The differences in behavior of chromium between lunar and analogous terrestrial materials have been ascribed to the differences in oxygen fugacities between Moon and Earth. In terrestrial basalts chromium is mainly present as Cr(III); Cr(II) has been invoked to explain the concentrations of chromium in mare basalts. Evidence for Cr(II) in lunar minerals has been drawn from inferences on charge balance constraints in lunar pyroxenes (1), high concentrations of chromium in some lunar olivines (2), spectroscopic measurements on olivines (3), and implications from compiled chemical data on lunar olivines and pyroxenes (4). However, despite attempts to detect the predicted Cr(II) conclusively in lunar rocks, much of the chromium present in lunar material is Cr(III), as evident from the presence of Cr(III)-bearing oxides such as spinel and chromite, spectroscopic measurements on lunar minerals (5), and analyses implying Cr(III)-Al(III) coupled substitutions in lunar pyroxenes (6).

In order to determine the effects of oxidation states of chromium on its mineralogical distribution, a study of the distribution of chromium among synthetic forsterite, clinoenstatite, diopside, spinel, and silicate liquid was done as a function of bulk composition, temperature, and oxygen fugacity. Two liquid compositions were chosen, FAD (25% Forsterite, 7% Anorthite, 68% Diopside, 0.7% Cr₂O₃) and FAS (53% Forsterite, 27% Anorthite, 20% Silica, 0.7% Cr₂O₃). Both melt at about 1500°C and crystallize forsterite over the first 100°C interval below their melting points, then forsterite plus clinopyroxene over the next 100°C interval. Iron was omitted to make the experiments simpler; its absence imposes limitations on the application of the results to natural systems. Electron microprobe analyses were used to determine the concentrations of elements among the phases. Estimates of the amount of each redox state of chromium present at the particular crystallization temperature were based on analyses of glasses by titration and by electron paramagnetic resonance measurements. The observed effects of phase, composition, temperature, and oxygen fugacity on the Nernst solid/liquid distribution coefficients of chromium are summarized in Figure 1.

As seen in Figure 1, changes in the oxidation state of chromium affect the crystal/liquid distribution of that element. In proceeding from an oxidizing to a reducing atmosphere, regions of Cr(VI)-Cr(III) equilibrium, predominantly Cr(III), Cr(III)-Cr(II) equilibrium, and predominantly Cr(II) are traversed. The clinopyroxenes greatly concentrate Cr(III) with respect to the residual liquid, which is in agreement with the extremely high octahedral site preference energy (crystal field theory) of that ion and the favorable pyroxene site. The large variation of the forsterite/melt distribution coefficient of Cr(III) over the experimental conditions can be explained by variation in the number of octahedral "structural" sites in the liquid.

Clinopyroxenes only slightly partition Cr(II) in favor of the melt. Based upon the distribution coefficients of other divalent transition metal ions in a similar system and predictions of crystal field theory, this
behavior of Cr(II) is exactly as expected. Similar arguments for the partition of Cr(II) between forsterite and melt, including the expectation that the distorted M1 site of olivine should stabilize the Cr(II) ion [71], indicate that forsterite should readily accept Cr(II) [815, intermediate to values for Ni(II) and Co(II)] as in Figure 2. However, the measured forsterite/melt D value for Cr(II) is conspicuously less than one. Possibly the large size of the Cr(II) ion [high spin radius intermediate to Fe(II) and Mn(II) as in Fig. 2] in the olivine lattice overwhelms the favorable crystal field energy. Barmina et al. [12] have also found that the olivine/liquid D value for Cr(II) in a melt crystallizing Fo0.85 was intermediate to those of Fe(II) and Mn(II), as predicted by size arguments. Dodd et al. [13] also present evidence that the size of the Cr(II) ion controls its substitution into meteoritic olivines. Although the size of the Cr(II) ion may be important in its partition into the olivine structure, it is not a limiting factor in its introduction into the clinopyroxene structure.

According to the experimental results from Figure 1, chromium should be present predominantly as Cr(II) for these synthetic compositions at the low partial pressure of oxygen typical of lunar petrogenesis. This is inconsistent with the apparent predominance of Cr(III) in lunar rocks. However, many factors could contribute to this apparent anomaly. Melt compositions have a profound effect on trace element redox equilibria as shown by previous work on Eu [14]. When compared to synthetic and terrestrial spinels, a lunar spinel which had formed under conditions reducing enough to contain Cr(II) only contained Cr(III) due to compositional constraints [15]. The presence of primary Cr(II) in the mare basalts may also have been lost through postulated equilibria such as Fe(II) + 2Cr(II) = 2Cr(III) + Fe(0) [16]. Others [17] have ascertained that oxygen partial pressures of greater than 10^-16 atmosphere have been imprinted in lunar rocks, which would also result in greater proportions of the oxidized species. Presently there is no compelling reason for any single rationale to explain quantitatively the relative concentrations of Cr(III) and Cr(II) on the Moon.

The high concentration of chromium in mare basalts is consistent with the chromium in the lunar interior being present mainly as Cr(II) so that the chromium is excluded from olivine at depth. As the mare basalts solidified, a major portion of the chromium behaved as if it was Cr(III). Experimentally the clinopyroxene/forsterite distribution coefficient was shown to decrease with a corresponding increase in the Cr(II)/Cr(III) ratio (or fall in oxygen partial pressure), which gives a foundation to the work of Jakes and Reid [4] relating the chromium contents of coexisting lunar olivines and pyroxenes to the redox state of the Moon at the various landing sites. These lunar values cover the experimental range of crystallization from a melt containing all Cr(III) to the other extreme of containing all Cr(II).

CR(III)-CR(II) DISTRIBUTION

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FIGURE 1a: Clinopyroxene (composition FAS).

FIGURE 1b: Forsterite from Liquid FAS.

FIGURE 1c: Forsterite from Liquid FAD.

FIGURE 2a: Distribution values for Ni, Co, and Mn from Bird (1971).

FIGURE 2b: Forsterite/Liquid.