Correlations of octahedral cations with OH\textsuperscript{−}, O\textsubscript{2}\textsuperscript{−}, Cl\textsuperscript{−}, and F\textsuperscript{−} in biotite from volcanic rocks and xenoliths

KEVIN RIGHTER,\textsuperscript{1,*} M. DARBY DYAR,\textsuperscript{2} JEREMY S. DELANEY,\textsuperscript{3} TORSTEN W. VENNEMANN,\textsuperscript{4} RICHARD L. HERVIG,\textsuperscript{5} AND PENELope L. KING\textsuperscript{6}

\textsuperscript{1}Lunar and Planetary Laboratory, University of Arizona, Tucson, Arizona 85721, U.S.A.
\textsuperscript{2}Department of Earth and Environment, Mount Holyoke College, 50 College Street, South Hadley, Massachusetts 01075, U.S.A.
\textsuperscript{3}Department of Geological Sciences, Rutgers University, Piscataway, New Jersey 08854, U.S.A.
\textsuperscript{4}Institute for Geochemistry, University of Tuebingen, Wilhelmstr. 56, 72074
\textsuperscript{5}Center for Solid State Science, P.O. Box 871704, Arizona State University, Tempe, Arizona 85287-1704, U.S.A.
\textsuperscript{6}Department of Earth Sciences, University of Western Ontario, London, Ontario N6A 5B7, Canada

ABSTRACT

To understand compositional variation in igneous biotite, full analyses of a suite of biotites of variable composition from volcanic and xenolith parageneses have been completed. Major and minor elements were determined by electron microprobe analysis, water was determined by manometry and SIMS analysis, and Fe\textsuperscript{3+}/Fe\textsuperscript{2+} was determined by microXANES and Mössbauer spectroscopy. Our new data, together with previous biotite analyses (total of 52 analyses), reveal correlations between O\textsubscript{2}\textsuperscript{−} (2-F-Cl-OH) and the sum of the octahedral cations Al + Ti + Fe\textsuperscript{3+} + Cr. This correlation allows estimation of either OH\textsuperscript{−} or Fe\textsuperscript{3+}/Fe\textsuperscript{2+} as long as one or the other has been determined. The hydroxyl site in most mantle micas contains at least 1.0 O\textsubscript{2}\textsuperscript{−} atoms per formula unit (apfu), indicating that the oxy-component cannot be ignored. The large oxy-component in melt inclusion micas from the martian meteorite Chassigny does not necessarily indicate oxidized or hydrous magmatic conditions because dehydrogenation may have occurred and/or because the oxy-component may be stable at low oxygen fugacity. The large variation in Ti, Al, and Fe\textsuperscript{3+} in natural igneous micas is most likely dependent upon bulk compositional differences in each specific system such as variation of a\textsubscript{TiO\textsubscript{2}} and a\textsubscript{Al\textsubscript{2}O\textsubscript{3}} in silicate melts.

BACKGROUND

Coupled substitution of different cations between tetrahedral (IV), octahedral (VI), and interlayer (XII) sites in micas is complicated, and has been examined in depth by many investigators (see Guo and Green 1990, and references therein), in part because accurate analyses of most of the major-element constituents in mica are possible with electron microprobe analysis (EMPA). For example, in phlogopite the prevalent substitution mechanisms are:

\begin{align*}
\text{vTi} + \text{v□} &= 2\text{vMg}, \\
\text{vTi} + 2\text{vAl} &= \text{vMg} + 2\text{vSi}, \text{ and} \\
\text{x□Ba} + \text{x□Mg} &= 2\text{vK},
\end{align*}

where □ denotes a vacancy substitution in a site of specified

INTRODUCTION

Biotite occurs in a wide variety of settings in igneous rocks and its compositional variation holds information about the conditions under which these rocks formed. Compositional variation is of four forms—that on the tetrahedral sites (cat-

ions such as Si, Al, Fe\textsuperscript{3+}), octahedral sites (Mg, Mn, Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Ti, Al, Cr), the interlayer sites (K, Na, Ba, □), and the “hy-

droxyl” site (OH\textsuperscript{−}, O\textsubscript{2}\textsuperscript{−}, Cl\textsuperscript{−}, F\textsuperscript{−}). Past efforts in understanding compositional variation in biotite have been stymied by a variety of problems. Most octahedral and interlayer site cations are easily measured by electron microprobe techniques, but many studies have excluded analysis of BaO, Cr\textsubscript{2}O\textsubscript{3}, and/or Na\textsubscript{2}O, the sum of which can exceed 3 wt% in some biotites. Similarly, some studies include analyses of H\textsubscript{2}O, but exclude F\textsuperscript{−} and Cl\textsuperscript{−} (and vice versa), thus allowing uncertainty in the nature of the hydroxyl site occupants. Finally, and perhaps most importantly, Fe\textsubscript{O} and Fe\textsubscript{2}O\textsubscript{3} are rarely measured in biotites, yet the equilibrium 2Fe\textsubscript{O} + 1\textsubscript{2} O\textsubscript{2} = Fe\textsubscript{2}O\textsubscript{3} is a function of water and oxygen fugacity and it is linked to the nature of the occupancy of the hydroxyl site. Although complete chemical characterizations including all these variables (and oxygen) are available for a large suite of metamorphic biotites (Dyar et al. 1991, 1993; Guidotti and Dyar 1991), no similar large data set exists for igneous samples.

To better understand the compositional variation in igne-

ous biotites, we have selected and characterized a suite of bi-

otite samples for complete analysis. In this study, we focus on volcanic localities, because their samples are less likely to have experienced re-equilibration of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} or lost OH\textsuperscript{−}. New data are presented for 16 samples, which together with published biotite analyses, provide new insight into the composition of both terrestrial and martian biotites.