Application of a new vanadium valence oxybarometer to basaltic glasses from the Earth, Moon, and Mars

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ABSTRACT

The redox states of volcanic and impact melts from the Earth, Moon, and Mars have been estimated from the valence state of V in basaltic glasses (Sutton et al. 2005). The V valence has been determined using synchrotron micro X-ray absorption near-edge structure spectroscopy (XANES) (Sutton et al. 2005), which allows for in situ measurements on samples with a micrometer spatial resolution and ~100 ppm elemental sensitivity. Here, we interpret those results for the natural samples and compare them to the literature. The results show that terrestrial melts are dominated by V4+, lunar samples by V3+, with Martian melts a mixture of both V3+ and V4+. The fO2 estimates derived from the V valence are consistent with those determined by other proven methods, whereby terrestrial basalts experience fO2 conditions within 1 or 2 log units of the QFM buffer, lunar basalts equilibrate at 1 to 2 log units below the IW buffer, and Martian basalts fall somewhere between the QFM and IW buffer. The results illustrate the usefulness of this technique; i.e., a robust oxybarometer covering over six orders of magnitude, applicable to samples that record fO2 conditions from reduced extraterrestrial bodies to the oxidized Earth.

Keywords: Oxygen fugacity, planetary basalts, vanadium, oxidation state, Mars, XANES

INTRODUCTION

As part of NASA’s Cosmochemistry Program and the Lunar and Planetary Institute’s “Oxygen in the Solar System” initiative, we have been developing V-valence oxybarometers as measured in basaltic phases. Vanadium exists as V3+, V4+, and V5+ on Earth (Canil 1999), exists as a mixture of both V3+ and V4+ on Mars (Papike et al. 2004), and exists mainly as V3+ on the Moon and asteroids (Karnet et al. 2005). Divalent V (V2+) may also occur in highly reduced systems, such as those that existed in the early solar nebula (Sutton et al. 2002). Vanadium partitioning between minerals and melt is redox sensitive (Lindstrom 1976; Canil 1997, 1999, 2002; Jessman and Rubie 1998; Jessman et al. 1999; Kilburn and Wood 1998; Connolly and Burnett 1999; Hanson and Jones 1997), and thus the variable V valences can be used to extract fO2 information from the most oxidized materials on Earth to the most reduced materials in the solar nebula. The importance of fO2 is that it significantly affects the valence-state partitioning of elements over crystallographic sites and phases in planetary basalts (Papike et al. 2005). We note that the crystallization sequence, mineral-melt partitioning, nature of fractionation, and thus melt evolution for one basaltic bulk composition can be profoundly different over a range of fO2 conditions from the reduced solar nebula to the oxidized Earth. This paper reports on the application of a new V-valence oxybarometer to basaltic glasses from the Earth, Moon, and Mars.

Vanadium valence in the basaltic glasses has been determined by synchrotron micro X-ray absorption near-edge structure (XANES) spectroscopy, which uses X-ray absorption associated with core-electronic transitions (absorption edges) to reveal features that relate to the valence state of the element of interest. Other techniques that determine the valence state of elements in materials, such as wet-chemical analysis, Mössbauer spectroscopy, or electron energy loss spectroscopy, have been reviewed by Delaney et al. (1998) and Berry et al. (2003). MicroXANES has advantages over these other techniques because measurements can be made non-destructively in air and in situ on conventional thin sections previously studied by other microanalytical techniques. Furthermore, the high-brilliance synchrotron source allows high spatial resolution in the micrometer range with elemental sensitivities of ~100 ppm. MicroXANES has been used successfully to determine the valence states of Fe (Bajt et al. 1994; Delaney et al. 1996; Dyr et al. 1998, 2002; Wilke et al. 2001), Cr (Sutton et al. 1993; Berry and O’Neill 2004), and V (Wong et al. 1984; Kallithrakas and Moshohoritou 1998; Delaney et al. 1999; Sutton et al. 2002, 2005; Sutton and Newville 2005; Guili et al. 2004) in planetary materials, and we continue this development here, measuring V valences in basaltic glasses to obtain fO2 estimates for these materials. This oxybarometer is very powerful because (1) V valence is measured in basaltic glasses that have been quenched at near-liquidus temperatures, thereby recording magmatic fO2 conditions; and (2) the method

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