
A growing body of experimental and observational data is pointing to low redox potentials on the moon during its cooling history. Information on the oxygen fugacities at the times of mineral crystallization may be derived from the identity of mixed oxidation states of the more abundant transition elements Fe, Ti, Cr and Mn in silicate and oxide minerals. We are utilizing Mössbauer and electronic absorption spectroscopy to identify the valencies and site occupancies of transition metal cations in minerals handpicked from crushed rocks or occurring in large single crystals (> 1 mm) in thick polished sections of rock chips. Preliminary work on the ferromagnesian silicate minerals in rocks 15058, 15499, 15555, 60315, 62295, 65015 and 68416 indicates the presence of significant amounts of Ti$^{3+}$ in rim pyroxenes, the presence of Cr$^{3+}$ in olivines and core pigeonites, and the absence of Fe$^{3+}$ and probably of Cr$^{2+}$ in pyroxenes and olivines.

The Mössbauer spectra of pyroxene fractions handpicked from Apollo 15 rocks 15058(1), 15499 and 15555 demonstrate that ferric ions are below the 1% detectability level of our spectrometer. Thus, no features in the absorption spectra need be attributed to the extremely weak, spin-forbidden transitions in Fe$^{3+}$ and to metal-metal charge transfer transitions involving Fe$^{3+}$ ions. This facilitates the interpretation of electronic absorption spectra of lunar minerals in the visible region.

For example, the absorption spectra in the visible region of three regions across a large zoned pyroxene phenocryst in rock 15058 are illustrated in figure 1. The doublet around 505 nm, interpreted by some groups as a feature due to Fe$^{3+}$ ions, represents a characteristic spin-forbidden transition in Fe$^{2+}$. Indeed, the relative intensities of the component peaks at 503 and 508 nm correlate with the Fe$^{2+}$ site occupancies of the M1 and M2 positions, respectively, derived from Mössbauer spectroscopy of the core pyroxene fraction. The increased Fe$^{2+}$ occupancy of the M1 positions and accentuated compositional zoning towards the perimeter of the grain, leads to loss of resolution and broadening of the peak at 505 nm (figures 1b and 1c). Other spin-forbidden transitions due to Fe$^{2+}$ include 400, 430, and 550 nm. The weak broad peaks around 450 and 600 nm in the core pigeonite (figure 1a) are attached to Cr$^{3+}$ ions. Similar features are observed in olivines from other Apollo rocks. These together with the absence of bands attributable to Cr$^{2+}$ ions, indicate that chromium in lunar pyroxenes and olivines is predominantly Cr$^{3+}$. 

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Figure 1. Polarized absorption spectra of three regions across a zoned pyroxene phenocryst in rock 15058. They are taken with light polarized along the Z indicatrix axis. Reference zero is at 1750 nm and the thickness of the polished section is approximately 100 microns.
Indeed, the formation of the Jahn-Teller unstable \( \text{Cr}^{2+} \) ion at the expense of octahedrally coordinated \( \text{Cr}^{3+} \) in pyroxenes is unlikely, since the latter has high crystal field stabilization energy. The broad bands centered around 470 and 650 nm in the spectra of rim pyroxenes (figure 1c) are best interpreted as spin-allowed transitions in \( \text{Ti}^{3+} \) ions, although alternative interpretations have been proposed for the 650 nm band (\( \text{Ti}^{3+} \rightarrow \text{Ti}^{4+} \) charge transfer) and 470 nm band (\( \text{Fe}^{2+} \rightarrow \text{Ti}^{4+} \) charge transfer). Nevertheless, the spectral data do indicate the presence of \( \text{Ti}^{3+} \) ions in the Apollo 15 pyroxene mantles.

The small grain size of the Apollo 16 rocks has prevented detailed Mössbauer measurements on handpicked mineral separates and absorption spectral measurements on the phenocrysts. However, Mössbauer spectra of crushed rock samples 60315 and 62295 showed the presence of pyroxene and olivine, small amounts of ilmenite, and traces of metallic iron and troilite. No \( \text{Fe}^{3+} \) ions could be detected in the pyroxenes. Spectral measurements of the olivines in rocks 65016 and 68416 revealed them to be magnesian varieties from peak maxima - composition curves published earlier (2).

References Cited