X-ray absorption characterization of Cr in forsterite within the MacAlpine Hills 88136 EL3 chondritic meteorite

DAVID A. McKEOWN1,*, ANDREW C. BUECHELE1, RYAN TAPPERO2, TIMOTHY J. MCCOY3 AND KATHRYN G. GARDNER-VANDY3

1Vitreous State Laboratory, The Catholic University of America, 620 Michigan Avenue NE, Washington, D.C. 20064, U.S.A.
2Photon Sciences Department, Brookhaven National Laboratory, Upton, New York 11793, U.S.A.
3Department of Mineral Sciences, National Museum of Natural History, Smithsonian Institution, Washington, D.C. 20560-0119, U.S.A.

ABSTRACT

Chromium K-edge X-ray absorption spectra were collected to characterize Cr in forsterite (Mg2SiO4) as well as sulfides within the MAC 88136 EL3 chondrite to determine Cr valence and to see whether forsterite within this meteorite can be used as a Cr2+-silicate standard. Spectra were measured on several areas within a nearly pure 100 × 200 μm forsterite grain containing 0.13 wt% Cr. XANES findings indicate highly reduced Cr2+ species, with no clear evidence of Cr3+ or Cr4+. EXAFS data indicate an average 2.02 Å Cr-O nearest-neighbor distance, consistent with Cr-O distances found in square-planar Cr2O4 sites observed in synthetic crystalline silicates, and an average 2.69 Å Cr-Si second-nearest neighbor distance, consistent with Cr2+ substituting for Mg2+ in the forsterite M(1) site. Nearest-neighbor Debye-Waller factor and coordination number parameters indicate Cr2+ is likely entering forsterite in disordered sites that are possible intermediates between M(1) and square-planar Cr2O4 configurations. Preliminary Cr XAS measurements on sulfides within this meteorite also indicate Cr2+ in CrS6 octahedra.

Keywords: Cr2+-silicate, meteorite, X-ray absorption spectroscopy

INTRODUCTION

Olivines [(Mg,Fe)2SiO4] within chondrules in chondritic meteorites sometimes contain significant amounts of chromium (Cr) incorporated into the silicate structure upon crystallization from the molten chondrule. Cr concentrations in unmetamorphosed chondrules can range upward to 1 wt% Cr2O3 (Weisberg et al. 2005). During subsequent thermal metamorphism, Cr diffuses from the olivine, providing a sensitive indicator of the relative degree of metamorphism (Weisberg et al. 2005, 2006; Grossman 2004). Consequently, olivine within most metamorphosed, chondritic meteorites typically has only trace amounts of Cr. Among those chondritic meteorites with Cr-bearing olivines, those with the most Cr in olivine are the least metamorphosed, including the CO3.0 chondrite Allan Hills (ALH) A77307, the LL3.0 chondrite Semarkona, and the EL3 chondrite MacAlpine Hills (MAC) 88136. MAC 88136 contains forsterite (Mg2SiO4) with relatively “high” Cr-concentrations of up to 0.7 wt% Cr2O3 (Weisberg et al. 1994, 2005).

The initial interest in characterizing chondritic Cr-bearing olivines is to identify a crystalline Cr2+-silicate standard to use for Cr valence X-ray absorption spectroscopy (XAS) studies of silicates synthesized under reducing conditions (McKeown et al. 2011). At the same time, understanding Cr valence states sheds light on the fO2 conditions of formation of these meteorites. Cr2+-silicates are not readily found in the oxidizing environments at or near the Earth’s crust, where Cr species are typically 6+ or 3+. In contrast, chondrule formation, crystallization, and chondrite metamorphism likely occurred under relatively reducing conditions, with fO2 ranging from ~IW (iron-wustite) to ~IW-8 (Fogel et al. 1989). Previous work has demonstrated the predominance of Cr2+ among chondrule olivines (Sutton et al. 1996), with the FeO-rich olivines in the CO3.0 chondrite ALH A77307 having a lower Cr2+/Cr3+ ratio (~0.3) than the FeO-poor olivines in the LL3.0 chondrite Semarkona (~0.9) (Sutton et al. 1996). Extending this trend, we have studied the relatively Cr-rich and FeO-poor olivines from the highly reduced EL3 chondrite MAC 88136 to improve the chances of collecting better signal-to-noise Cr2+-silicate XAS data.

An X-ray absorption spectrum is divided into two regions: the X-ray absorption near edge structure (XANES) that includes an absorption edge of the element of interest, and the extended X-ray absorption fine structure (EXAFS). The slope and shape of the absorption edge rise as well as the overall edge energy are sensitive to the valence of the absorbing element, where the overall edge energy increases with higher (more oxidized) valences. Relatively narrow features at the absorption edge can be due to single and multiple scattering contributions from the local atomic environment surrounding the absorbing element. The EXAFS data, by convention, are extracted from a spectrum at approximately 20 eV beyond the absorption edge to higher energies. In many cases, EXAFS oscillations are due primarily to single scattering of the spherical electron wave emitted by the absorbing atom (in this case Cr) from the arrangement of atoms surrounding the absorber. Through fitting procedures, EXAFS data are analyzed to quantitatively determine average bond distance [r (Å)], coordination number [n (atoms)], and disorder or Debye-Waller factor [σ² (Å²)] of shells of atoms around the absorber.