LETTER

Comparative planetary mineralogy: V/(Cr + Al) systematics in chromite as an indicator of relative oxygen fugacity

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ABSTRACT

We have been developing oxygen barometers based largely on the behavior of V, which can occur in four valence states (V^{2+}, V^{3+}, V^{4+}, and V^{5+}), and record at least 8 orders of magnitude variation in oxygen fugacity ($f_{O_2}$). Our first efforts in measuring these valence proportions were by XANES techniques in basaltic glasses from Earth, Moon, and Mars. We now address the behavior of V valence states in chromite from basaltic glasses from these bodies with a technique that uses the electron microprobe. Our first insights into this new technique resulted from running electron probe traverses across spinel grains from core to rim on grains that show zoning from chromite to ulvöspinel. The zoning profiles showed the normal trends of core to rim decreases of Cr, Al, and Mg, and increases of Fe, Ti, and Mn. However, the behavior of V was very different for Moon and Earth, with Mars in between. In terrestrial basalts V^{3+} > V^{4+}, in lunar basalts V^{4+} > V^{3+}, and in martian basalts V^{4+} and V^{5+} are both significant. The trends (core to rim) for the Moon show a strong positive correlation of V and Cr and negative correlation of V and Ti. For the Earth, the trends are just the opposite, with a strong negative correlation for V and Cr and a strong positive correlation of V and Ti. Chromite in martian basalts showed trends somewhere in between. We found that a convenient way to display these data for chromite is a plot showing the relative V/(Cr + Al) ratios. These ratios nicely reflect the oxygen fugacity ranges for Moon, Mars, and Earth.

INTRODUCTION

As our part of the new “Oxygen in the Solar System” initiative of the Lunar and Planetary Institute, we have been developing oxybarometers largely based on the behavior of V, which can occur in four valence states (V^{2+}, V^{3+}, V^{4+}, and V^{5+}) and record at least 8 orders of magnitude variation in oxygen fugacity ($f_{O_2}$) (Sutton et al. 2004). Figure 1 illustrates the relationship between the V valence-state transitions and the valence-state transitions of other selected multivalent cations. Our first efforts in measuring these valence proportions were by X-ray Absorption Near Edge Structure (XANES) techniques in basaltic glasses from Earth, Moon, and Mars (Sutton et al. 2004; Karner et al. 2004a). We now address the behavior of V valence states in chromite in basaltic glasses from these bodies. We have been looking for a “V in chromite oxybarometer” that works with data collected by the electron microprobe and thus is readily accessible to a large segment of the planetary materials community. This paper describes our results in this effort.

Previous work recognized the potential of V for estimates of $f_{O_2}$. Lindstrom (1976) was the first to report experimental results confirming that the partitioning behavior of V is dependent on $f_{O_2}$. Canil (1999) studied V partitioning among orthopyroxene, spinel, and silicate melt and the redox states of mantle source regions for primary magmas. Pearce et al. (2000) used V vs. Yb systematics to assess $f_{O_2}$ in fore-arc peridotites. Canil and Fedorchouk (2001) addressed olivine - liquid partitioning of V, with applications to modern and ancient picrites. Shervais (1982) used Ti-V plots to understand the petrogenesis of modern and ophiolitic magmas. Canil (2002) studied V in peridotites, mantle redox, and tectonic environments. It is this paper that is most relevant to our present work because Canil (2002) did partitioning studies of V between several basalt and chromite compositions and showed that for spinel with high Cr/Al, the D-values for V (spinel/melt) increases dramatically from ~2 at high $f_{O_2}$ [Iron-Wustite (IW) + 5] to ~32 at low $f_{O_2}$ (IW-2). Connolly and Burnett (2003) studied the $f_{O_2}$ dependence of D-values for V and Ti.

Therefore, with this background we initiated the present study, which is a part of our continuing efforts in comparative planetary mineralogy. Two of our recent studies in this area are Karner et al. (2003), on olivine from planetary basalts, and Karner et al. (2004b) on plagioclase from planetary basalts. Thus this paper, on chromite from planetary basalts, will be the third in this series. The sample suites we used for this study are described in Table 1.

ANALYTICAL TECHNIQUES

Chromite grains in thin sections from 11 samples (see Table 1) were analyzed to determine their major- and minor-element compositions. Samples were selected that contained chromite as an early liquidus phase. Analyses were made at the University of New Mexico’s microbeam facilities using a JEOL JXA 8200 microprobe equipped with a back-scattered electron detector, a thin-window energy dispersive spectrometer, and five wavelength-dispersive spectrometers. Chromite analyses were made using an accelerating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 1 μm. The analytical routine included calibration of Ti on olivine, Ti on rutile, Mg, Al, and Cr on chromite, Mn on spessartine, Fe on pure Fe metal, and V on pure V metal. All the standards were from the C.M. Taylor Corporation. Wavelength dispersive spectrometer counting times were as follows: 20 s on peak and 10 s on backgrounds for Si, Al, Cr, Fe, and Mg; 30 s on peak and 15 s on backgrounds for Ti; and 40 s on peak and 20 s on backgrounds for V and Mn. Vanadium concentrations were corrected for interference from the Ti Kα peak by the procedure described in Snetsinger et al. (1968), and resulted in ~5% of the total Ti counts being subtracted from the total V counts. Likewise, Mn was corrected for interference from the Cr Kα peak, and resulted in ~0.1% of the total Cr counts being subtracted from the total Mn counts. All data were reduced using a ZAF correction program and cast as oxide wt% with Fe as FeO, Cr as Cr₂O₃, and V as V₂O₃.

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