Amphibole fractionation and its potential redox effect on arc crust: Evidence from the Kohistan arc cumulates

JINGBO ZHANG1†, RUI WANG1,*, and JUN HONG2

1State Key Laboratory of Geological Processes and Mineral Resources, Institute of Earth Sciences, China University of Geosciences, Beijing 100083, China
2MNR Key Laboratory for the Study of Focused Magmatism and Giant Ore Deposits, Xi’an Center of Geological Survey, CGS, Xi’an 710054, China

ABSTRACT

Arc magmas, a major contributor to continental crust growth, are thought to be more oxidized than mid-ocean ridge basalts as reflected by an enrichment in ferric iron relative to ferrous iron. But how arc magmas become oxidized is hotly debated. It is acknowledged that the fractionation of common Fe-rich phases (e.g., amphibole) may change the Fe valence of the derivative melt. Amphibole has Fe-rich compositions commonly found in arc systems. We present high-precision (±0.01%) Fe valence data of amphibole and cumulates from the Kohistan arc determined by Mössbauer spectroscopy and bulk cumulate Fe³⁺/ΣFe ratios by wet chemistry. We evaluate the Fe³⁺/ΣFe trend of Fe-rich amphibole during arc magma fractionation. Our results show that bulk Fe³⁺/ΣFe ratio of cumulates in mature island arc settings is mainly controlled by amphibole due to its abundance and decreases (from 0.4 to 0.2) with decreasing Mg# as Fe³⁺/ΣFe ratios decrease in amphibole (from 0.35 to 0.2). Our modeling suggests that amphibole fractionation from parental arc magmas to Fe³⁺/ΣFe above 0.2 may lead to an increase in Fe³⁺/ΣFe ratios of middle–late stage residual melts by 0.1–0.3, and the partitioning of ferrous Fe into amphibole increases with the evolution of arc magmas. Our findings highlight the importance of petrological processes in the magma that contribute to the production of fertile arc crust.

Keywords: Amphibole, iron valence, Kohistan cumulate, redox state, porphyry deposit

INTRODUCTION

The oxidation state reflected by oxygen fugacity (fO₂) plays an important role in many physical and chemical processes, including metasomatism, magma genesis, ore-forming processes, and atmospheric evolution (e.g., Cottrell and Kelley 2011; Frost and McCammon 2008). Previous studies indicate that arc magmas are oxidized with AFMQ (relative to fayalite-magnetite-quartz buffer) of +0.5 to +2, and locally may be greater than +3 (Richards 2015; and references therein). However, there is a debate on whether the oxidized nature of arc magmas is inherited from the mantle source or acquired by magmatic differentiation, crustal interaction, or degassing during magma upwelling (e.g., Brunce et al. 2014; Burgisser and Scailliet 2007; De Hoog et al. 2004; Kelley and Cottrell 2009; Lee et al. 2010).

Iron is the most abundant multi-valence element in magmatic systems; thus, Fe-bearing minerals play an important role in modulating redox conditions. One hypothesis suggests that garnet fractionation in thick continental arcs results in the oxidation of the residual melt due to its preference for Fe³⁺ over Fe²⁺ (Tang et al. 2018, 2019a). Although garnet may crystallize at the base of mature island arcs built on crust >30 km thick, such as Talkeetna arc in south-central Alaska (Buchholz and Kelemen 2019; Kelemen et al. 2014), its redox effect may be much less significant due to its generally low proportions in island arc cumulates. Amphibole fractionation is more common in arc systems (Davidson et al. 2007; Dessimoz et al. 2012), and amphibole-bearing cumulates are frequently observed at convergent margins (Jagoutz and Schmidt 2012; Santana et al. 2020; Xu et al. 2019; Zhang et al. 2021; Zhu et al. 2019). Previous studies focused on the partitioning of Fe³⁺/ΣFe [atomic Fe³⁺/(Fe³⁺+Fe²⁺)] between synthetic amphibole and basanitic melt at 1100–1175 °C and 1.5–2.0 GPa (King et al. 2000). However, these conditions are not equivalent to those in arc magmas, and whether amphibole fractionation can control the Fe³⁺/ΣFe of evolving arc magmas is still unclear.

The Kohistan arc in Northern Pakistan is a mature island arc with exposures of a continuous section from the lithospheric mantle through lower crustal cumulates to mid-crustal gabbros and granitoids (Dhuime et al. 2007; Jagoutz 2014; Jagoutz and Schmidt 2012). The cumulates represent early products of crystallization during hydrous, high-pressure fractionation starting from a mantle-derived basaltic melt (Jagoutz et al. 2011), and they have not experienced subsequent crustal processes, such as assimilation or degassing (Jagoutz and Schmidt 2012). There is a complementary relationship between the ultramafic to mafic cumulates and shallow-level intermediate-to-felsic arc magmas; the granitoids in the Kohistan batholith can be successfully modeled by crustal fractionation of the minerals present in the cumulates (Jagoutz et al. 2009; Jagoutz 2010). Thereby, these cumulates provide an ideal case to study the evolution of the Fe³⁺/ΣFe ratio and potential redox state of arc magmas. In this