted ultramafic rock. During serpentinization various elements are exchanged between fluid and rock transforming

the chemical composition of both the interacting fluid (e.g. ocean water) and the exposed mantle rock (e.g. Früh-Green et al., 2004; Janeky and Seyfried, 1986). In continental environments, serpentinization produces very similar fluid chemistries to those found in oceanic settings – Ca-rich, highly alkaline fluids (pH  $\geq$  9–12) that are rich in  $\text{H}_2$  and  $\text{CH}_4$ , but poor in Mg and are typically strongly depleted in total dissolved carbon contents (Boschetti and Toscani, 2008; Cipolli et al., 2004; Kelley et al., 2001; Marques et al., 2008; Neal and Stanger, 1983). Interaction of these Ca-rich, alkaline fluids with dissolved carbonate in seawater or atmospheric  $\text{CO}_2$  results in the formation of widespread carbonate deposits (Clark and Fontes, 1990; Kelley et al., 2001; Schwarzenbach et al., 2013a). Thus, in recent years peridotite-hosted systems have also been studied due to their potential capacity to sequester  $\text{CO}_2$  over long, geologically relevant time-scales (Boschi et al., 2009; Kelemen and Matter, 2008; Schwarzenbach et al.,

\* Corresponding author at: Institute of Geological Sciences, Freie Universität Berlin, 12249 Berlin, Germany. Tel.: +49 30 838 58 952; fax: +49 30 838 70763.

E-mail address: [esther.schwarzenbach@fu-berlin.de](mailto:esther.schwarzenbach@fu-berlin.de) (E.M. Schwarzenbach).

2013b). Furthermore, the abundant availability of H<sub>2</sub> and reduced organic compounds in these systems has led to the hypothesis that they may have served as the origin for early life on Earth and that such environments may host life forms on other planetary bodies (Martin and Russell, 2007; McCollom, 1999; Russell et al., 2010). In this regard, the accessibility of environments that host continental serpentinization makes these systems a natural laboratory to study low temperature peridotite alteration and their role in supporting microbial life.

Continental serpentinization systems have been described at numerous locations globally, including the Western USA (Barnes et al., 1967), Oman (Neal and Stanger, 1983), the Voltri Massif in Italy (Schwarzenbach et al., 2013b), in Greece (Etiopie et al., 2013), Portugal (Marques et al., 2008), and Newfoundland (Szponar et al., 2012). In this study, we will focus on a recently described system in the Santa Elena Ophiolite of Costa Rica (Sanchez-Murillo et al., 2014). We present a study of the carbon and sulfur geochemistry of the ultramafic basement and the carbonate deposits in this ophiolite sequence and compare them to the recorded geochemical signatures of other similar serpentinization systems. In particular, we identify and differentiate between the processes occurring during different stages of the evolution of the ultramafic rocks. Obducted serpentinites typically record evidence for a large range of processes that took place on the ocean floor, possibly during obduction, and during interaction with meteoric water after their emplacement on the continent.

The sulfur and carbon geochemistry of these rocks records both biogenic and abiogenic processes that take place during water–rock interaction. Seawater-derived fluids can mix with mantle-derived fluids, microbes utilize sulfur and carbon-species, and at higher temperatures abiogenic redox reactions may occur. Previous studies have shown that microbial activity is abundant in oceanic serpentinization environments; sulfate-reducers are present in the chimneys and the subsurface of the Lost City hydrothermal field along the Mid-Atlantic Ridge (e.g. Brazelton et al., 2006; Kelley et al., 2005; Schrenk et al., 2004), and evidence for microbial sulfate reduction has also been detected in sulfur isotope signatures of ancient, oceanic peridotite-hosted hydrothermal systems such as in calcite-veined serpentinites from the Iberian Margin and the Northern Apennine ophiolite (Alt and Shanks, 1998; Schwarzenbach et al., 2012). Similarly, microbial communities are found in association with continental serpentinization environments and may primarily be supported by the serpentinization fluids (e.g. Brazelton et al., 2013). While microbial life appears abundant in these systems, various studies have shown that the alkaline end-member fluids in serpentinization environments are extremely depleted in dissolved inorganic carbon or DIC (Lang et al., 2012; Schwarzenbach et al., 2013b), which is essential for the abiogenic production of reduced organic compounds that are an energy source for microbial life (Lang et al., 2010, 2012). In this study, we specifically aim to distinguish between primary mantle signatures, ocean floor and later low-temperature, continental alteration in order to provide better insight into the source and speciation of carbon and sulfur during the serpentinization process in these environments. This will further allow us to determine the role of these elements in facilitating microbial activity specifically during the less well-studied continental water–rock interaction.

## 2. Geological setting

The Santa Elena ophiolite is located on the northwest coast of Costa Rica and covers an area of 250 km<sup>2</sup> of mostly mafic and ultramafic lithologies that were emplaced during the Upper Cretaceous (Fig. 1; Baumgartner and Denyer, 2006; Denyer and Gazel, 2009; Gazel et al., 2006). The ophiolite is predominantly comprised of variably serpentinized peridotites (lherzolites, harzburgites and dunites), locally layered gabbros, and mafic dikes that intrude the peridotites (Gazel et al., 2006; Madrigal et al., 2015). To the east, the peridotites are covered by rudist reef limestones of Campanian age. To the south, the

Santa Elena peninsula is made up of the Santa Rosa accretionary complex, which is composed of basaltic lavas and various sedimentary lithologies: radiolarian cherts, tuffaceous mudstones, pelagic limestones, black shales, sandstones, turbidites, breccias and conglomerates (Baumgartner and Denyer, 2006; Denyer and Gazel, 2009). The Santa Rosa accretionary complex is locally also exposed in a tectonic window in the center of the peninsula (Fig. 1).

The Santa Elena ophiolite was formed along an ultra-slow to slow-spreading oceanic ridge with emplacement of the mafic dikes around 131–116 Ma (Madrigal et al., 2015). The mafic lithologies are locally hydrothermally altered, which has been attributed to ocean floor metasomatism (Gazel et al., 2006). The peridotites are variably serpentinized (30–100%) with estimated serpentinization temperatures < 250 °C based on mineralogical evidence (Schwarzenbach et al., 2014). The sulfide and metal mineral assemblages indicate highly reducing conditions and low (<1) water–rock ratios during serpentinization. They also preserve unusual Cu-rich metals and sulfides, which has been attributed to the introduction of a high-temperature fluid most likely post-dating serpentinization (Schwarzenbach et al., 2014). The specific tectonic evolution of this ophiolite sequence is still controversial and subject of current research (Escuder-Virueite and Baumgartner, 2014; Madrigal et al., 2015). However, there is increasing evidence that serpentinization occurred primarily when sections of the upper mantle were exposed to seawater along a mid-ocean ridge, though, fluid infiltration was limited (Schwarzenbach et al., 2014). Later, subsequent emplacement on the continent allowed for continued serpentinization induced by the infiltration of meteoric water.

## 3. Sampling and analytical methods

### 3.1. Previous studies and sampling

The springs of the Santa Elena Ophiolite have been studied as part of a collaborative project with focus on the fluid chemistry, microbiology and geochemistry of the carbonate deposits and basement rocks (Sanchez-Murillo et al., 2014). The location of the sampled springs and ultramafic rocks are shown in Fig. 1. The water chemistry of the springs ranges from Mg–HCO<sub>3</sub>-rich fluids to highly alkaline Ca–OH spring waters. Detailed fluid chemistry data and initial gene sequence data can be found in Sanchez-Murillo et al. (2014) and here we use the same names of the springs as found in that study.

Carbonate deposits associated with Mg–HCO<sub>3</sub> and Ca–OH springs in the eastern part of the ophiolite (Fig. 1) were sampled at various locations within the riverbeds. Ultramafic basement rocks were sampled throughout the Santa Elena ophiolite. We distinguish between two groups of ultramafic rocks: Group A includes the peridotite basement that was not in any obvious way affected by interaction with alkaline fluids. Group B includes the spring serpentinites, which are the serpentinite samples that were taken in the vicinity of the Mg–HCO<sub>3</sub> to Ca–OH type spring waters. However, we note that none of these serpentinites were in direct contact with spring water at the time of sampling. Though, sampling took place during the dry season and it is possible that the serpentinites interacted with spring waters during the wet season.

### 3.2. Analytical methods

#### 3.2.1. Sample preparation and mineralogy

All analytical measurements and sample preparation of the Santa Elena peridotites and carbonates were performed at the Department of Geosciences at Virginia Tech. The carbonate samples were prepared by drilling out individual depositional layers of carbonates to reveal heterogeneities within different layers or crushed with an agate mortar for bulk rock analysis. Carbonate precipitates from the rivers were first dried at 40 °C in the oven. Before sample analyses all samples were homogenized by hand with the agate mortar. The mineralogy of the

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