The distribution and abundance of halogens in eclogites: An in situ SIMS perspective of the Raspas Complex (Ecuador)

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ABSTRACT

We present in situ secondary ion mass spectrometry (SIMS) and electron microprobe analyses of coexisting garnet, omphacite, phengite, amphibole, and apatite, combined with pyrohydrolysis bulk-rock analyses to constrain the distribution, abundance, and behavior of halogens (F and Cl) in six MORB-like eclogites from the Raspas Complex (Southern Ecuador). In all cases concerning lattice-hosted halogens, F compatibility decreases from apatite (1.47–3.25 wt%), to amphibole (563–4727 μg/g), phengite (610–1822 μg/g), omphacite (6.5–54.1 μg/g), and garnet (1.7–8.9 μg/g). The relative compatibility of Cl in the assemblage is greatest for apatite (192–515 μg/g), followed by amphibole (0.64–82.7 μg/g), phengite (1.2–2.1 μg/g), omphacite (<0.05–1.0 μg/g), and garnet (<0.05 μg/g). Congruence between SIMS-reconstructed F bulk abundances and yield-corrected bulk pyrohydrolysis analyses indicates that F is primarily hosted within the crystal lattice of eclogitic minerals. However, SIMS-reconstructed Cl abundances are a factor of five lower, on average, than pyrohydrolysis-derived bulk concentrations. This discrepancy results from the contribution of fluid inclusions, which may host at least 80% of the bulk rock Cl. The combination of SIMS and pyrohydrolysis is highly complementary. Whereas SIMS is well suited to determine bulk F abundances, pyrohydrolysis better quantifies bulk Cl concentrations, which include the contribution of fluid inclusion-hosted Cl. Raspas eclogites contain 145–258 μg/g F and at least 7–11 μg/g Cl. We estimate that ~95% of F is retained in the slab through eclogitization and returned to the upper mantle during subduction, whereas at least 95% of subducted Cl is removed from the rock by the time the slab equilibrates at eclogite facies conditions. Our calculations provide further evidence for the fractionation of F from Cl during high-pressure metamorphism in subduction zones. Although the HIMU (high U/Pb) mantle source (dehydrated oceanic crust) is often associated with enrichments in Cl/K and F/Nd, Raspas eclogites show relatively low halogen ratios identical within uncertainty to depleted MORB mantle (DMM). Thus, the observed halogen enrichments in HIMU ocean island basalts require either further fractionation during mantle processing or recycling of a halogen-enriched carrier lithology such as serpentinite into the mantle.

Keywords: Eclogite, halogens, subduction, SIMS, nominally anhydrous minerals, HIMU; Halogens in Planetary Bodies

INTRODUCTION

Our understanding of the abundance and distribution of halogens in subducted slabs is limited. Hydrothermally altered oceanic crust (AOC) is thought to be a major halogen carrier during subduction, where F and Cl substitute into the hydroxyl sites of hydrous minerals such as amphibole and mica (Ito et al. 1983; Philippot et al. 1998; Van den Bleeken and Koga 2015; Barnes et al. 2018). Bulk estimates of pre-subduction AOC vary from 50–253 μg/g Cl and 216–400 μg/g F (Ito et al. 1983; Straub and Layne 2003; Barnes and Cisneros 2012; Van den Bleeken and Koga 2015; Chavrit et al. 2016). More recently, primary halogen measurements of altered oceanic crust from the East Pacific Rise (Penrose-type oceanic crust) and Atlantis Bank (SWIR, ultra-slow spreading) have shown extreme variability with both stratigraphic depth and lithology (Kendrick 2019a, 2019b). Bulk halogen measurements of blueschists and eclogites thought to represent high-pressure metamorphic AOC are also sparse. In a study of mélangé rocks from Syros, Greece, Marshall et al. (2009) measured the bulk Cl content of eclogites (28–60 μg/g) and called into question previous estimates of eclogitized AOC Cl abundances, e.g., 100–200 μg/g Cl of Philippot et al. (1998), speculating that they may be overestimated. Pagé et al. (2016) analyzed a suite of blueschists from northwest Turkey; their results (8–22 μg/g Cl) also indicate that bulk eclogitized AOC could host less Cl than previously thought. Debret et al. (2016) reconstructed bulk halogen concentrations (57–79 μg/g Cl and 10–62 μg/g F) from in situ secondary ion mass spectrometry (SIMS) analyses for both blueschists and eclogites from the Western Alps, cautioning that typical bulk halogen measurements are...