Oxidation of arcs and mantle wedges by reduction of manganese in pelagic sediments during seafloor subduction

SHUGUANG SONG1,*, SHITING YE1, MARK B. ALLEN2, YAOLING NIU3, WEIDONG SUN3, AND LIFEI ZHANG1

1MOE Key Laboratory of Orogenic Belt and Crustal Evolution, School of Earth and Space Sciences, Peking University, Beijing 100871, China
2Department of Earth Sciences, Durham University, Durham DH1 3LE, U.K.
3Center of Deep Sea Research, Institute of Oceanography, Chinese Academy of Sciences, Qingdao 266071, China

ABSTRACT

Plate subduction links the Earth’s surface and interior and may change the redox state of the Earth’s mantle. Mantle wedges above subduction zones have high oxygen fugacity compared with other mantle reservoirs, but the cause is debated. Here we analyze high-pressure metamorphic rocks derived from ferromanganese pelagic sediments in the Qilian subduction complex, northwest (NW) China. We show that progressive metamorphism is a process of reducing reactions, in which Mn$^{2+}$ is reduced to Mn$^{3+}$. On the global scale, such reactions would release significant amounts of oxygen ($\sim 1.27 \times 10^{12}$ g year$^{-1}$), estimated from the global flux of MnO in sediments passing into subduction zones. This budget is sufficient to raise the oxygen fugacity of the mantle wedge, hence arc magmas, to a higher level than other mantle reservoirs. In contrast, ferric iron (Fe$^{3+}$) enters hematite, aegirine, and garnet, without valence change and plays little role in the oxidation of the mantle wedge. Fe$^{3+}$ remains stable to depths of $>100$ km but will transfer to the deeper mantle along with the subducting slab. The manganese reduction process provides a new explanation for high oxygen fugacity in the mantle wedge.

Keywords: Ferromanganese pelagic sediments, high-pressure metamorphism, reductive reactions, subduction zone, mantle oxidation

INTRODUCTION

Subduction zones are key places for understanding the dynamics of the Earth and play an important role in the oxidation state and recirculation of oxygen and water (Wood et al. 1990; Frost and McCammon 2008; Evans 2012; Kelley and Cottrell 2009; Debret et al. 2014). It has been demonstrated that mantle wedges above subduction zones are more oxidized than oceanic or ancient cratonic mantle by the high oxidation state of both island-arc tholeiites and peridotites from the mantle wedges (Arculus 1985; Parkinson and Arculus 1999; Evans and Tomkins 2011; Richards 2015; Buchholz and Kelemen 2019). Redox reactions in oceanic subduction zones must play important roles in controlling the oxidation state of the mantle wedge and the generation of island-arc tholeiites and also in dictating the circulation of oxygen during whole-mantle convection.

The major factors controlling mantle oxygen fugacity, including volatile budgets and mineral assemblages, and how tectonic processes drive its secular evolution, are still debated (Kelley and Cottrell 2009; Lee et al. 2010). Dehydration fluids produced by high-pressure metamorphism in subduction channels are thought to be responsible for the oxidation and partial melting of the mantle wedge (Brandon and Draper 1996; Song et al. 2009; Foley 2011), either directly through the addition of volatiles, or indirectly if hydrous fluids carry dissolved Fe$^{3+}$ or sulfate (Kelley and Cottrell 2009; Malaspina et al. 2017). Previous work suggested that oxidized Fe, C, and S in sediments, altered ocean crust, and partially serpentinitized lithospheric mantle in the subduction zones could also be important controls of the redox state of the mantle (Evans and Tomkins 2011; Evans 2012; Debret 2014; Bénard et al. 2018). However, large amounts of organic carbon and sulfides in pelagic sediments (Alt 1995; Evans 2012; Plank and Langmuir 1998; Plank 2014) are in a reduced state and may need extra oxygen, while carbonates and sulfates can be stable at depths $>100$ km (Frost and McCammon 2008; Wang et al. 2016). Li et al. (2020) demonstrated that slab-derived fluids provide negligible sulfate to oxidize the sub-arc mantle. Thus, S may not play an important role as an oxidizer in subduction zones. Several aspects of the redox state in subduction zones remain unclear, notably: (1) how to generate high-$f_O$, fluid and the quantification of fluid fluxes, and (2) the behavior of Fe$^{3+}$ in subduction channels. The details of redox reactions in subduction zones are poorly known.

Ferromanganese (Fe-Mn) chert is a common pelagic sedimentary rock both on the modern ocean floor and in subduction-zone complexes preserved in orogenic belts. The majority of iron and manganese in oceanic sediments is held in Mn-rich polymetallic nodules/crusts and banded Fe-Mn layers developed in deep ocean basins (Bonatti and Nayudu 1965). These rocks are carried to mantle depths during subduction and interact with mantle wedge as redox factors (Thamdrup et al. 1994; Tumiati et al. 2015). In this paper, we present detailed petrologic studies of Mn-rich, high-pressure metasedimentary rocks from a representative, exhumed, ancient subduction complex to define the Mn mineral