Comparative planetary mineralogy: Valence state partitioning of Cr, Fe, Ti, and V among crystallographic sites in olivine, pyroxene, and spinel from planetary basalts

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ABSTRACT
This is a comparative planetary mineralogy study emphasizing the valence-state partitioning of Cr, Fe, Ti, and V over crystallographic sites in olivine, pyroxene, and spinel from planetary basalts. The sites that accommodate these cations are the M2 site (6 to 8-coordinated) and M1 site (6-coordinated) in pyroxene, the M2 site (6- to 8-coordinated) and M1 (6-coordinated site) in olivine, and the tetrahedral and octahedral sites in spinel. The samples we studied are basalts from Earth, Moon, and Mars, and range in oxygen fugacity conditions from IW-2 (Moon) to IW+6 (Earth), with Mars somewhere in between (IW to IW+2). The significant elemental valence-states at these fO2 conditions are (from low to high fO2): Ti4+, V3+, Fe2+, Cr2+, Cr3+, V4+, and Fe3+. V2+ and Ti3+ play a minor role in these phases in oxidized terrestrial basalts because it is probably lower in abundance than V4+, and has an ionic radius that is so small (0.054 nm, 6-coordinated), that it is almost at the lower limit for octahedral coordination, and can even be tetrahedrally coordinated. The role of Cr3+ in the Moon is significant, as Cr2+ predominates in basaltic melts at fO2 less than IW-1. Lunar olivine has been found to contain mostly Cr2+, whereas coexisting pyroxene contains mostly Cr3+. Fe3+ is very important in Earth, less so in Mars, and nonexistent in the Moon. The importance of the Fe2+ to Fe3+ transition cannot be overstated and, indeed, their crystal-chemical differences, in terms of behavior (based on size and charge), are similar to the differences between Mg and Al. We note that for pyroxene in six of the seven terrestrial suites we studied, Fe3+ (in the M1 site) coupled with Al (in the tetrahedral site) is one of the two most important charge-balance substitutions. This substitution is of lesser importance in Mars and does not exist in lunar basalts.

INTRODUCTION
This is a comparative planetary mineralogy study emphasizing the valence-state partitioning of Cr, Fe, Ti, and V over crystallographic sites in olivine, pyroxene, and spinel from planetary basalts. We concentrate on planetary basalts because basaltic volcanism is a fundamental process that has occurred on the Earth, Moon, Mars, and asteroids (especially 4 Vesta), from the beginning of the solar system at 4.56 Ga, to the present time. As partial melts of planetary interiors, basalts have compositions that are the product of many physical and chemical factors including the thermodynamic history of a planet, composition and mineralogy of the planet’s interior, and post-extraction processes (e.g., Bence et al. 1980, 1981). Ultimately, many of these factors may be related to the origin and early evolution of the planetary body. Many studies have concentrated on the bulk-rock compositions of basalts to understand differences among basalt systems, and the influences of a planetary environment on a basalt system, in a comparative planetology context (Consolmagno and Drake 1977; Stolper 1979; Bence et al. 1980, 1981; Drake et al. 1989; Goodrich and Delaney 2000). This method works well when the basalts represent liquids erupted onto a planetary surface with little loss or gain of material (assimilation and/or cumulate processes).

A slight variation to the basalt bulk composition approach is to explore the compositions of the minerals in basalts, as they reflect the differing chemical and physical conditions of the melts from which they crystallized. Several studies have explored the composition of the silicate phases in planetary basalts to understand similarities and differences in a comparative context and/or to use individual minerals as petrogenetic and geochemical recorders (e.g., Bence and Papike 1972; Papike 1981, 1998). We have extended this philosophy to a set of comparative planetary mineralogy studies that combine major-, minor-, and trace-element data to correlate chemical trends in basaltic minerals with planetary origin and setting (e.g., Papike 1996; Papike et al. 1996). Our most recent studies (Karner et al. 2003, 2004b) reported the composition of olivine and plagioclase grains from 13 planetary basalt suites, relating the similarities and differences to the effects of igneous process, possible early solar system differentiation processes and planetary parentage. Studies, such as these, that concentrate on individual minerals in basalts are important because many present and future samples (Zolensky et al. 2000) of extraterrestrial planetary bodies are and will be from soils or regoliths, and may be too small to represent bulk-rock compositions. These “regolith” samples will have key information recorded in individual minerals, and this information can tell us not only about the source region of the rocks, but also...