Halogens in amphibole and mica from mantle xenoliths: Implications for the halogen distribution and halogen budget of the metasomatized continental lithosphere

JOHANNES G. HECKER¹, MICHAEL A.W. MARKS¹,*,†, THOMAS WENZEL¹, AND GREGOR MARKL¹

¹Department of Geosciences, Eberhard-Karls-Universität Tübingen, Wilhelmstrasse 56, 72074 Tübingen, Germany

ABSTRACT

This study reports halogen contents (F and Cl) of amphibole and phlogopite derived from mantle xenoliths and one peridotite massif, for amphibole and phlogopite megacrysts and ultramafic magmatic cumulates (hornblendites) found in alkaline volcanic rocks from 12 localities in Europe and Africa. Amphibole and phlogopite contain more F than Cl with F/Cl ratios reaching about 160 in phlogopites and 50 in amphiboles. Phlogopites are higher in F (median of 3400 μg/g) than amphibole (median of 1000 μg/g), while median Cl contents are higher in amphibole (290 μg/g) compared to phlogopite (180 μg/g).

The Cl contents and the F/Cl ratios in amphibole and phlogopite from mantle xenoliths exhibit large differences between samples of the same region, recording very large variations of halogen contents in the continental lithosphere. We suggest that the halogen content in such samples largely depends on the initial composition of percolating melts and fluids in the continental lithosphere. During reaction of these agents with peridotitic wall-rocks, Cl is preferentially retained in the fluid as it is much more incompatible compared to water and F. This desiccation effect continuously increases salinity (Cl content) and decreases the F/Cl ratio in the agent with time, causing variable Cl contents and F/Cl ratios in amphibole and phlogopite at a specific locality. Subsequent partial melting processes may then sequester and re-distribute, especially Cl among amphibole, phlogopite and melts/fluids as a result of its strong incompatibility, whereas F is much less affected as it behaves slightly compatible. The impact of even small amounts of amphibole and mica on the total halogen budget in the continental lithosphere is significant and both minerals can effectively contribute to the high halogen contents typical of alkaline melts.

Keywords: Continental lithosphere, halogens, amphibole, phlogopite, metasomatism; Halogens in Planetary Systems

INTRODUCTION

The Earth’s lithospheric mantle contains significant amounts of halogens (F, Cl, Br, and I) with clear differences between different reservoirs (e.g., Klemme and Stalder 2018; Frezzotti and Ferrando 2018). The major process for transferring halogens from the Earth’s surface into the lithospheric mantle is their transport through subduction zones, either through marine pore fluids or rocks rich in hydrous silicates in the subducted crust or serpentinites (e.g., Rüpke et al. 2002; Kendrick et al. 2011, 2017; Kendrick 2018; Barnes et al. 2018; Pagé and Hattori 2019). Eventually, halogens may return to the surface via arc magmatism, which is believed to be important for the heavier halogens (Cl, Br, and I), while F is thought to be retained much longer in the subducted slab and, thus, may be transported to greater mantle depths (e.g., Barnes et al. 2018 and references therein). Most of the heavy halogens are released from the subducted slab between the lizardite-antigorite transition and the eclogite facies boundary (e.g., John et al. 2011; Debret et al. 2014). Very shallowly released halogenates (at depths of less than 30 km) could even be directly recycled back into the oceanic crust (e.g., Hattori and Guillot 2003; Marschall et al. 2009, Pagé et al. 2019).

Metasomatism in the continental lithosphere may happen through silicate and carbonate metamorphism or through fluids and brines; Selverstone and Sharp (2011) propose three different settings for such metasomatic events: Rift settings, plume settings, and subduction settings. Rift and plume settings can result in metasomatic processes through silicate or carbonate melts, whereas subduction zones mostly release fluids and brines that will interact with the overlying mantle wedge. Two major categories of mineral hosts for halogens exist in the continental lithosphere: (1) volatile-bearing minerals (apatite, amphibole, and mica) that formed by metasomatism in the lithospheric mantle (Smith 1981; Smith et al. 1981; Ionov et al. 1997; Klemme and Stalder 2018) and (2) nominally anhydrous mantle (NAM) minerals, such as olivine, garnet, orthopyroxene, and clinopyroxene (e.g., Mosenfelder and Rossman 2013a, 2013b; Grützner et al. 2017; Uran et al. 2017).

The metasomatized continental lithosphere is an important source of alkaline magmas (Pilet et al. 2008; Mayer et al. 2014), which are known to be exceptionally halogen-rich (e.g., Bailey and Hampton 1990; Köhler et al. 2009). Therefore, mantle xenoliths from alkaline magmatic provinces represent the perfect sample type when studying modal mantle metasomatism with respect to halogens and their potential connection to halogen-rich magmatism. For the present study, we investigated amphibole- and phlogopite-bearing mantle rocks and amphibole and phlogopite megacrysts hosted by alkaline igneous rocks. For comparison, we also analyzed amphibole from several mafic magmatic cumulates (hornblendites). The data derived from this comprehensive sample