Normal to inverse transition in martian spinel:

Understanding the interplay between chromium, vanadium, and iron valence state partitioning through a crystal-chemical lens

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ABSTRACT

Spinel is a very important rock-forming mineral that is found in basalts from Earth, Mars, the Earth’s Moon, and basaltic meteorites. Spinel can be used as a sensitive indicator of petrologic and geochemical processes that occur in its host rock. This paper highlights the role of increasing $f_{O_2}$ (from IW-1 to FMQ+2) in converting a $\sim$90% normal spinel to an $\sim$25% magnetite (inverse) spinel, the trajectory of $D_V^{\text{spinel/melt}}$ as it relates to the ratio of $V^{3+}/V^{4+}$ in the melt, and the crystal chemical attributes of the spinel that control the intrinsic compatibility of both $V^{3+}$ and $V^{4+}$. This work examines the nuances of the $V$ partitioning and provides a crystal chemical basis for understanding $Fe^{3+}$, Cr, and $V$ substitution into the octahedral sites of spinel. Understanding this interplay is critical for using spinels as both indicators of planetary parentage and reconstructing the redox history of magmatic systems on the terrestrial planets. Three
potential examples for this use are provided. In addition this work helps explain the ubiquitous miscibility gap between spinels with changing ulvospinel contents.

INTRODUCTION

Spinels are a common accessory phase in many terrestrial and extraterrestrial materials and their structure and composition are uniquely responsive to changing conditions (e.g. Haggerty 1972, 1976; Lindsley 1976, 1991; Basaltic Volcanism Study Project 1981; McKay et al. 2004a,b; Righter et al. 2006; Ishizawa et al. 2014). Specifically, the spinel structure and its inherent ability to accommodate multi-valent cations such as V, Cr, and Fe is highly sensitive to changing temperature and fO2 conditions (e.g. Hill and Roeder 1974, McKay et al. 2004a,b; Muan et al. 1972, Righter et al. 2006).

Papike et al. (2004) suggested that zoned, magmatic spinels could be used to determine relative oxygen fugacities and planetary parentage. This study specifically noted that the behavior of V is very different when comparing terrestrial, lunar, and martian basalts. In terrestrial basaltic liquids, typically V4+ > V3+, whereas in lunar basalts V3+ > V4+, and in martian basalts V3+ and V4+ are both significant. The core to rim trends for lunar spinels show a strong positive correlation of V and Cr and negative correlation of V and Ti. For the Earth, the trends are just the opposite, with a strong negative correlation of V and Cr and strong positive correlation of V and Ti. Chromite in martian basalts shows intermediate trends. These systematics suggest that at high oxygen fugacity (Earth), V4+ follows Ti4+, whereas at low oxygen fugacity (Moon), V3+ follows Cr3+.

These qualitative interpretations of vanadium behavior were subsequently investigated using a series of experiments to better understand the potential of V behavior in spinels as an oxybarometer (e.g. Papike et al. 2004, 2005, 2013, 2014). The experiments illustrated the
relationships between $\text{Fe}^{2+}$-$\text{Fe}^{3+}$ and $\text{V}^{3+}$-$\text{V}^{4+}$, in which the vanadium in spinel, $\text{V}^{3+}$ is best incorporated in normal spinel as $\text{IVFe}^{2+}\text{V}^{3+}\text{O}_4$ (coulsonite) and $\text{V}^{4+}$ as $\text{IVFe}^{2+}\text{V}^{4+}$-$\text{Fe}^{2+}\text{V}^{4+}\text{O}_4$ (synthetic compound, inverse spinel) (Rodgers et al. 1963).

The intent of this study is to explore the relationships between $\text{V}$ partitioning behavior and spinel crystal chemistry at magmatic conditions over several orders of magnitude in $f\text{O}_2$. In particular, we examine (1) the interplay among normal-inverse spinel structure, $\text{Fe}^{2+}$-$\text{Fe}^{3+}$, and $\text{V}$ partitioning and (2) the importance of using this interaction for interpreting petrologic conditions for the origin of extraterrestrial materials.

**CRYSTAL CHEMISTRY OF SPINEL**

The potential interplay between vanadium and iron valence states in the context of the spinel crystal chemistry is partially illustrated in Figure 1. This figure shows the crystal structure of both normal and inverse spinel. The normal spinel structure (Fig. 1a) is represented by magnesiocoulsonite, $\text{IVMgV}^{3+}\text{O}_4$ (see Papike et al. 2005 and references therein). In naturally occurring normal spinel, the sixteen octahedral sites per unit cell (Papike et al. 2005) are occupied by trivalent cations Cr, Al, $\text{V}^{3+}$, etc., while the eight tetrahedral sites per unit cell are occupied mainly by Mg and $\text{Fe}^{2+}$. The inverse spinel structure (Fig. 1b) is represented by magnetite, $\text{IVFe}^{3+}\text{VI(Fe}^{2+}\text{Fe}^{3+})\text{O}_4$. In naturally occurring inverse spinel, the sixteen octahedral sites per unit cell are occupied by tetravalent, trivalent, and divalent cations, Ti$^{4+}$, $\text{Fe}^{3+}$, $\text{Cr}^{3+}$, Al$^{3+}$, $\text{V}^{3+}$, $\text{Fe}^{2+}$, while the eight tetrahedral sites per unit cell are occupied mainly by cations such as $\text{Fe}^{3+}$. In Figure 1c, synthetic inverse vanadium spinel is represented by $\text{IVFe}^{2+}\text{VI(Fe}^{2+}\text{V}^{4+})\text{O}_4$ (Rodgers et al. 1963). This spinel is referred to as $\text{V}$-inverse in this paper. This synthetic compound has the same structure as ulvöspinel, with $\text{V}^{4+}$ taking the place of Ti$^{4+}$. In a study by Wechsler et al. (1984), the authors point out that (based on neutron diffraction), all Ti is confined
to the sixteen octahedral sites per unit cell, none enters the eight tetrahedral sites. We assume that
the same holds true in our own experiments. Thus even in spinel at reducing conditions such as
IW-1, which is largely chromite with the normal spinel structure $^{\text{IV}}(\text{Mg, Fe}^{2+})^{\text{VI}}\text{Cr}^{3+}2\text{O}_4$, small
domains of the inverse structure must exist in order to accommodate Ti.

Spinels with chromite contents between 0.00 and 0.48 mole fraction are characterized by
domains that are dominantly “normal” spinel, while those with ülvospinel contents greater than
0.88 mole fraction ülvospinel contain domains that are dominantly “inverse.” See Haggerty
(1972) for documentation of this miscibility gap. The result is that the lowest free energy
assemblage is a two-phase region of a chromite-rich spinel and an ülvospinel-rich spinel
coexisting across a miscibility gap. This explains the ubiquitous miscibility gap between spinels
with ülvospinel contents less than 0.48 mole fraction ülvospinel/(ülvospinel + chromite) and
those with greater than 0.88 mole fraction ülvospinel.

EXPERIMENTAL AND ANALYTICAL APPROACHES

Experiments

All of the Yamato 980459 (Y98) composition partitioning experiments were conducted in
the gas mixing laboratory at NASA Johnson Space Center. The majority of the experiments were
performed using Re wire loops to prevent Fe-loss. Experiments run at oxygen fugacities at or
above the FMQ buffer employed Pt/Rh-alloy wire loops. Experimental $f$O$_2$ was controlled using
CO/CO$_2$ gas mixtures that were calibrated with a Y-stabilized zirconia electrochemical oxygen
sensor, specifically the SIRO2 from COF-Australia, housed in a dedicated reference furnace.
Experiments were conducted at discrete $f$O$_2$ intervals separated by approximately 1 log unit. The
experimental $f$O$_2$ values ranged from $\Delta$IW-1 to $\Delta$IW+5.4. Experiments were conducted with an
initial, eight hour super-liquidus dwell at 1450°C. At the end of the super-liquidus soak, the
temperature was dropped at 0.25°C sec\(^{-1}\) until reaching the final target temperature of 1200°C. Experiments were terminated by drop quenching the charge into water. The synthetic Y98 composition used in the experiments was made from a mixture of synthetic oxide powders that were fused to form a homogenous glass. This glass was milled to a fine-grained powder prior to being used in the experiments. The composition of the glass was patterned after the reported composition of the bulk Y98 meteorite. Additionally, starting glass was also doped with 0.20 wt. % V\(_2\)O\(_3\), EuO\(_2\) and CeO\(_2\).

**Electron microprobe (EPMA)**

Analyses were collected on the JEOL JXA 8200 electron microprobe at the Institute of Meteoritics (IOM) and Department of Earth and Planetary Sciences (E&PS), at the University of New Mexico (UNM). Backscattered electron imaging and analyses were collected at an accelerating voltage of 15 kV. Oxide phases were analyzed using a probe current of 20 nA, and a spot size of 0-2 µm. Glass analyses were collected at a beam current of 10 nA, and a spot size of 5 µm to limit beam volatilization. Elements were calibrated using C.M. Taylor Co. EPMA standards, as well as additional standards developed in-house; a separate calibration was used for the oxides and the glass. Vanadium measurements were made under typical analytical conditions, i.e., 40 second peak counting and 20 seconds on both background positions. The Ti interference on V was specifically determined for our spectrometer configuration (with the Ti K\(\beta\) peak representing a known interference for V K\(\alpha\)), as was the Cr K\(\beta\) interference on Mn K\(\alpha\). Ferric iron in the spinel was calculated using the methodology of Droop (1987).

Uncertainties associated with the calculated partition coefficient values (e.g., for D\(_V^{\text{spinel/glass}}\)) were propagated using the 1σ standard deviations and the mean of the EPMA determined vanadium analyses. Typically, the 1σ standard deviation for a given population of
vanadium analyses was greater than the 2σ analytical uncertainty derived from x-ray counting statistics; therefore, we feel the use of the 1σ standard deviation is a more accurate portrayal of the actual uncertainties that arise from subtle compositional inhomogeneity.

RESULTS

Major and minor element chemistry of both spinel and glass are presented in Table 1. Analyses were collected in samples spanning the fO2 range of IW-1 to FMQ+2. Analytical conditions were tailored to the phases being analyzed, and are discussed in detail in the experimental and analytical approach section above.

The major element chemistry of the spinels is generally defined by an increase in magnetite component at the expense of the chromite and spinel components with increasing fO2. This can be seen in changes in the concentration of the elements that define those components. The average aluminum content of the spinels drops from 8.62 wt.% Al2O3 at IW-1 to 5.96 wt.% at FMQ; at FMQ+1 and FMQ+2, Al2O3 jumps up slightly to 7.30 and 6.95 wt.%, respectively. Chromium initially increases from 46.06 wt.% Cr2O3 at IW-1 to 54.87 wt.% at FMQ, but increasing fO2 results in a drop in Cr2O3 to 39.83 and 40.42 wt.% at FMQ+1 and FMQ+2, respectively. The calculated Fe2O3 concentration increases from 0.94 wt.% to 8.12 wt.% at FMQ; increasing the fO2 results in further increases in Fe2O3, where at FMQ+1 and FMQ+2, it was calculated to be 17.27 and 17.53 wt.%, respectively (Fig. 2a). Figure 2b shows the modeled Cr3+/ total Cr in glass (discussed more below). Figure 2c illustrates measured vanadium in spinel, and Figure 2d presents modeled ferric iron in the liquid. All of these are discussed below.

Vanadium concentration in spinel initially shows a decrease with increasing fO2. The V2O3 concentration of the spinel drops from 9.16 wt.% to 1.58 wt.% in the IW-1 and FMQ experiments, respectively (Fig. 2c). Increasing fO2 further results in a slight bump in V, to 2.40
and 2.22 wt.% V$_2$O$_3$, at FMQ+1 and FMQ+2, respectively. Remaining major and minor element chemistry in the spinels is detailed in Table 1.

Analyses collected in the glasses in the experiments indicate that Cr decreases in the melt with increasing $f$O$_2$, while V increases (Table 1). The Cr$_2$O$_3$ concentration varies from 0.37 wt.% in the IW-1 experiment to 0.12 wt.% in the FMQ+2 experiment. The V$_2$O$_3$ concentration increases from 0.20 wt.% in the IW-1 experiment, to a high of 0.33 wt.% in the FMQ+2 experiment. Partition coefficient values, calculated for V between spinel and melt ($D_V^{\text{spinel/melt}}$), generally drop from the low $f$O$_2$ experiments through the more oxidized samples (Fig. 3, Table 1). The calculated values range from 45.2 at IW-1, down to 6.2 at FMQ. The experiments at even higher $f$O$_2$ show some variability in the partition coefficient; $D_V^{\text{spinel/melt}}$ is calculated at 7.6 and 6.8 at FMQ+1 and FMQ+2, respectively.

DISCUSSION

The Effect of $f$O$_2$ on Spinel Composition and the Compatibility of V$^{3+}$ and V$^{4+}$

Not only does $f$O$_2$ profoundly change the spinel-melt partitioning systematics of V, but it also exerts a significant influence on the valence ratios of Fe$^{3+}$ to Fe$^{2+}$ and Cr$^{3+}$ to Cr$^{2+}$ in the melt. The availabilities of Cr$^{3+}$, Fe$^{2+}$, and Fe$^{3+}$ in the melt should, in some way, also be manifested in the equilibrium composition of the spinel. Changes in the major element composition of spinel have been indirectly observed to have important consequences for the compatibility of V in the spinel structure (Canil 2002; Righter et al. 2006 and Mallmann and O’Neill 2009). The underlying crystal chemical reasons for these effects are discussed in detail in the following section. In this section we focus the discussion on how changes in Cr and Fe valence influence both the composition and structure of the equilibrium spinels.
The spinel components have been plotted as a function of \(fO_2\) in Figure 4. This figure clearly illustrates two important points: (1) the major element composition of the spinel is relatively constant as \(fO_2\) is increased from IW-1 to IW+3.4 (i.e., FMQ), and (2) at \(fO_2\) values >IW+3.4, the composition of the spinel shows a significant increase in its magnetite component accompanied by a reduction in the spinel and ferro-chromite components.

The availability of Cr\(^{3+}\) in the melt is an important parameter that plays a critical role in defining the stability field of spinel with respect to both its position on the liquidus, as well as its equilibrium composition, and therefore has important implications for V stability in spinel as well. Several recent studies have demonstrated the Cr\(^{3+}/\text{Cr}^{\text{total}}\) (Fig. 2b) in basaltic melts changes dramatically as \(fO_2\) is increased from values near the IW buffer to values near the FMQ buffer (Hanson and Jones 1998; Berry et al. 2006 and Bell et al. 2014). Curiously, the increase in Cr\(^{3+}/\text{Cr}^{2+}\) of the melt does not appear to significantly increase the chromite content of the experimental spinels. Importantly, this observation suggests that \(fO_2\) has only a minor effect on spinel composition in the \(fO_2\) space where the concentration of ferric iron in the melt is minimal. The increase in the Cr\(^{3+}/\text{Cr}^{2+}\) ratio that accompanies the oxidation of the melt appears to be accommodated through the crystallization of additional Cr-rich spinel. This observation is corroborated by the monotonic decrease in the Cr\(^{\text{total}}\) content of the melt that occurs with increasing \(fO_2\). In contrast, the effect of ferric iron on the composition of the spinel is relatively pronounced. The increasing abundance of Fe\(^{3+}\) in the melt results in the spinel being steadily enriched in the magnetite component and depleted in the MgAl\(_2\)O\(_4\) component.

From a structural point of view, the observed change in spinel composition can be understood as follows: at low oxygen fugacity, ~IW-1 to IW+3, the structure is that of normal spinel, in which the sixteen octahedral sites per unit cell (Papike et al. 2005) are occupied by...
trivalent cations, Cr, Al, V$^{3+}$ etc., while the eight tetrahedral sites per unit cell are occupied mainly by Mg and Fe$^{2+}$. Spinel at IW-1 to IW+3 must be dominated by the normal spinel structure, only containing isolated domains of the inverse structure to accommodate elements such as Ti$^{4+}$ and limited quantities of Fe$^{3+}$. However, in the oxygen fugacity range above IW+3, the increasing Fe$_2$O$_3$ in the melt causes a significant shift in the spinel composition, where domains of the inverse spinel structure (which have lower free energy than the normal spinel structure) become increasingly prevalent.

The observed changes in the spinel composition have important implications for the compatibility of V$^{3+}$ and V$^{4+}$ in the octahedral sites of the spinel. For example, V$^{3+}$ is highly compatible in Cr-rich normal spinel as it can readily substitute for Cr$^{3+}$. Normal spinels have difficulty accommodating higher valence cations in the octahedral sites due to charge balance issues, therefore small, highly charged cations such as Ti$^{4+}$ and V$^{4+}$ only partition weakly into these sites. In contrast to this behavior, 4$^+$ cations are much more compatible in the inverse spinel structure where divalent cations occupy the tetrahedral sites in order to maintain charge balance. The consequences of this change in spinel composition and structure will be explored in detail in the next section of the work.

**The variation of $D_V^{\text{spinel/glass}}$ with Oxygen Fugacity**

The observed trend in the vanadium partition coefficients (Fig. 3a) must be interpreted with respect to both the ratio of V$^{3+}$ to V$^{4+}$ in the melt, as well the changing major element composition and structure of the spinel. It is represented schematically in Figure 5. In an attempt to disentangle the crystal chemical effects on $D_V^{\text{spinel/glass}}$ from that of the changing V$^{3+}$/V$^{4+}$ in the melt, we have modeled the $D_V^{\text{spinel/glass}}$ as a function of $f$O$_2$ for the experimental spinels (Fig. 3b). It is clear from this figure that increasing $f$O$_2$ depresses the $D_V^{\text{spinel/glass}}$ value. The model
assumes that: 1) $V^{3+}$ and $V^{4+}$ are the two valence states present in the melt and 2) the $D_{V^{3+}}$ and $D_{V^{4+}}$ values are static (i.e., they are independent of the major element composition of the spinel and comply with Henry’s Law). The total partition coefficient for vanadium can therefore be expressed as:

$$D_{V_{\text{spinel/melt}}} = (x_{V^{3+}_{\text{melt}}} D_{V^{3+}}) + (x_{V^{4+}_{\text{melt}}} D_{V^{4+}})$$

In the case of our experiments, the effects of $fO_2$ on the major element compositions of the experimental spinels are minimal at $fO_2$ values lower than IW+2. Therefore, the use of static $D$ values in this $fO_2$ range is justified. However, calculating the $D_{V_{\text{spinel/melt}}}$ (effective) requires knowledge of the molar concentrations of $V^{3+}$ and $V^{4+}$ in the melt. Previous spectroscopic studies of V valence in silicate melts have convincingly demonstrated that $V^{3+}$ comprises >80% of the total V in melts of basaltic compositions (Righter et al. 2006 and Sutton et al. 2005) at reduced conditions (i.e., $fO_2 < IW$). Through trial and error, we found that modeling the $D_{V_{\text{spinel/melt}}}$ curve using a $V^{3+}/V^{total}$ value of 0.90 for the IW-1 experiment and $D_{V^{3+}_{\text{spinel/melt}}} \approx 48$ and $D_{V^{4+}_{\text{spinel/melt}}} = 3$ yielded the best match for the observed trend of our partitioning data.

This modeling also helps clarify the role of $Fe^{3+}$ on the inverse component of the spinel. In the most oxidized experiments, the model curve shows a significant divergence from the measured $D_{V_{\text{spinel/melt}}}$ curve. The divergence of the model curve and measured $D_{V_{\text{spinel/melt}}}$ values can be explained by an increase in the compatibility of $V^{4+}$ in the spinel structure (Papike et al. 2004, 2005), as it becomes more inverse. This change in structure is facilitated by the increasing concentration of $Fe^{3+}$ in both the spinel (as magnetite) and the melt. Furthermore, the modeling clearly shows that in the spinels that contain little $Fe^{3+}$ and have a constant Cr/Al, the $D_{V_{\text{spinel/melt}}}$...
can be modeled as a simple function of the V$^{3+}$/V$^{4+}$ present in the melt. This simplified approach, however, cannot be used for spinels that have a substantial portion of inverse domains. In the case of our experiments, the rise of the inverse structure coincides with rise of Fe$^{3+}$ in the melt with increasing $f_{O_2}$. Although not explicitly addressed by our experiments, this effect is also important for spinels enriched in the ülvospinel component.

Spinels as indicators of planetary parentage and redox histories

This manuscript illustrates the interplay among multivalent cations (Fe$^{2+}$,$^{3+}$, Cr$^{2+}$,$^{3+}$, V$^{3+}$,$^{4+}$), the spinel structure, and oxygen fugacity in determining the partitioning behavior of vanadium. Understanding this interplay is critical for using spinels as both indicators of planetary parentage and reconstructing the redox history of magmatic systems on the terrestrial planets. Three examples for this use are given below.

Example 1. Papike et al. (2005) and Karner et al. (2003) illustrated the usefulness of silicates (olivine, pyroxene, and plagioclase) for determining planetary parentage of extraterrestrial materials. These approaches have been used in countless studies of meteorites (e.g. Fagan et al. 2002; Agee et al. 2013; Elardo et al. 2013). Papike et al. (2004, 2013) illustrated the qualitative usefulness in relating spinel chemistry to both a parent body source and the $f_{O_2}$ of a planetary body mantle and its associated basalt systems. As discussed in those papers, differences in $f_{O_2}$ among basaltic systems associated with the Earth’s moon and primitive, differentiated small bodies such as the eucrite parent body (~IW-1), the Earth (FMQ±1), and Mars (IW+1 to FMQ) have profound implications for the valence state of multi-valent cations and the spinel structure. The planetary environments that are reduced will be dominated by normal spinels and the reduced species of multi-valent cations. More oxidizing environments, such as the Earth (FMQ±1), and Mars (IW+1 to FMQ), will be dominated by the
transition between normal and inverse spinels and the more oxidized species of multi-valence cations. These differences strongly influence partitioning behavior during mantle melting and subsequent crystallization, and thereby result in differences in spinel compositions.

Example 2. A prominent geochemical feature of the shergottites is the large range in initial Sr isotopic ratios (~0.702 – 0.724) and initial $\varepsilon^{\text{Nd}}$ values (~ -10 to +50) (e.g., Nyquist et al. 2006; Borg et al. 2012; Brandon et al. 2012; Shearer et al. 2008; Symes et al. 2008). Within this range of isotopic characteristics, the shergottites also exhibit a systematic variation in the oxygen fugacity of crystallization (Wadhwa 2001; Herd 2006; Borg et al. 2003, 2005; Borg and Drake 2005; Shearer et al. 2008; Symes et al. 2008). To decipher the petrogenesis of the shergottites, a fuller understanding of the petrologic linkages between these geochemical characteristics and intensive parameters ($f_{O_2}$) must be reached. One approach to deciphering these petrogenetic linkages is to examine the crystallization history preserved in spinel compositions of a single magma and compare the history preserved by spinel populations in different magmas.

Spinels in the shergottites exhibit substantial compositional differences among early spinels from different shergottites and along crystallization trajectories within individual shergottites (e.g. Goodrich et al. 2003; McKay et al. 2004a,b; Peslier et al. 2010; Gross et al. 2011). Early spinels in the isotopically depleted shergottites such as Y980459, NWA 5789, SaU 005, and Dhofar 019 have relatively low magnetite (1 to 2%) and inverse spinel components (magnetite + ülvospinel ~ 4 to 5%). Therefore, $f_{O_2}$ estimates from V partitioning in these lithologies should be relatively unaffected by the presence of an inverse structural component. Comparison with our data suggests an $f_{O_2}$ of crystallization for Y980459 of IW+1.

On the other hand, the more isotopically enriched shergottites such as NWA 1110 and EETA 79001 have early spinel with higher magnetite (3 to 6%) and inverse spinel components
Based on comparison with our data, the $f_{O_2}$ of crystallization for the enriched shergottites is more oxidizing than IW+2. All of the early spinels have similar chromite-ülvospinel-spinel components and overlapping $V_2O_3$. This suggests similar bulk $D_{V^{\text{spinel/melt}}}$ and slightly different bulk V in the magma. Examining the spinel crystallization trajectories, the magnetite and inverse spinel components increase only slightly, with the magnetite component increasing to 2-5% and the inverse spinel component increasing (magnetite + ülvospinel ~ 8 to 15%). Also, there is an overall increase in the V component in these spinels. Based on our results, this suggests only a subtle increase in $f_{O_2}$ during crystallization.

In contrast, several of the depleted olivine-phyric shergottites exhibit a substantial increase in both the magnetite (13-15%) and the inverse spinel components (magnetite + ülvospinel ~ 18 to 20%). These data suggest that the $f_{O_2}$ becomes increasingly oxidized during crystallization. Very little V data exists for these spinels, but based our analysis would predict an overall decrease in bulk $D_{V^{\text{spinel/melt}}}$ and therefore a decrease in the V content of the late spinels. These initial observations are only the beginning. Combining the experimental data and interpretations with a much more detailed analytical dataset of spinels from the shergottites would yield a much more profound understanding of the $f_{O_2}$ record preserved in martian spinels.

Example 3. The differentiation of asteroids is one of the most fundamental processes to have occurred in the early Solar System. There are numerous families of achondrite meteorites that represent partial melting of these small parent bodies (e.g. eucrites, diogenites, acapulcoites, lodranites, brachinites, and unclassified Na-rich achondrites such as GRA 06129/06128). Several of these achondrites represent magmatism on parent bodies with a well-defined $f_{O_2}$ (e.g. eucrites and diogenites ~ IW-1). Other achondrites are derived from parent bodies with $f_{O_2}$ that are not well-defined (e.g. brachinites, unclassified Na-rich achondrites such as GRA 06129/06128). As
has been demonstrated, differences in the $fO_2$ (IW-1 to IW+2) during partial melting on these parent bodies will produce considerably different melt compositions (e.g. Jurewicz et al. 1995; Garder-Vandy et al. 2013; Usui et al. 2014). Several studies have linked brachinites to unique sodium feldspar-rich achondrite GRA 06129/06128 (e.g. Shearer et al. 2010; Usui et al. 2014). Usui et al. (2014) illustrated that partial melting of a chondritic precursor would yield a brachinite residuum and a GRA 06129 melt, under specific $fO_2$ conditions. As both lithologies contain Cr-spinels, examining the systematic relationship between their chemistries and $fO_2$ would allow for an analysis of conditions of melting and crystallization. The spinels in brachinites have a $Cr/(Cr+Al)$ of 0.73 to 0.83. The extent of the magnetite component is debated, but is thought to be approximately 1 to 3%. Complicating the interpretation of this data is the subsolidus reequilibration experienced by both of these primitive lithologies.

This work demonstrates the nuances of the V partitioning and provides a crystal chemical basis for understanding Fe$^{3+}$, Cr, and V substitution into the octahedral sites of spinel. The above examples illustrate the importance of understanding this interplay for using spinels as both indicators of planetary parentage and reconstructing the redox history of magmatic systems on the terrestrial planets.

**IMPLICATIONS**

We seek to understand the origin and evolution of the solar system. There are many ways to do this: theory, experimental approaches and space missions with orbital and landed experiments. Arguably, the most powerful approach is to have a sample from the specific body we want to understand. In some cases this is not currently possible given the costs or the lack of critical technology to enable such missions (e.g., obtaining samples from Europa or the center of Jupiter). The book “Basaltic volcanism in the terrestrial planets” (Basaltic Volcanism Study
Project, 1981) was an early attempt to address the issue of understanding processes in the solar system as recorded by basalts. A team led by the first author (JJP) participated in this exciting study by pulling together information on the silicates from planetary basalts. In the present study we follow giants in the field (Haggerty 1976; Lindsley 1976, 1991; Basaltic Volcanism Study Project, 1981) including S.E. Haggerty (Haggerty 1976; his contribution to Basaltic Volcanism Study Project, 1981) who was a leader in the study of spinels. We hope our work, both preceding and specifically in this paper, will make the use of spinel chemistry, crystal chemistry, and valence state partitioning even more powerful.

The use of a single zoned spinel from (normal spinel, chromite) to (inverse spinel ülvospinel-magnetite) can, with use of the ratios of $\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Cr}^{2+}, \text{Cr}^{3+}, V^{2+,3+,4+,5+}$ compared to the other elements in the core to rim zoning trend of a single spinel crystal, identify the planetary parentage of the grain and (if the melt composition is known) the quantitative oxygen fugacity trajectory during crystallization of the host basalt.

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FIGURE CAPTIONS

Figure 1. Spinel structural diagrams. a. The normal spinel structure represents 
magnesiocoulsonite, \(^{IV}\)Mg\(^{VI}\)V\(^{3+}\)\(_2\)O\(_4\) (see Papike et al. 2005 and references therein). b. The inverse 
spinel structure (magnetite IVFe\(^{5+}\) VI(Fe\(^{2+}\)Fe\(^{3+}\))O\(_4\)). c. The V-inverse synthetic spinel structure 
(IVFe\(^{2+}\) VI(Fe\(^{2+}\)V\(^{4+}\))O\(_4\)). The structures are color coded as follows: Light blue represents oxygen 
ligands in all structures. Magnesiocoulsonite has yellow representing both Mg\(^{2+}\)-containing
tetrahedra and spheres. Red represents $V^{3+}$ and $V^{4+}$ octahedra and spheres. Magnetite has purple representing $Fe^{3+}$ tetrahedra, octahedra, and spheres, and green representing $Fe^{2+}$. V-inverse has green representing Fe (both ferrous and ferric) and red representing $V^{4+}$. As the structure evolves, from (a) normal spinel/ magnesiocoulsonite to (b) magnetite and from (a) to (c), with increasing oxygen fugacity, $V^{3+}$ in normal spinel is replaced by $V^{4+}$ in inverse spinel and by $Fe^{2+}$ and $Fe^{3+}$ in magnetite (an inverse spinel).

Figure 2. a. Shows the variation of Fe$_2$O$_3$ in spinel (wt.%). b. Shows modeled Cr$^{3+}$/total Cr in melt. Error bars represent the 1σ standard deviation. c. Shows V$_2$O$_3$ in spinel (wt. %). d. Shows modeled Fe$_2$O$_3$ in the liquid (wt. %). The modeled Cr valence in the melt was produced with the data and methods described in Bell et al. (2014). The ferric/ferrous ratios of the melts were modeled using the Kress and Carmichael (1991) equation and the EPMA determined melt composition.

Figure 3. a. $D_{V^{\text{spinel/melt}}}$ (partition coefficient). Error bars represent the 1σ propagated error. b. Measured $D_{V^{\text{spinel/melt}}}$, as in Figure 3a., with modeled partitioning curve overlain.

Figure 4. Spinel components chromite, magnetite, and other normal spinel, as a function of $fO_2$.

Figure 5. A cartoon that illustrates the combined effects of vanadium valence in the melt and the increase in the magnetite component of the spinel.
### Table 1. Experimental average values. Standard deviation (1σ) shown in parentheses.

<table>
<thead>
<tr>
<th>/O₂</th>
<th>IW-1</th>
<th>IW</th>
<th>IW+1</th>
<th>IW+2.2</th>
<th>FMQ</th>
<th>FMQ+1</th>
<th>FMQ+2</th>
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<tr>
<td>Sample ID:</td>
<td>Y98C-21</td>
<td>Y98C-15</td>
<td>Y98C-10</td>
<td>Y98C-40</td>
<td>Y98C-19</td>
<td>Y98C-29</td>
<td>Y98C-31</td>
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<tr>
<td>Oxide (Wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>SiO₂</td>
<td>0.26 (0.03)</td>
<td>0.18 (0.02)</td>
<td>0.26 (0.03)</td>
<td>0.16 (0.03)</td>
<td>0.15 (0.02)</td>
<td>0.17 (0.03)</td>
<td>0.17 (0.03)</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.62 (1.94)</td>
<td>8.40 (1.12)</td>
<td>8.14 (0.78)</td>
<td>6.74 (0.21)</td>
<td>5.96 (0.12)</td>
<td>7.30 (0.05)</td>
<td>6.95 (0.11)</td>
</tr>
<tr>
<td>Fe₂O₃*</td>
<td>0.94 (0.25)</td>
<td>2.35 (0.24)</td>
<td>3.59 (0.41)</td>
<td>6.30 (0.33)</td>
<td>8.12 (0.25)</td>
<td>17.27 (0.29)</td>
<td>17.53 (0.39)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.79 (0.21)</td>
<td>2.37 (0.25)</td>
<td>2.04 (0.05)</td>
<td>1.42 (0.14)</td>
<td>0.90 (0.04)</td>
<td>1.89 (0.02)</td>
<td>1.72 (0.07)</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>46.06 (1.94)</td>
<td>48.43 (1.74)</td>
<td>49.08 (1.81)</td>
<td>51.68 (0.63)</td>
<td>54.87 (0.42)</td>
<td>39.83 (0.11)</td>
<td>40.42 (0.76)</td>
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<tr>
<td>MgO</td>
<td>6.76 (0.24)</td>
<td>6.67 (0.21)</td>
<td>6.97 (0.18)</td>
<td>6.66 (0.11)</td>
<td>9.44 (0.08)</td>
<td>7.45 (0.04)</td>
<td>7.39 (0.07)</td>
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<tr>
<td>FeO</td>
<td>25.64 (0.31)</td>
<td>25.26 (0.25)</td>
<td>24.50 (0.23)</td>
<td>23.82 (0.12)</td>
<td>19.17 (0.13)</td>
<td>22.79 (0.06)</td>
<td>22.65 (0.19)</td>
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<tr>
<td>MnO</td>
<td>0.60 (0.02)</td>
<td>0.57 (0.01)</td>
<td>0.58 (0.01)</td>
<td>0.60 (0.02)</td>
<td>0.53 (0.02)</td>
<td>0.60 (0.02)</td>
<td>0.62 (0.02)</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>9.16 (0.44)</td>
<td>6.56 (0.40)</td>
<td>5.58 (0.23)</td>
<td>2.80 (0.53)</td>
<td>1.58 (0.05)</td>
<td>2.40 (0.01)</td>
<td>2.22 (0.07)</td>
</tr>
<tr>
<td>Total</td>
<td>100.83</td>
<td>100.78</td>
<td>100.74</td>
<td>100.19</td>
<td>100.72</td>
<td>99.69</td>
<td>99.67</td>
</tr>
</tbody>
</table>

| A.F.U. | | | | | | | |
| Si | 0.01 (0.00) | 0.01 (0.00) | 0.01 (0.00) | 0.01 (0.00) | 0.01 (0.00) | 0.01 (0.00) | 0.01 (0.00) |
| Al | 0.34 (0.07) | 0.33 (0.04) | 0.32 (0.03) | 0.27 (0.01) | 0.24 (0.00) | 0.30 (0.00) | 0.28 (0.01) |
| Fe³⁺ | 0.02 (0.01) | 0.06 (0.01) | 0.09 (0.01) | 0.16 (0.01) | 0.21 (0.01) | 0.45 (0.01) | 0.45 (0.01) |
| Ti | 0.07 (0.01) | 0.06 (0.01) | 0.05 (0.00) | 0.04 (0.00) | 0.02 (0.00) | 0.05 (0.00) | 0.04 (0.00) |
| Cr | 1.23 (0.06) | 1.29 (0.05) | 1.31 (0.05) | 1.40 (0.02) | 1.46 (0.01) | 1.08 (0.00) | 1.10 (0.02) |
| Mg | 0.34 (0.01) | 0.34 (0.01) | 0.35 (0.01) | 0.34 (0.01) | 0.47 (0.00) | 0.38 (0.00) | 0.38 (0.00) |
| Fe²⁺ | 0.72 (0.01) | 0.71 (0.01) | 0.69 (0.01) | 0.68 (0.00) | 0.54 (0.00) | 0.66 (0.00) | 0.65 (0.00) |
| Mn | 0.02 (0.00) | 0.02 (0.00) | 0.02 (0.00) | 0.02 (0.00) | 0.02 (0.00) | 0.02 (0.00) | 0.02 (0.00) |
| V | 0.25 (0.01) | 0.18 (0.01) | 0.15 (0.01) | 0.08 (0.01) | 0.04 (0.00) | 0.07 (0.00) | 0.06 (0.00) |
| Total | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 | 3.00 |

| Components (Mol.%) | | | | | | | |
| Chromite | 0.77 | 0.77 | 0.76 | 0.76 | 0.77 | 0.59 | 0.60 |
| Spinel | 0.21 | 0.20 | 0.19 | 0.15 | 0.12 | 0.16 | 0.15 |
| Magnetite | 0.01 | 0.04 | 0.05 | 0.09 | 0.11 | 0.24 | 0.25 |

| Glass (Wt.%) | | | | | | | |
| Cr₂O₃ | 0.37 (0.02) | 0.22 (0.03) | 0.20 (0.02) | 0.13 (0.02) | 0.13 (0.04) | 0.12 (0.02) | 0.12 (0.02) |
| V₂O₃ | 0.20 (0.02) | 0.18 (0.02) | 0.21 (0.01) | 0.23 (0.02) | 0.26 (0.03) | 0.32 (0.02) | 0.33 (0.02) |

<table>
<thead>
<tr>
<th>Partition Coefficient</th>
<th>D_V²spinel/melt</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Y98C-21</td>
<td>45.19</td>
<td>36.75</td>
<td>26.52</td>
<td>12.37</td>
<td>6.19</td>
<td>7.55</td>
<td>6.77</td>
</tr>
</tbody>
</table>

*Estimated using the methodology of Droop (1987).*
Magnesiocoulsonite

Mg$^{2+}$

V$^{3+}$

Fe$^{2+}$

Fe$^{3+}$

V$^{4+}$

Magnetite

V-Inverse
Figure 3.

Model Curve Parameters:

DV^{3+} = 50
DV^{4+} = 3
V^{3+}/V^{Total}@IW-1 = 0.90

Assumes Henrian behavior for “FeV_{2}O_{4}” component in spinel and V^{3+} and V^{4+} are the only valence states present in the melt.
Figure 5.

Increasing $V^{4+}$ in melt (decreasing $V^{3+}/V^{4+}$)

$$D_{V}^{\text{eff}} = (xV^{3+}\text{ melt } DV^{3+}) + (xV^{4+}\text{ melt } DV^{4+})$$

"Spinel" Contains Ferric Iron ~

$D_{V}^{4+}$ increases & $D_{V}^{3+}$ decreases with $Fe_3O_4$ content of spinel  
(i.e. the D values, themselves, are a function the system $fO_2$)

Fe-Free "Spinels"~

$D_{V}^{4+}$ & $D_{V}^{3+}$ are constant  
and $D_{V}^{4+} \ll D_{V}^{3+}$