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Geochimica et Cosmochimica Acta 187 (2016) 294–310

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

The effect of site geometry, Ti content and Ti oxidation state on the Ti K-edge XANES spectrum of synthetic hibonite

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Received 11 February 2015; accepted in revised form 1 May 2016; available online 12 May 2016

Abstract

The Al-rich oxide hibonite ($CaAl_{12}O_{19}$) is modeled to be the second mineral to condense from a gas of solar composition and is found within calcium–aluminum-rich inclusions and the matrix of chondritic meteorites. Both Ti^{3+} and Ti^{4+} are reported in meteoritic hibonite, so hibonite has been proposed as a single mineral oxybarometer that could be used to elucidate conditions within the first 0.2 Myrs of the Solar System.

Synthetic hibonites with $Ti^{3+}/(Ti^{3+} + Ti^{4+})$ (hereafter $Ti^{3+}/\Sigma Ti$) ranging between 0 and 1 were prepared as matrix-matched standards for meteoritic hibonite. The largest yield of both Ti-free and Ti-bearing hibonite at ~1300 and ~1400 °C was obtained by a single sinter under reducing conditions.

In situ micro-beam Ti K-edge X-ray absorption near edge structure (XANES) spectra were recorded from the synthetic hibonites, as well as from terrestrial hibonite. Spectral features in the post-crest region were shown to correlate with the Ti^{4+} content. Furthermore, Ti^{4+} on the M2 trigonal bipyramidal and the adjoining M4 octahedral sites appears to cause variability in the post-crest region as a function of orientation. For this suite of synthetic hibonites it was observed that the pre-edge peak region is not influenced by orientation, but is controlled by $Ti^{3+}/\Sigma Ti$, site geometry and/or Ti concentration. In particular, the pre-edge peak intensities reflect Ti coordination environment and distortion of the M4 octahedral site. Therefore, although pre-edge peak intensities have previously been used to determine $Ti^{3+}/\Sigma Ti$ in meteoritic minerals, we excluded use of the pre-edge peak intensities for quantifying Ti valence states in hibonite.

The energy of the absorption edge at a normalized intensity of 0.8 ($E_{0.8}$) and the energy of the minimum between the pre-edge region and the absorption edge (E_{m1}) were found to vary systematically with $Ti^{3+}/\Sigma Ti$. $Ti^{3+}/\Sigma Ti$ in hibonite as a function of E_{m1} was modeled by a quadratic function that may be used to quantify $Ti^{3+}/\Sigma Ti$ in meteoritic hibonite when the synthetic hibonite standards are crystal-chemically matched to the natural samples and are measured during the same analytical session as the meteoritic hibonites.

Keywords: Hibonite; Synthesis; XANES spectroscopy; Ti^{3+}/Ti^{4+}; Valence state

1. INTRODUCTION

Hibonite is found in the matrix of chondritic meteorites and in calcium–aluminum-rich inclusions (CAIs), the oldest Solar System materials dated (Connelly et al., 2012). Many CAIs form by condensation and may then undergo multiple reprocessing events (Ireland, 1990) within the first 0.2 Myrs

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http://dx.doi.org/10.1016/j.gca.2016.05.001

of the Solar System (Connelly et al., 2012; Kita et al., 2013). As such, the composition and textural relationships of hibonite can be used to elucidate early Solar System processes.

The refractory element Ti (Lodders, 2003) may be accommodated within the hibonite structure as both Ti^{3+} and Ti^{4+}, so hibonite is potentially a single-mineral oxybarometer (Beckett et al., 1988). $Ti^{3+}/\Sigma Ti$ in hibonite may be determined stoichiometrically as Ti is often a major component within hibonite; Ti^{3+} substitutes directly for Al^{3+}, whereas Ti^{4+} undergoes a coupled substitution with Mg^{2+} for two Al^{3+} (Allen et al., 1978) such that Ti in excess of the amount of Mg (Fig. 1A) is inferred to be Ti^{3+}. Stoichiometric calculations are used for determining the Ti^{3+} content of fassaite (Haggerty, 1978; Simon et al., 1991; Simon et al., 2005; Grossman et al., 2008; Dyl et al., 2011). However, three reasons make it advantageous to measure the Ti^{3+}/Ti^{4+} ratio in hibonite directly. Firstly, the inclusion of additional redox-variable elements within meteoritic hibonites (*c.f.* Fig. 1B and C) complicates the stoichiometric calculation of $Ti^{3+}/\Sigma Ti$. Secondly, oxygen vacancies and/or cation defects (Beckett et al., 1988) in a chemically complex mineral such as hibonite may compromise stoichiometric calculations. Thirdly, many meteoritic hibonite grains are very small (e.g. with diameters of <3 μm), making contamination of elemental analyses by underlying phases and/or by adjacent minerals sometimes unavoidable (e.g., Weber and Bischoff, 1994).

$Ti^{3+}/\Sigma Ti$ has previously been determined for glasses and meteoritic hibonite using bulk analysis techniques such as titration (Schreiber et al., 1978; Tranell et al., 2002) and electron spin resonance (ESR) spectroscopy (Beckett et al., 1988), respectively. Titration is suitable for analysis of Fe-free compositions, but produces anomalously high $Ti^{3+}/\Sigma Ti$ values in Fe-bearing systems, as shown by Whipple (1979). ESR spectroscopy is restricted to the analysis of paramagnetic elements, so $Ti^{3+}/\Sigma Ti$ is determined by measuring the concentration of Ti^{3+}. Furthermore, ESR spectra may be complicated by the presence of other paramagnetic elements (Schreiber et al., 1978) and are interpreted in light of available structural data. For example, of the five Al sites in hibonite, Beckett et al. (1988) inferred from ESR spectra that Ti^{3+} occupied the M2 trigonal bipyramidal site, a key requirement for their proposed oxybarometer. However, a recent neutron powder diffraction (NPD) study by Doyle et al. (2014) showed that Ti^{3+} does not occupy the M2 site, but instead occupies the M4 octahedral site, and Ti^{4+} partitions between the M2 trigonal bipyramidal site and the M4 octahedral site.

Spectroscopic techniques such as X-ray absorption near edge structure (XANES) spectroscopy and electron energy-loss spectroscopy (EELS) may be used to determine the ratio of oxidation states for redox-variable elements directly as both methods explore the electronic structure of an atom. These techniques offer μm to nm spatial resolution (Smith et al., 2004; Schofield et al., 2010), are element-specific and are applicable to a range of elements, e.g., Ti (Waychunas, 1987; Stoyanov et al., 2007) and Fe (van Aken and Liebscher, 2002; Berry et al., 2008).

Approximately 100 nm thick sections are required for EELS analysis, for which focused ion beam (FIB) sections are extracted from polished sections. So, whether or not the samples are stable during EELS analysis, the sample preparation required for EELS is destructive. In contrast, XANES spectra can be recorded from samples mounted as unpolished grains or (preferably) polished sections

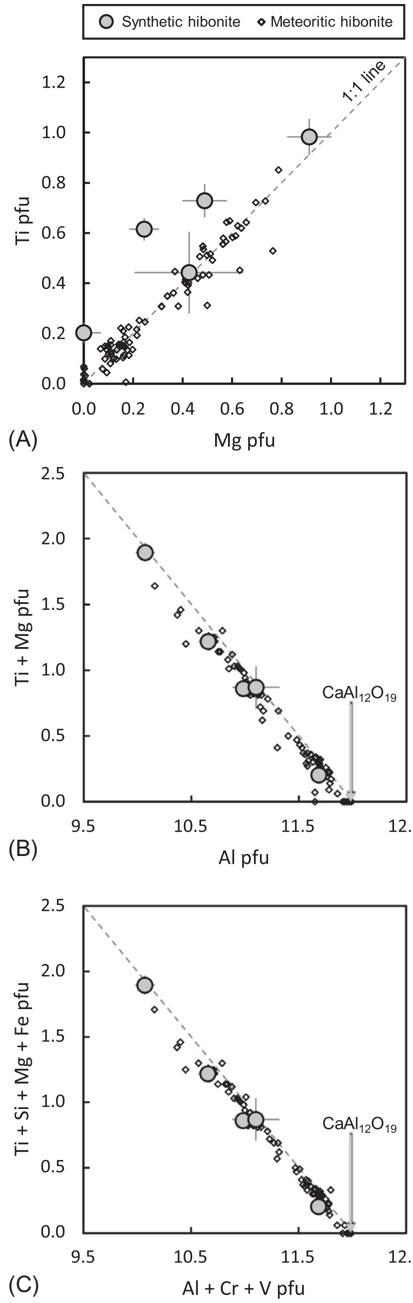

Fig. 1. Cations per formula unit (pfu) in synthetic and meteoritic hibonite: (A) Ti as a function of Mg; (B) Ti and Mg as a function of Al; and (C) Ti, Si, Mg and Fe as a function of Al, Cr and V. The dashed lines indicate the expected stoichiometric relationship between the cations ($y = 12 - x$). The meteoritic data are from Fuchs et al. (1973), Allen et al. (1978), Armstrong et al. (1982), Davis et al. (1982), Burns and Burns (1984), Ireland (1988), Weber and Bischoff (1994), Simon et al. (1997), Bischoff and Srinivasan (2003), Krot et al. (2004), Krot et al. (2006), Ushikubo et al. (2007), Rout et al. (2009) and Doyle (2012).