

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 f_{O_2} . 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 f_{O_2} 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 (D_s) 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 f_{O_2} , from IW-0.7 during early pyroxene crystallization, to IW+0.5 during later episodes of pyroxene crystallization. In addition to f_{O_2} , 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