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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We have considered 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 (6-8 coordinated) and M1 site (6 coordinated) in pyroxene, the M2 site (6-8 coordinated) and M1 site (6 coordinated) in olivine, and the tetrahedral and octahedral sites in spinel. The samples we studied are basalts from Earth, Moon, and Mars, which have fO_2 conditions that range from IW-2 (Moon) to IW+6 (Earth) with Mars somewhere between at IW to IW+2. In this range of fO_2 the significant elemental valences are (from low to high fO_2) Ti^{4+}, V^{3+}, Fe^{2+}, Cr^{2+}, Cr^{3+}, V^{3+}, V^{4+}, and Fe^{3+}. V^{2+} and Ti^{3+} play a minor role in the phases considered for the Moon, and are probably in very low concentrations. V^{5+} plays a minor role in these phases in terrestrial basalts because it is probably in lower abundance than V^{4+} and it has an ionic radii that is so small (0.054 nm, 6- coordinated,[1]) that it is almost at the lower limit for octahedral coordination. The role of Cr^{2+} in the Moon is significant, as Sutton et al. [2] found that lunar olivine contains mostly Cr^{2+} while coexisting pyroxene contains mostly Cr^{3+}. Hanson and Jones [3] showed that Cr^{2+} predominates in basaltic melts at fO_2 less than IW-1. Fe^{3+} is very important in Earth and less so in Mars and nonexistent in the Moon. The importance of the Fe^{2+} to Fe^{3+} transition cannot be overstated, as the crystal chemical differences, in terms of behavior (based on size and charge), is comparable to the differences between Mg and Al. We note that for pyroxene in six of the seven terrestrial suites that we studied [4, 5], Fe^{3+} (in the M1 site) coupled with Al (in the tetrahedral site) is one of the top two most important substitutions. This is of lesser importance in Mars and is not important in the Moon. The V^{3+} to V^{4+} transition is important and very useful for olivine oxygen barometry [6] because D for V^{3+} is significantly higher than D for V^{4+}. We rationalize this observation in the following way: Most V^{3+} and V^{4+} substitutions into the olivine structure (other than Na in the M2 site coupled with say V^{3+} in the M1 site) involve vacancies, which are quite incompatible in crystal structures. For V^{3+}, one vacancy can accommodate two V^{3+} cations whereas for V^{4+}

one vacancy only accommodates one V^{4+}. Thus more vacancies are required in V^{4+} substitutions into olivine. In the Moon V^{3+} is much more abundant than V^{4+} [7, 8]. Thus in lunar chromite V^{3+} follows Cr^{3+}, whereas in Earth V^{4+} (which is much greater in abundance than V^{3+}) follows Ti^{4+} (eg in ulvöspinel). We could go on in this vein for some time but space limitations do not permit us to do so. It is much more efficient to present our observations in table form (Table 1).

We note that this review is very different than those we have been involved with in the past. Most reviews are written about a field of study that is mature and may have already "peaked". However, we are writing about a field "valence-state partitioning over crystallographic sites and phases" that really is in its infancy. It certainly has not reached full bloom! We have done this because we feel strongly that this research direction is very important and we would like more crystal chemists, mineralogists, petrologists, and geochemists to participate. We note that the crystallization sequence, mineral-melt partitioning, nature of fractionation and thus melt evolution for one bulk composition (for example MORB) can be profoundly different over a range of fO_2 from IW-2 to IW + 6. We must better understand the atomistics of valence-state partitioning. What is needed is more experimental work at controlled fO_2. However, of much more importance is the characterization of the mineral phases with advanced techniques (for example XANES) that are capable of not only determining valence states of the element of interest but which can determine which crystallographic sites the valence states are going into. We will also have to understand this process as a function of temperature and pressure.

REFERENCES [1] Shannon and Prewitt (1969) *Acta Cryst.* B25, 925-946. [2] Sutton et al. (1993) *GCA* 57, 461-468. [3] Hanson and Jones (1998) *Am. Min.* 83, 669-684. [4] Papike and White (1979) *Geophys. R. Lett.* 6, 913-916 [5] Papike (1980) *RIM* 7, 495-525. [6] Canil and Fedortchouk (2001) *Can. Min.* 39, 319-330. [7] Canil (2002) *EPSL* 195, 75-90. [8] Papike et al. (2004) *Am. Min.* 89, 1557-1560.

Table 1. How fO$_2$ conditions for the planets affect the presence and distribution of Fe, Cr, V, and Ti valence states.

fO$_2$ range for planetary basalts		
Moon: IW-2 to IW	**Mars: IW to IW+2**	**Earth: IW+2 to IW+6**
Multivalent elements in basaltic melts		
No Fe^{3+}	Fe^{3+} moderate	Fe^{3+} high
Cr^{3+} moderate, Cr^{2+} high	Cr^{3+} high, Cr^{2+} low	mostly Cr^{3+}, Cr^{2+} very low
$V^{3+} > V^{4+}$, low V^{2+}	$V^{4+} \approx V^{3+}$	$V^{4+} > V^{3+}$, V^{5+}
Ti^{4+}, Ti^{3+} low	all Ti^{4+}	all Ti^{4+}
Olivine components and charge balance couples = "others"		
none	$^{M2}\square - {}^{M1}2Fe^{3+}$	$^{M2}\square - {}^{M1}2Fe^{3+}$
low	$^{M2}\square - {}^{M1}2Cr^{3+}$	$^{M2}\square - {}^{M1}2Cr^{3+}$
none	$^{M2}Na - {}^{M1}Cr^{3+}$	$^{M2}Na - {}^{M1}Cr^{3+}$
Cr^{2+} for Mg or Fe^{2+}	little	none
low	$^{M2}\square - {}^{M1}V^{4+}$	$^{M2}\square - {}^{M1}V^{4+}$
$^{M2}\square - {}^{M1}2V^{3+}$	$^{M2}\square - {}^{M1}2V^{3+}$	low
none	$^{M2}Na - {}^{M1}V^{3+}$	low
V^{2+} for Mg or Fe^{2+} (low)	none	none
$^{M2}\square - {}^{M1}Ti^{4+}$	$^{M2}\square - {}^{M1}Ti^{4+}$	$^{M2}\square - {}^{M1}Ti^{4+}$
$^{M2}\square - {}^{M1}2Ti^{3+}$	none	none
Pyroxene charge balance couples = "others"		
none	$^{VI}Fe^{3+} - {}^{IV}Al$	$^{VI}Fe^{3+} - {}^{IV}Al$
none	$^{M2}Na - {}^{M1}Fe^{3+}$	$^{M2}Na - {}^{M1}Fe^{3+}$
$^{M1}Cr^{3+} - {}^{IV}Al$	$^{M1}Cr^{3+} - {}^{IV}Al$	$^{M1}Cr^{3+} - {}^{IV}Al$
none	$^{M2}Na - {}^{M1}Cr^{3+}$	$^{M2}Na - {}^{M1}Cr^{3+}$
Cr^{2+} for Mg or Fe^{2+}	low	none
none	$^{M2}Na{}^{M1}V^{4+\ IV}Al$	$^{M2}Na{}^{M1}V^{4+\ IV}Al$
low	$^{M1}V^{4+} - 2^{IV}Al$	$^{M1}V^{4+} - 2^{IV}Al$
none	$^{M2}Na - {}^{M1}V^{3+}$	low
$^{M1}V^{3+} - {}^{IV}Al$	low	none
V^{2+} for Ca, Mg, Fe^{2+}	none	none
$^{M1}Ti^{3+} - {}^{IV}Al$	none	none
$^{M1}Ti^{4+} - 2^{IV}Al$	$^{M1}Ti^{4+} - 2^{IV}Al$	$^{M1}Ti^{4+} - 2^{IV}Al$
Spinel components		
none	Moderate	$^{IV}Fe^{3+}(Fe^{3+}\ Fe^{2+})O_4$ (Magnetite)
$^{IV}Fe^{2+\ VI}(Fe^{2+}\ Ti^{4+})O_4$ (Ulvöspinel)	present	present
$^{IV}(Fe^{2+},\ Mg)\ ^{VI}Ti^{3+}_2\ O_4$ (Predicted)	none	none
$^{IV}Cr^{2+\ VI}Cr^{3+}_2\ O_4$ (Predicted)	low	none
$(Fe^{2+},\ Mg)\ ^{VI}V^{3+}_2\ O_4$ (Coulsonite)	low	none
low	$^{IV}Fe^{2+\ VI}(Fe^{2+}\ V^{4+})O_4$ (Predicted)	some
V^{2+} for $(Fe^{2+},\ Mg)$	none	none