The oxidation state of sulfur in lunar apatite

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ABSTRACT

Lunar apatites contain hundreds to thousands of parts per million of sulfur. This is puzzling because lunar basalts are thought to form in low oxygen fugacity ($f_{O_2}$) conditions where sulfur can only exist in its reduced form ($S^{2-}$), a substitution not previously observed in natural apatite. We present measurements of the oxidation state of S in lunar apatites and associated mesostasis glass that show that lunar apatites and glass contain dominantly $S^{6+}$, whereas natural apatites from Earth are only known to contain $S^{2-}$. It is likely that many terrestrial and martian igneous rocks contain apatites with mixed sulfur oxidation states. The $S^{6+}/S^{2-}$ ratios of such apatites could be used to quantify the $f_{O_2}$ values at which they crystallized, given information on the portioning of $S^{6+}$ and $S^{2-}$ between apatite and melt and on the $S^{6+}/S^{2-}$ ratios of melts as functions of $f_{O_2}$ and melt composition. Such a well-calibrated oxybarometer based on this the oxidation state of S in apatite would have wide application.

Keywords: Moon, oxygen, apatite, sulfur

INTRODUCTION

Lunar apatites, melt inclusions, and glass beads contain concentrations of H, C, S, and Cl that suggest that at least some portions of the lunar crust, mantle, or both contain higher concentrations of these volatile elements than previously thought and perhaps even in concentrations similar to those observed for Earth (Saal et al. 2008; Boyce et al. 2010; Greenwood et al. 2011; Hauri et al. 2011; Chen et al. 2015; McCubbin et al. 2015; Wetzel et al. 2015). This information has led to significant recent interest in lunar volatiles and to efforts to explain these results in the context of models for the formation of the Moon. A puzzling aspect of the unexpectedly high volatile contents of lunar materials was the observation of hundreds to thousands of parts per million of S in apatite, similar to the levels observed in terrestrial igneous apatite (Boyce et al. 2010).

Terrestrial magmas typically formed at $f_{O_2}$ levels 4–5 orders of magnitude higher than the iron-wüstite oxygen buffer (referred to as IW+4 to IW+5). At these $f_{O_2}$ values, sulfur dissolved in the silicate liquids from which terrestrial apatites crystallize is present as sulfate (i.e., $SO_4^{2-}$ or $S^{6+}$) and sulfide (i.e., $S^{2-}$), but it has been generally believed that the sulfur in terrestrial apatites is present entirely as sulfide (Fleet 2005), with the sulfate anion in the apatite substituting for the phosphate anionic group, coupled with $SiO_2^4-$ or Na$^+$ to maintain charge balance (Pan and Fleet 2002). However, lunar rocks reflect much lower $f_{O_2}$ conditions, including at the point of apatite saturation and crystallization. Lunar apatites crystallize in the interstices of lunar basalts from late-stage, highly differentiated liquids, since only in such liquids does phosphorus reach sufficient concentrations for the liquids to become saturated with respect to apatite. The $f_{O_2}$ of these late-stage liquids in lunar basalts are constrained from petrographic descriptions of the phases present in the interstices (e.g., coexistence of Fe-metal, ulvospinel, ilmenite, and sometimes fayalite and/or silica) and are as low as IW-1 (e.g., El Goresy 1976). This is more than 4 orders of magnitude lower than the $f_{O_2}$ values required to begin to stabilize sulfate in basaltic and andesitic liquids (~IW+3.5; Botcharnikov et al. 2010; Jugo et al. 2010), and more than 3 orders of magnitude lower than needed in Fe-free or Fe-poor soda-lime, K$_2$Si$_2$O$_6$, albite, and haplo-trondhjemite liquids (~IW+2.5; Klimm et al. 2012). Thus, under the reducing conditions of lunar petrogenesis, it is anticipated that nearly all S dissolved in the interstitial silicate melts in these lunar magmas will be dissolved as sulfide ($S^{2-}$), and that crystalline phases in equilibrium with the interstitial silicate melts likely contain nearly entirely sulfide. Since at the time of the discovery of hundreds to thousands of parts per million of S in lunar apatites sulfur was only known to be present in naturally occurring apatite as sulfate groups, it was not clear how to explain the incorporation of sulfur in lunar apatites (Boyce et al. 2010).

Boyce et al. (2010) speculated that the elevated S abundance of lunar apatite was due to sulfide substitution into the column anion site in apatite where $F^-$, $OH^-$, and Cl$^-$ anions normally sit. Although this hypothesized substitution has until now not been observed in natural apatites, in support of their speculation, Boyce et al. (2010) pointed out that fully $S^{2-}$-substituted apatites had been synthesized experimentally (Suiitch et al. 1986; Taitai and Lacout 1989; Henning et al. 2000), and since then, apatites that exhibit S-XANES spectral evidence for both sulfide and sulfate (Konecke et al. 2017a) have been synthesized. The speculation that this occurs at the column anion site also is supported by ab initio calculations, which show that this substi-