Quantitative microscale Fe redox imaging by multiple energy X-ray fluorescence mapping at the Fe K pre-edge peak

ERIC T. ELLISON1,*, LISA E. MAYHEW1, HANNAH M. MILLER1, AND ALEXIS S. TEMPLETON1

1Department of Geological Sciences, UCB 399, University of Colorado–Boulder, Boulder, Colorado 80309, U.S.A.

ABSTRACT

Fe oxidation/reduction reactions play a fundamental role in a wide variety of geological processes. In natural materials, Fe redox state commonly varies across small spatial scales at reaction interfaces, yet the approaches available for quantitatively mapping the Fe redox state at the microscale are limited. We have designed an optimized synchrotron-based X-ray spectroscopic approach that allows microscale quantitative mapping of Fe valence state by extending the Fe XANES pre-edge technique. An area of interest is mapped at nine energies between 7109–7118 eV and at 7200 eV, allowing reconstruction, baseline subtraction, and integration of the pre-edge feature to determine Fe(III)/ΣFe with 2 μm spatial resolution. By combining the Fe redox mapping approach with hyperspectral Raman mineralogy mapping, the Fe oxidation state distributions of the major mineral phases are revealed. In this work, the method is applied to a partially serpentinized peridotite with various Fe-bearing secondary mineral phases to trace the Fe transformations and redox changes that occurred during its alteration. Analysis with the Fe redox mapping technique revealed that the peridotite contained relict olivine with abundant Fe(II), while serpentine, pyroaurite, and another hydroxide phase are secondary mineral reservoirs of Fe(III). Although serpentine is not Fe-rich, it contained approximately 74% ± 14% Fe(III)/ΣFe. These analytical results are integral to interpreting the sequence of alteration reactions; serpentization of primary olivine formed Fe(II)-rich brucite and oxidized serpentine, which could have contributed to H2 production during serpentization. Subsequent weathering by oxidizing, CO2-bearing fluids led to the partial carbonation and oxidation of brucite, forming pyroaurite and a hydroxide phase containing dominantly Fe(III). This Fe redox imaging approach is applicable to standard petrographic thin sections or grain mounts and can be applied to various geologic and biogeochemical systems.

Keywords: Iron, redox, oxidation state, X-ray fluorescence mapping, microscale, pre-edge, serpentinization, Oman ophiolite

INTRODUCTION

Fe oxidation and reduction reactions during mineral dissolution and precipitation play a dominant role in numerous geological and environmental processes; thus, determining the Fe redox state [Fe(III)/ΣFe] of natural materials has many applications. For example, Fe redox reactions exert a fundamental control on chemical weathering in mine drainage systems (Johnson et al. 2014), bedrock weathering and saprolitization (Buss et al. 2008), soil nutrient cycling and availability (Prietzel et al. 2007; Colombo et al. 2014), iron transport and bioavailability in the oceans (Lam et al. 2012; Toner et al. 2012), and stabilization or mobilization of groundwater contaminants including uranium, selenium, and arsenic (Myneni et al. 1997; O’Loughlin et al. 2003; Essilifie-Dughan et al. 2013; Ying et al. 2013). Additionally, iron valence can help constrain the oxygen fugacity of geological materials, revealing key insights into mantle processes and planetary formation (Berry et al. 2008; Cottrell and Kelley 2011; Elmaleh et al. 2015; Le Guillou et al. 2015).

There is a need for spatially resolved methods to determine Fe redox in complex systems at the microscale. The progression of Fe redox reactions in many systems may be recorded by gra-