Chromium, vanadium, and titanium valence systematics in Solar System pyroxene as a recorder of oxygen fugacity, planetary provenance, and processes

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ABSTRACT

Pyroxene is arguably the most powerful, single-phase geochemical and petrologic recorder of Solar System processes, from nebular condensation through planetary evolution, over a wide range of temperatures, pressures, and fO2. It is an important mineral phase in the crusts and mantles of evolved planets, in undifferentiated and differentiated asteroids, and in refractory inclusions—the earliest Solar System materials. Here, we review the valence state partitioning behavior of Cr (Cr2+, Cr3+), Ti (Ti3+, Ti4+), and V (V2+, V3+, V4+, V5+) among crystallographic sites in pyroxene over a range of fO2, from approximately fayalite-magnetite-quartz (FMQ) to ~7 log units below iron-wüstite (IW-7), and decipher how pyroxene can be used as a recorder of conditions of planetary and nebular environments and planetary parentage. The most important crystallographic site in pyroxene with respect to its influence on mineral/melt partitioning is M2; its Ca content has a huge effect on partitioning behavior, because the large Ca cation expands the structure. As a result, distribution coefficients (Ds) for Cr and V increase with increasing Ca content from orthopyroxene to pigeonite to augite. In addition, it is noted that V3+ is favored over V4+ in olivine and pyroxene. In pyroxene in refractory inclusions, Ti3+ is favored over Ti4+ and incorporation of Ti is facilitated by the high availability of Al for coupled substitution. The most important results from analysis of pyroxene in martian meteorites (e.g., QUE 94201) are the oxygen fugacity estimates of IW+0.2 and IW+0.9 derived from partitioning and valence data for Cr and V, respectively, obtained from experiments using appropriate temperatures and melt compositions. In angrites, changes in V valence state may translate to changes in fO2, from IW-0.7 during early pyroxene crystallization, to IW+0.5 during later episodes of pyroxene crystallization. In addition to fO2, the partitioning behavior of Cr, V, and Ti between pyroxene and melt is also dependent upon availability of other cations, especially Al, for charge-balancing coupled substitutions.

Keywords: Pyroxene, oxygen fugacity, partitioning, chromium, vanadium, titanium, valence state

INTRODUCTION

This is a comparative planetary mineralogy review emphasizing the valence-state partitioning behavior of Cr, V, and Ti between the pyroxene M1 and M2 sites and coexisting equilibrium melt over the oxygen fugacity range from the fayalite-magnetite-quartz (FMQ) buffer to approximately seven log units below the iron-wüstite buffer (~IW-7). We focus primarily on pyroxenes from planetary basalts, as they record fundamental igneous mineral-melt processes that have occurred on the Moon, Mars, Earth, and small planetary bodies (e.g., angrite and eucrite parent bodies) from ~4.5 Ga to the present time.

Some lithophile elements can have more than one oxidation state under conditions relevant to the formation of planetary materials. The oxygen fugacities at which important lithophile elements have multiple valences and the environments in which they occur are summarized in Figure 1. Changing the valence of an element affects its ionic radius, which affects its compatibility in a given crystallographic site and its partitioning behavior into a given mineral. The range of the ionic radii of the cations considered here is illustrated in Figure 2. Understanding the fundamental interactions between the behavior of multivalent cations and a mineral structure is critical to deciphering the fO2 of a planetary body and fingerprinting planetary parentage. This crystal chemical approach has led to the development of several “valence state oxybarometers,” such as a semi-quantitative V-valence spinel oxybarometer (Papike et al. 2004); a V-valence glass oxybarometer (Sutton et al. 2005; Karner et al. 2006); and a Cr- and V-valence pyroxene oxybarometer (Karner et al. 2007a, 2007b, 2008). Papike et al. (2013) further developed and compared four vanadium valence state oxybarometers: (1) spinel-melt; (2) olivine-melt; (3) spinel-olivine; and (4) V(Cr+Al) in spinel-melt. Papike et al. (2015) illustrated the relationships between the valence state of Cr, V, and Fe and their relationship to spinel stability and composition in martian basalts. Bell et al. (2014) explored by X-ray absorption near-edge structure (XANES) spectroscopy the Cr valence in olivine and its application to understanding the evolution of fO2 in planetary basalts.