Ti-V plots and the petrogenesis of modern and ophiolitic lavas

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Plots of Ti vs. V for many modern volcanic rock associations are diagnostic of tectonic setting and can be used to determine possible tectonic settings of ophiolites as well. The basis of this plot is the variation in the crystal/liquid partition coefficients for vanadium, which range with increasing oxygen fugacity from > 1 to < 1. Since the partition coefficients for Ti are almost always << 1, the depletion of V relative to Ti is a function of the $f_{O_2}$ of the magma and its source, the degree of partial melting, and subsequent fractional crystallization. Volcanic rocks from modern island arcs have Ti/V ratios of ~20, except for calc-alkaline volcanics which show the effects of magnetite fractionation. MORB and continental flood basalts have Ti/V ratios of about 20–50 and alkaline rocks have Ti/V generally >50. Back-arc basin basalts may have either arc-like or MORB-like Ti/V ratios, and sample suites from single back-arc basins may have Ti/V ratios ranging from 10 to 50. This range in Ti/V ratios in samples from a restricted geographical area may be diagnostic of the back-arc setting. The Ti/V plot is applied here to published data on ophiolites from a variety of postulated settings and in general supports the conclusions of previous investigators. Ophiolites from the western Mediterranean (Corsica, northern Apennines) and the “lower” Karmøy volcanics have Ti/V trends similar to MORB; the “upper” Karmøy volcanics have alkaline Ti/V ratios. Lavas and tonalites in the Papuan ultramafic belt, the high-Mg andesites of Cape Vogel, and the upper pillow lavas at Troodos all have Ti/V ratios < 20, consistent with formation in an island arc setting. More specific evaluation of the tectonic setting of these and other ophiolites requires application of detailed geologic and petrologic data as well as geochemistry. The Ti/V discrimination diagram, however, is a potentially powerful adjunct to these techniques.

1. Introduction

Ophiolites are commonly considered to represent fragments of oceanic crust formed at spreading ridges, and emplaced tectonically in orogenic zones. Since only the uppermost parts of in situ oceanic crust are exposed or sampled by drilling, most models of ocean crust formation draw heavily on comparisons with ophiolite complexes. It has become clear, however, that ophiolites may form in a variety of tectonic settings, e.g., back-arc basins, island arcs, ocean islands and intra-arc rifts, as well as at mid-ocean ridges. Each of these settings will have profound significance in reconstructing the geologic history of the region in which the ophiolite is found, and also severely constrains the extent to which models of ocean crust formation may be based on specific ophiolite complexes.

Because ophiolites are commonly in tectonic contact with adjacent terranes, and because low-temperature alteration and metamorphism are ubiquitous in ophiolite complexes, structural relationships and major element geochemistry are not definitive of origin in most cases. Trace elements that are relatively immobile during metamorphism have been used successfully as discriminants of ophiolite petrogenesis [1,2] and that approach will be explored further in this paper. Data presented

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here show that plots of Ti vs. V from many modern volcanic rock associations are diagnostic of tectonic setting and may be used to discriminate among possible tectonic settings of ophiolite volcanic rocks as well. This is because the crystal/liquid partition coefficients for V vary from > 1 to << 1 with increasing oxygen fugacity, making it a sensitive indicator of \( f_{O_2} \) conditions. The depletion of V relative to the incompatible element Ti is a measure of this variation and thus the relative \( f_{O_2} \) of the magma and its source. Recent data show that the volatile content (and thus \( f_{O_2} \)) of magmas erupted in oceanic settings increases in the order: MORB < ocean islands < back-arc basins < island arcs [3-5]. However, as we shall see, the actual Ti/V relationships are somewhat complex, for reasons explored below.

Titanium and vanadium are present in basaltic and intermediate rocks in abundances that greatly exceed their detection limit in routine XRF analysis [6], making accurate determination reasonably easy. The problem of Ti-K\(_\beta\) interference on V-K\(_\alpha\) may be dealt with using interference standards, as discussed by Nisbet et al. [6].

### 2. Trace element behavior

#### 2.1 Theory

The use of immobile trace elements as discriminants of ophiolite petrogenesis was pioneered by Pearce and Cann [1,2,7,8] and has since been applied by many others. Trace element discriminant diagrams have been largely empirical until recently when papers by Saunders et al. [9], Pearce and Norry [10], and Pearce [8] have attempted to place them on a firmer theoretical basis. Saunders et al. [9] have proposed a division of magmatophile elements into two groups (excluding REE) based on the ionic character of the elements. Elements with large ionic radii, low charges and high radius/charge ratios are called “low-field strength” (LFS) cations. These cations, which are equivalent to the “LIL” cation group of Schilling [11], have been shown to be mobile during low-temperature alteration (e.g. [12,13]). This mobility renders the “LFS” (LIL) group of questionable value in evaluating older, ophiolite-related volcanics. Elements having small ionic radii and low radius/charge ratios are called “high-field strength” (HFS) cations; they tend to be strongly incompatible, having very small bulk partition coefficients in most situations and are considered immobile during low-temperature alteration [9]. Elements whose cations are in this group include Zr, Hf, Ti, P, Nb and Ta; however, only Zr, Ti and P occur in basaltic rocks in concentration high enough to be determined accurately by XRF analysis. Many of the transition metals (Ni, Co, Sc, Ti, V, Cr) are also immobile during alteration and metamorphism, but with the important exceptions of Ti (a HFS cation) and V, they are compatible elements which are moderately to strongly partitioned into refractory residual phases during partial melting and into early-liquidus mafic phases during crystallization. The geochemical behavior of Ti, which occurs terrestrially in only one valence state, is relatively well known and is a commonly used discriminator (e.g. [2]). The remainder of this discussion will focus on the geochemical behavior of vanadium under differing conditions.

#### 2.2 Vanadium

Vanadium like chromium, differs from the other trace transition metals (Ni, Co, Sc, Ti), in having three common valence states under terrestrial conditions that exhibit strongly contrasting geochemical behavior. Table 1 compares the ionic charge, radius, and radius/charge ratio of vanadium to the incompatible HFS element titanium, and to the compatible transition metals, chromium, scandium, nickel and cobalt. Also shown for comparison are aluminum and the mafic major elements magnesium and iron. All of these elements have ionic radii in the range 0.6–0.8 Å. The mafic major elements and the compatible trace transition metals have similar charges (+2, +3) and relatively large radius/charge ratios (\( > 0.21 \)). These similarities account for the strongly compatible character of these trace elements in the presence of refractory or fractionating mafic minerals, where they occur in octahedrally coordinated sites. In contrast, titanium, with its high charge and small radius/charge ratio, is a HFS cation [9] which has
TABLE 1
Ionic characteristics of vanadium, titanium and related species in octahedral coordination, listed in order increasing radius/charge ratio [61].

<table>
<thead>
<tr>
<th>Species</th>
<th>V$^{3+}$</th>
<th>V$^{4+}$</th>
<th>Ti$^{4+}$</th>
<th>Al$^{3+}$</th>
<th>Cr$^{3+}$</th>
<th>V$^{3+}$</th>
<th>Fe$^{3+}$</th>
<th>Fe$^{2+}$</th>
<th>Sc$^{3+}$</th>
<th>Ni$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>Fe$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radius (Å)</td>
<td>0.62</td>
<td>0.67</td>
<td>0.69</td>
<td>0.61</td>
<td>0.70</td>
<td>0.72</td>
<td>0.73</td>
<td>0.83</td>
<td>0.77</td>
<td>0.80</td>
<td>0.83</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>Radius/charge</td>
<td>0.12</td>
<td>0.17</td>
<td>0.17</td>
<td>0.20</td>
<td>0.23</td>
<td>0.24</td>
<td>0.24</td>
<td>0.28</td>
<td>0.39</td>
<td>0.40</td>
<td>0.42</td>
<td>0.43</td>
<td></td>
</tr>
</tbody>
</table>

very small crystal/liquid partition coefficients for most minerals, with the important exception of magnetite solid solutions [14–17]. Reduced vanadium (V$^{3+}$) has ionic characteristics similar to the compatible trace transition metals and commonly substitutes for other trivalent cations in spinel and pyroxene. The more oxidized species (V$^{4+}$, V$^{5+}$) are HFS cations with high charges and low radius/charge ratios ($\leq 0.17$), similar to titanium (Table 1).

Experimental determinations of the crystal/melt partitioning of vanadium by Lindstrom [18] has shown the $D_V^{\text{ol/1}}$ for pyroxenes (both high and low calcium) and magnetite vary by over two orders of magnitude as a function of oxygen fugacity. At low oxygen fugacities (Fe-Wü buffer, $f_{O_2} = 10^{-11}$ to 10$^{-12}$ at about 1200°C) V$^{3+}$ is the dominant species and partition coefficients are much greater than one; at high oxygen fugacities ($f_{O_2} = 10^{-4.5}$) V$^{5+}$ is the dominant species and partition coefficients are much less than one (Table 2). Varying proportions of V$^{3+}$, V$^{4+}$ and V$^{5+}$ are expected to exist under intermediate $f_{O_2}$ conditions. Table 2 summarizes the experimentally determined partition coefficients of Lindstrom [18] and some empirically derived partition coefficients from literature.

TABLE 2
Crystal/liquid partition coefficients

<table>
<thead>
<tr>
<th>Augite</th>
<th>Low-Ca pyroxene</th>
<th>Olivine</th>
<th>Plagioclase</th>
<th>Magnetite</th>
<th>Hornblende</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Titanium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 (1100°C)</td>
<td>0.6</td>
<td>0.024</td>
<td>&lt;0.05</td>
<td>9–16</td>
<td>4.3–6.8</td>
</tr>
<tr>
<td>0.5 (1220°C)</td>
<td>0.3</td>
<td>(1112–1134°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2–0.8</td>
<td>0.14–0.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Vanadium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 (log $f_{O_2} = -12$)</td>
<td>2.5</td>
<td>0.03</td>
<td>$\sim 0.0$</td>
<td>0.11 (log $f_{O_2} &gt; -4.2$)</td>
<td>6.3–13</td>
</tr>
<tr>
<td>1 (log $f_{O_2} = -10$)</td>
<td>0.5</td>
<td></td>
<td></td>
<td>23 (log $f_{O_2} = -10$)</td>
<td></td>
</tr>
<tr>
<td>0.05 (log $f_{O_2} = -6$)</td>
<td>0.025</td>
<td>(1112–1134°C; QFM buffer)</td>
<td></td>
<td>67 (log $f_{O_2} = -13$)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>23–190</td>
<td>5–100</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Note</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Lindstrom [18].</td>
</tr>
<tr>
<td>b</td>
<td>For same $T$ as augite, using $D_{V^{3+}}^{\text{ol/1}} = 0.6$ [18].</td>
</tr>
<tr>
<td>c</td>
<td>For same $f_{O_2}$ as augite, using $D_{V^{3+}}^{\text{ol/1}} = 0.5$ [14].</td>
</tr>
<tr>
<td>d</td>
<td>Ewart et al. [14]: basalt to andesite.</td>
</tr>
<tr>
<td>e</td>
<td>Leeman et al. [16,17]: ferrobasalt to ferrolatite.</td>
</tr>
<tr>
<td>f</td>
<td>Luhr and Carmichael [26].</td>
</tr>
</tbody>
</table>
2.3 Partial melting and fractional crystallization

The experiments of Lindstrom [18] confirm the predictions from ionic characteristics that vanadium is a sensitive indicator of oxygen fugacity conditions during both partial melting and fractional crystallization. Fig. 1 shows partial melting curves based on a fixed bulk partition coefficient for titanium, and on bulk partition coefficients for vanadium which vary as a function of oxygen fugacity. The bulk partition coefficient for titanium ($D_{\text{Ti}} = 0.15$) was calculated from the data in Table 2 and assumed refractory mantle mineralogies ranging from spinel lherzolite to harzburgite (see Appendix A for a more detailed discussion of the parameters and methods used in the construction of Fig. 1). The bulk partition coefficient for vanadium, $D_{\text{V}}$, for the same refractory mineralogies varies from $\sim 0.15$ ($f_{O_2} \approx 10^{-7}$) to about $1.15$ ($f_{O_2} \approx 10^{-12}$) which spans the range of naturally-occurring oxygen fugacities in most magmatic systems from the reducing conditions prevalent in the source of MORB to the more oxidizing conditions found in many convergent margin settings [3,4,19,20,25]. Curves are drawn for $D_{\text{V}} = 0.15$, 0.45, 0.75, 1.0 and 1.15. The curves have been calculated from the Berthelot-Nernst equilibrium melting equation assuming the bulk earth Ti and V abundances of Ganapathy and Anders [21]. These abundances are slightly higher than chondritic but have about the same Ti/V ratio (bulk earth Ti/V = 10; chondritic Ti/V = 8.4–10 [22]) and are convenient for illustration. Also shown are trend lines of constant initial Ti/V for 20% and 30% partial melts. It is readily apparent (Fig. 1) that the Ti/V ratios of “primary” mantle melts increase with (a) decreasing fraction of melt produced and (b) increasing $D_{\text{V}}$. Primary melts produced by 20–30% partial melting under relatively reducing conditions like MORB ($f_{O_2} = 10^{-11}$ to $10^{-12}$; $D_{\text{V}} > 0.6$) will have initial Ti/V ratios of about 20–50. Similar melts produced under more oxidizing conditions (such as the mantle wedge overlying a de-volatilizing, subducting oceanic slab) should have $D_{\text{V}} < 0.5$ and initial Ti/V ratios of around 10–20. Subsequent silicate fractionation in the latter case (high $f_{O_2}$) will parallel or sub-parallel the constant Ti/V trend lines as long as $D_{\text{Ti}}$ and $D_{\text{V}}$ remain
similar and less than one. This will be true of most fractionating assemblages under oxidizing conditions until the onset of magnetite or hornblende fractionation, which will strongly deplete both Ti and V \[16,17,23,24-26\].

The effects of magnetite fractionation are shown in Fig. 1, as calculated from magnetite/liquid partition coefficients (10% magnetite removal) and as deduced from the trend of calc-alkaline andesites and dacites. These paths are virtually identical and support the origin of these dacites by 10–15% magnetite fractionation. Hornblende/liquid partition coefficients are about half those of magnetite, with \(D_{V}^{bh} / D_{Ti}^{bh} \approx 1.5–2.5 \times D_{V}^{bh} / D_{Ti}^{bh} \) [26]. This means that hornblende and magnetite will have the same relative effect on Ti and V concentrations, but that approximately twice as much hornblende as magnetite must separate (Fig. 1). Recent studies of arc volcanism have shown that hornblende is in general a late crystallizing phase, and is less important than magnetite in creating calc-alkaline trends (e.g. \[25\]). In any case, samples subject to either or both magnetite/hornblende fractionation will have negative trends on plots of Ti (or V) vs. SiO\(_2\), Zr, or FeO*/MgO [23]; these samples will have anomalously high Ti/V ratios and should not be used to discriminate tectonic setting on Ti-V plots.

In case of low-fo\(_2\) conditions (MORB-type magmas) fractionation dominated by olivine and plagioclase will follow the constant initial Ti/V trend lines because of their small crystal/liquid partition coefficients for Ti and V under any conditions. Clinopyroxene or spinel fractionation will cause curved fractionation trends that cross the constant Ti/V ratio lines at low angles. Fig. 1 shows a hypothetical fractionation path of the assemblages ol, ol + plg, ol + plg + cpx (the crystallization sequence of most MORB) starting from a 30% partial melt with an initial Ti/V ratio of 20. It should be noted that because \(D_{V}^{Ti} \) is always greater than \(D_{Ti}^{Ti} \), fractionation cannot drive magmas to lower Ti/V ratios than those inherited from the parental melt. This means that even if high \(f_{O2}\) conditions arise at some stage during the evolution of a mid-ocean ridge magma system (e.g., near a fracture zone), silicate fractionation will evolve magmas that have Ti/V ratios the same as or greater than primary MORB.

An important implication of the chondritic or near chondritic trends in the Ti/V ratios of island arc tholeiites is that their low Ti (and by analogy other HFS cation) abundances cannot be due to retention of Ti-rich minor phases (e.g., ilmenite, rutile) in the refractory residue unless that phase also retains V in chondritic proportion to Ti, or unless V is retained by other refractory phases in just the right modal proportions to maintain chondritic Ti/V ratios. Neither of these possibilities seems likely. The low HFS cation contents of arc tholeiites are thus more probably due to greater degrees of partial melting, followed by extensive closed system fractional crystallization (e.g. \[10\]). Similar arguments may also apply to calc-alkaline magmas.

### 2.4. Stability of Ti and V during alteration and metamorphism

Since the use of trace element plots to investigate ophiolite petrogenesis involves the application of criteria based on more-or-less fresh samples to ancient rocks which may have undergone several episodes of alteration and metamorphism, it is necessary to evaluate briefly the effect of these processes on Ti-V distributions. These processes include low-temperature sea floor weathering ("halmyrosis"), greenschist facies hydrothermal alteration and, possibly, subsequent regional metamorphism. The effect of seawater/basalt interaction at low and high temperatures has been studied both experimentally (e.g. \[27,28, and references therein\]) and on natural samples from dredge hauls and DSDP cores (e.g. \[28,29\]). These studies have shown that Ti and V are stable over a wide range of temperatures and water/rock ratios, even in samples which have been converted entirely to chlorite + quartz [28]. Absolute concentrations may decrease due to dilution by hydration or by the precipitation of anhydrite or calcite, and may increase by passive accumulation as more mobile elements are leached (e.g., Si, Ca). The largest changes are observed during palagonitization of glassy pillow rims, where Ti and V abundances may drop by as much as 50% compared to fresh cores [29]. Alteration of the crystalline interiors of massive flows and pillows may either increase or
decrease Ti and V by 20% or more [29]. In most cases, Ti and V show coherent behavior during alteration, so that the Ti/V ratio remains about the same in the altered rock as in the fresh rock. The data plotted in Fig. 2 (next section) include many altered samples, although relatively fresh rocks dominate. The altered samples plot in the same tectonic setting, suggesting that seawater alteration effects on Ti and V are negligible.

Ophiolites may also undergo regional metamorphism at intermediate to high grades either during or after emplacement. Recent studies of trace element mobility during amphibolite and granulite facies metamorphism suggest that Ti and V are relatively immobile under these conditions [30,31]. In summary, Ti and V appear to be stable over a wide range of temperatures during both seafloor and regional metamorphism. The glassy rims of pillows are most susceptible to changes in Ti/V during alteration. However, this problem can be overcome by judicious sampling in the field.

3. Ti/V plots of modern volcanic rocks

There are four basic tectonic settings in which thick sections of basaltic rocks may accumulate: ocean basins, island arcs, back-arc basins and continental interiors. Each of these settings may be further subdivided on a geochemical or geological basis (e.g., ridge basalts vs. oceanic islands). Alkaline rocks may occur in any of these settings. Fig. 2A–D presents the Ti and V abundances of samples from a number of specific localities or regions representative of these settings and their subdivisions. These data have been compiled from the sources listed in Appendix B.

3.1 MORB

MORB are confined almost entirely to Ti/V ratios between 20 and 50 regardless of whether they are "normal" or "enriched" in LREE and LIL (e.g. [32]; Fig. 2A). This is consistent with the model presented in the preceding section: 20–30% partial melting of a source with chondritic Ti/V = 10, and with the difference $\delta [D_{\text{Ti}} - D_{\text{V}}] = -0.6$ to $-1.0$ (Fig. 1). The crystallization sequence observed in MORB (ol = sp, ol + plg, ol + plg + cpx) is also consistent with the hypothetical fractionation path depicted in Fig. 1 for MORB: increasing Ti and V along the ratio inherited from the primary melt by olivine ± plagioclase fractionation, followed by a curved trajectory across the constant ratio lines during olivine-gabbro fractionation. There is a tendency for "enriched" MORB to have higher absolute abundances of both Ti and V than "normal" MORB, but both types span the same range in Ti/V ratios. There is also a pronounced tendency toward regional variation: basalts from the Pacific and Indian Oceans extend to higher Ti and V abundances than those from the Atlantic ocean, and are seldom as depleted (Fig. 2A). The MORB field is overlapped in part by the field of back-arc basin basalts; this will be discussed further below.

3.2 Flood basalts

Tholeiitic flood basalts of the Columbia River plateau are similar to MORB, being derived by large degrees of partial melting (20–30%) under conditions of low volatile fugacities [33]. The Columbia River basalts have the same range in Ti/V ratios as MORB, but tend to have higher absolute abundances (Fig. 2D). The contrasts in flow morphology and associated sediments between continental flood basalts and MORB makes it unlikely that these settings will be confused, despite their similarity in Ti/V ratios.

3.3 Alkali basalts

Tholeiitic and alkalic basalts from both continents and oceans plot in distinct fields with a minimum of overlap, separated by a Ti/V ratio of about 50 (Fig. 2A, B; [34,35]). Since both tholeiitic and alkalic basalts form relatively deep in the mantle under low $f_O$, conditions, the difference $\delta [D_{\text{Ti}} - D_{\text{V}}]$ should be about the same in both cases. The consistent difference in Ti/V ratios between tholeiitic and alkalic basalts may reflect either (a) primary differences in the Ti/V ratios of their respective sources, (b) retention of contrasting refractory assemblages during partial melting of their sources, (c) derivation of alkali basalts
Fig. 2. Ti/V plots of modern volcanic rocks, showing fields for specific regions and trend lines of constant Ti/V ratios = 10, 20, 50 and 100 for reference. Data sources are listed in Appendix B. A. MORB: Atlantic Ocean (n = 61); Pacific Ocean (n = 47); Indian Ocean (n = 23) and the Red Sea axis basalts (n = 4). Fields drawn by eye to include the majority of samples for each given region.

from smaller amounts of partial melting, or (d) formation of alkalic magmas by partial melting under high CO₂ activities, which will reduce the activities of both oxygen and water. It is not possible to distinguish between these possibilities with Ti/V data, and all may be operative in varying degrees (e.g. [11,28]).

Alkali basalts in ocean basins may occur at spreading centers, but are most common off-axis as oceanic islands and seamounts. Off-axis sills which intrude sediment in the Shikoku Basin (DSDP Leg 38, Hole 444; [36]) are either tholeiitic
(Ti/V = 30–50) or transitional to alkaline (Ti/V = 35–70). Transitional basalts from small seamounts near the East Pacific Rise [37] have Ti/V ratios of 40–50, while Hawaiian tholeiites [38] range from 42 to 60 and Hawaiian alkali basalts [39] range from 50 to 110 (Fig. 2B). This suggests that seamounts which form off-axis may begin as tholeiitic basalts similar to “enriched” MORB and evolve toward more alkalic Ti/V ratios and compositions [40].

3.4 Island arc lavas

Volcanic rocks from island arc-related settings may be divided into at least three suites [41]:
island arc tholeiite (Fig. 2C), calc-alkaline (Fig. 2D) and shoshonite (Fig. 2D). Recent work in many intra-oceanic arcs has shown that all gradations exist between tholeiitic and calc-alkaline suites [25]. These terms will be retained here, however, because they are representative of the gross geochemical variations possible within arc terrains and because they exhibit contrasting behavior with respect to Ti and V. The arc tholeiite and calc-alkaline series are each represented by both basic
(SiO$_2$ < 58–60%) and more fractionated intermediate rocks (SiO$_2$ > 58–60%). Shoshonites are all relatively basic. Other, less common rock suites which may occur in an island arc setting are the boninite suite [42,43] and the picrite-ankaramite association [44,45].

Arc tholeiite series. Arc tholeiites with silica < 60% plot almost exclusively on or near chondritic trends and have Ti/V ratios < 20 (Fig. 2C). There is minor overlap with MORB ratios (20–27) when V is less than 350 ppm; however, suites of related samples with a range of Ti and V abundances will
display the distinctive "chondritic" trend that clearly distinguishes arc tholeiites from MORB. The more evolved rocks of the arc tholeiite suite (SiO₂ > 58–60%) show the effects of titanomagnetite fractionation: sudden drastic reduction in Ti and V abundances and increasing Ti/V ratios. The effects of magnetite fractionation are discussed in more detail below.

**Calc-alkaline series.** In contrast to the arc tholeiite series, calc-alkaline series eruptives have negative slopes on plots of Ti (or V) vs. Zr, FeO*/MgO, or SiO₂ regardless of their silica content, which implies magnetite fractionation throughout their evolution [23]. As a result, calc-alkaline volcanic rocks define trends on Ti-V diagrams (Fig. 2D) that are parallel to magnetite fractionation paths (Fig. 1) calculated from empirically-derived magnetite/liquid partition coefficients [16,17]. The V abundances of both tholeiitic and calc-alkaline dacites are consistent with 10–15% magnetite fractionation from basalts containing 300–350 ppm V (i.e., the same as the most V-rich calc-alkaline basalts shown in Fig. 2D). Magnetite fractionation causes Ti/V ratios to increase, so that calc-alkaline rocks have Ti/V > 15 (Fig. 2D). The influence of magnetite control can be easily ascertained by the use of supplementary plots of Ti and V against an independent fractionation index such as Zr, FeO*/MgO or SiO₂ [23]. Rock suites with negative slopes throughout their evolution are calc-alkaline with obvious island arc affinities and the Ti/V plot is not applicable or needed. Rock suites with positive slopes at low Zr (or SiO₂) and negative slopes at high Zr (or SiO₂) are tholeiitic, and samples from the positive slope may be plotted on the Ti/V diagram to distinguish the nature of their original tectonic setting.

**Shoshonites.** Shoshonitic basalts from Fiji [46] have Ti/V ratios and abundances similar to arc tholeiites, although Ti/V may be as low as 4.5 (Fig. 2D). Vanadium generally decreases with increasing silica, but Ti varies irregularly so that the effect of magnetite fractionation is unclear. There is, however, a rough positive correlation between in creasing Ti/V and K₂O/Na₂O in the Fiji shoshonites (Fig. 3). This coupled with the very low Ti/V ratios (~ 1/2 chondritic) in samples with the lowest K₂O/Na₂O ratios, suggests that Ti and K₂O were selectively added to a source region that had been previously melted to create the low Ti/V ratios, or that a previously unmelted phase rich in TiO₂ and K₂O (e.g., Ti-phlogopite) began to participate during progressive melting. Models similar to the latter have been proposed by Jakeš and White [41]. Shoshonites are clearly distinguished from intra-oceanic and continental alkali basalts by their arc-like Ti/V ratios.

**Boninites.** Boninites are petrographically and geochemically distinctive rocks which have been found only in the fore-arc region of modern oceanic arcs [42,43]. They have low Ti/V ratios of about 10 or less, but with lower Ti and V abundances than most arc tholeiites (Ti < 2500 ppm; V < 200 ppm).
This is consistent with their proposed origin by hydrous melting of a source previously depleted by arc tholeiite formation [42,43]. Meijer [43] has described more fractionated rocks from the Marianas which appear to be derived from a boninite parent. These “boninite series” rocks would be expected to have Ti and V abundances somewhat higher than true boninites, but still depleted relative to equivalent arc tholeiites.

Ankaramites. The picrite-ankaramite association has been documented in several island arcs, most notably at New Georgia in the Solomons arc [44], and throughout the New Hebrides arc (e.g. [45]). These olivine and clinopyroxene-rich lavas are sub-alkaline to mildly alkaline and appear to be related to extensional tectonics within the Solomons and New Hebrides arcs. Ankaramites from the New Hebrides arc have Ti/V ratios ranging from 7 to 27, but most are between 10 and 20 (Fig. 2C). Ankaramites have the same range in Ti and V concentrations, and the same “chondritic” trend on the Ti-V plot, as the island arc tholeiites with which they are commonly associated.

3.5 Back-arc basins

Basaltic rocks from back-arc basins [9, 47] define a field on the Ti/V plot that overlaps both MORB and island arc volcanic rocks, although MORB-like abundances are most common (Fig. 2B). This tendency to show overlapping or transitional geochemical characteristics has been noted by many investigators for other geochemical data (e.g. [9,47]). It appears that the conditions of melting and fractionation vary between the two extremes of oxygen fugacity in a back-arc basin setting. However, back-arc basin basalts tend to show less enrichment in Ti and V than is seen in either MORB or island arc basalts. This may be related to slow, diffuse spreading centers in back-arc basins, which lack well-developed magma chambers [47].

3.6 Summary

It is clear from the foregoing discussion and from Fig. 2 that Ti/V ratios alone are not sufficient to define the tectonic setting of any given volcanic rock in most cases. More important are the trends defined by suites of related samples that exhibit a range of Ti and V abundances. The Ti/V plot is also poorly constrained (a) after the onset of magnetite (± hornblende) fractionation, and (b) for volcanic rocks of the calc-alkaline suite. The first difficulty may be circumvented by first plotting either/or both Ti, V against an independent fractionation index, e.g., Zr, FeO*/MgO or SiO₂, and omitting those data points that indicate magnetite control. This will also reveal whether the rocks are calc-alkaline or tholeiitic [23]. The difficulties with calc-alkaline rocks are not serious, since calc-alkaline series volcanic rocks in the geologic record are seldom mistaken for ophiolites, and they are easily distinguished by their negative slopes on Ti vs. Zr or SiO₂ plots. Shoshonites are more problematical, but are generally spatially associated with calc-alkaline rocks, and have arc-related Ti/V and Zr abundances (e.g. [46]). Island arc tholeiites, boninites and ankaramites, however, may form “ophiolite” assemblages. The Ti/V plot promises to be useful in distinguishing these from MORB ophiolites and ocean islands. Distinguishing back-arc basin related ophiolites will require careful study of local and regional geology as well as geochemistry.

4. Application of Ti/V plots to ophiolite volcanics

In testing the applicability of a new discriminant diagram to older ophiolite terrains, it is desirable to apply it first to familiar, well-studied examples whose tectonic settings are reasonably well-constrained by previous geochemical and geologic investigations. Unfortunately, vanadium is not commonly determined (or reported) for many of these (e.g., Samail, Bay of Islands). Published examples for which vanadium analyses are available include: Corsica [48]; the northern Apennines [49]; Troodos [50] (ranges and means only reported by [48]); the Karmøy Complex in Norway [51]; and Papua-New Guinea [52,53]. These data are presented in Fig. 4.

Western Mediterranean. The ophiolites of Corsica and the northern Apennines have volcanic rocks
Fig. 4. Ti-V plots of ophiolites. Ophiolite volcanic rocks from Corsica [48], the northern Apennines [49] and the Karmøy Complex in Norway [51] have Ti/V ratios between about 30 and 55, except for rare alkaline basalts in the western Mediterranean. The strong linear trends in these suites imply fractionation dominated by olivine ± plagioclase (see Fig. 1). These ratios and trends are consistent with their origin as MORB (see text). Alkaline basalts which are intercalated with sediments that overlie the Karmøy ophiolite have Ti/V > 50, consistent with their proposed origin as an oceanic island [51]. V analyses for Troodos are unpublished [50], but the means and ranges reported by Beccaluva et al. [48] are shown here: TL = Troodos lower pillow lavas; TU = Troodos upper pillow lavas; large circles = respective means. The Troodos upper pillow lavas and the lavas and tonalites of the Papuan ultramafic belt [52] and the high-Mg andesites of Cape Vogel [53], all have Ti/V < 20, which implies their formation near a convergent plate boundary (e.g., within an island arc, or in a small back-arc basin). Ranges reported for the Troodos lower pillow lavas [50] are too large for definite interpretation, but the low mean (~11) implies origin in a setting similar to the Troodos upper lavas.

with Ti/V ratios between 30 and 50, with rare examples of alkaline basalt with Ti/V > 50 (Fig. 4). These Ti/V ratios and trends are consistent with an origin as MORB, an interpretation supported by the primary investigators [8,48,49, 54,55]. Pearce [8] has also noted the tendency toward alkalinity in these rocks which he attributes to their origin in small ocean basins along a rifted continental margin.

**Troodos.** Troodos, in the eastern Mediterranean, has been a controversial subject since Miyashiro [55] first suggested that it was related to island arc volcanism. Subsequent data appear to support his
contention (e.g. [7,8,42,56]), especially in regard to the “Upper Pillow Lavas”. The mean and ranges of Ti and V from the “Upper” and “Lower” volcanic sequences are shown in Fig. 4 [48,49]. The means for both lava groups plot on the chondritic trend of Ti/V ~ 10, however, the ranges for the lower volcanic sequence are too large to draw any definite conclusions. The ranges of Ti and V from the upper pillow lavas are restricted to ratios close to 10, suggesting that these rocks at least were formed in a high volatile environment such as an island arc or intra-arc basin. This conclusion is consistent with Pearce [7,8], Cameron et al. [42], and Dick et al. [56], but at odds with older interpretations [57,58].

**KarrraCy.** The Caledonian Karmøy Complex in Norway consists of two greenstone units: a lower unit of ophiolitic lavas (Visne Group) and an upper unit of alkaline basalts (Vikingstad Greenstone), which is intercalated with 700 m of hemipelagic sediments [51]. The Visne and Vikingstad units have been interpreted by Sturt et al. [51] to represent ocean crust and oceanic island rocks, respectively. This conclusion is supported by their Ti and V abundances, which show MORB and alkaline characteristics, respectively (Fig. 4). Note the distinct linearity sub-parallel to constant Ti/V ratios exhibited by the Karmøy lava suites, and by the western Mediterranean ophiolite lavas, which suggest that fractionation of these lavas was dominated by olivine and plagioclase.

**Papua-New Guinea.** The high-magnesium andesites (HMA) of Cape Vogel are similar to both komatiites and boninites in their low abundances of incompatible elements and high abundances of MgO, Cr and Ni [53]. These rocks have very low absolute abundances of Ti (< 2600 ppm) and V (< 211 ppm) and low to very low Ti/V ratios, ranging from 4.3 to 16.7 (9.3 average) [53]. These rations and abundance levels are consistent with their origin by relatively large percentages of fusion of a previously depleted source, as suggested by Jenner [53] for the Cape Vogel rocks, and by others for boninites from Bonin-Marianas arc [42,43]. This refractory source was enriched in LREE shortly before the second melting event [53]. Jenner [53] claims that this component has an oceanic island or continental affinity, and is not similar to that found in island arcs. We have seen, however, that alkalic rocks and transitional tholeiites from both ocean basins and continents have high Ti/V ratios (> 35 about). Arc-related alkalic rocks (shoshonites) have low Ti/V ratios similar to arc tholeiites. This suggests that the Cape Vogel high Mg-andesites are related to some phase of island arc volcanism, and that by inference the LREE component added may have been derived from a subduction related source.

The Papuan ultramafic belt (PUB) comprises a full ophiolite sequence which has been intruded by Eocene tonalities [52]. The tonalities have Ti/V ratios of 10–20 and very low abundances (Ti < 2000 ppm; V < 150 ppm), consistent with their proposed origin as early island arc magmas related to the HMA of Cape Vogel [52]. Ophiolite basalts of the PUB have Ti/V ratios of 15–18 and V abundances of 450–500 ppm. There is no overlap between MORB and arc tholeiites at these abundance levels, and the island arc affinities of these basalts are clearly demonstrated. Jaques and Chappell [52] inferred that the PUB volcanics were most similar to MORB, but noted many dissimilarities from MORB as well, such as low Ti, Zr and HREE at high FeO*/MgO, and the presence of cumulate orthopyroxene in the plutonic section. Geophysical evidence suggests that the PUB formed in a marginal basin [59,60]. If so, it must have been a small basin close to the subduction zone since the Ti/V ratios imply hydrous melting of the mantle source. The high V abundances and the presence of cumulate orthopyroxene are more suggestive of arc tholeite magmas than of most “back-arc” basin basalts.

5. Conclusions

The data presented here show that plots of Ti vs. V clearly distinguish arc related tholeiites, MORB and alkali basalts. The Ti/V ratio of individual samples is not as diagnostic as the trends defined by suites of related samples that exhibit a range in Ti and V abundances. The theoretical basis of this plot can be modelled assuming a
chondritic mantle (for Ti and V), reasonable refractory mineral assemblages, and bulk partition coefficients for V which vary as a function of oxygen fugacity. The results of this modelling are consistent with what is known about the physical conditions under which each magma series is generated and with experimental determinations of crystal/liquid partition coefficients for vanadium and titanium. Calc-alkaline magmas may be generated under conditions similar to arc tholeiites, but they are dominated by magnetite fractionation throughout their evolution causing variable Ti/V ratios which overlap MORB and alkali basalt ratios at low abundance levels. This makes it necessary to use supplementary plots of V vs. Zr, FeO*/MgO or SiO₂ in order to distinguish the calc-alkaline series (which is definitely arc-related), and to eliminate tholeiite samples which are dominated by magnetite fractionation. Shoshonites have Ti/V ratios similar to arc tholeiites, which serves to distinguish them from other basalts. Although V vs. SiO₂ plots imply magnetite control, the source of shoshonites appears to have been enriched in Ti, so that Ti vs. SiO₂ plots are inconclusive. The only criteria by which “back-arc” basin basalts may be recognized on this plot are variable Ti/V ratios in a suite of samples from a single geographic area, and possibly by a lack of enrichment in either Ti or V, relative to the other magma series.

The use of V as a discriminant offers advantages over plots based on less abundant elements (e.g., Ta, La, Nb, Ce, etc.) because it is easily analyzed by routine XRF techniques (e.g., [6]), having concentrations in basaltic rocks (50–600 ppm) which greatly exceed the detection limit (~3 ppm). Application of this technique to ophiolite volcanic rocks yields interpretations which are consistent with conclusions based on other geochemical techniques and on recent petrologic and structural investigations.

The problems associated with transitional tectonic settings such as back-arc basins or incipient ocean islands, however, require the application of careful geologic, petrologic and structural investigations in addition to various geochemical methods to elucidate the origin of ophiolites formed in these settings.

### Acknowledgements

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### Appendix A

The bulk partition coefficients (Dᵢ) for Ti and V used to construct Fig. 1 were calculated from the relationship:

$$Dᵢ = α₁ Dᵢ^{p/v} + β₁ Dᵢ^{β₁/v} + δ₁ Dᵢ^{δ₁/v} + ... + ψ₁ Dᵢ^{ψ₁/v}$$

where α = weight proportion of phase a, such that α + β + δ + ... + ψ = 1.0, and Dᵢ^{p/v} = partition coefficient for element i between phase α and the liquid. Two refractory mineralogies were assumed: spinel lherzolite (65% ol, 20% opx, 12% cpx, 3% Cr-spinel) and spinel harzburgite (70% ol, 24% opx, 3% cpx, 3% Cr-spinel). These should span the range in the refractory source regions of arcs and MORB, but probably not that of alkali basalts. Spinel/liquid partition coefficients for Ti (≈ 1.2) and V (≈ 6.5) were estimated from an unpublished spinel–whole rock pair (an arc-related ankaramite, corrected for phenocryst content). Other partition coefficients are from Lindstrom [18]; most of these values are summarized in Table 2. Dₚ was calculated from the high-temperature values in Table 2: lherzolite Dₚ ≈ 0.17; harzburgite Dₚ ≈ 0.14; an “average” of 0.15 is assumed since residual harzburgite is more likely for moderate to large degrees of melting. D_v was calculated from the data below for both spinel lherzolite and spinel harzburgite at three nominal oxygen fugacities, and are also listed below:

<table>
<thead>
<tr>
<th>log f_O₂</th>
<th>0</th>
<th>0.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>D_p^{v/1}</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>D_p^{v/1}</td>
<td>0.05</td>
<td>0.50</td>
</tr>
<tr>
<td>D_p^{v/1}</td>
<td>0.10</td>
<td>1.00</td>
</tr>
<tr>
<td>D_p^{v/1}</td>
<td>6.50</td>
<td>6.50</td>
</tr>
<tr>
<td>D_v (harzburgite)</td>
<td>0.23</td>
<td>0.37</td>
</tr>
<tr>
<td>D_v (lherzolite)</td>
<td>0.24</td>
<td>0.44</td>
</tr>
</tbody>
</table>

D_v = D_p (≈ 0.15) is assumed to be the limiting case for high f_O₂ conditions. Due to uncertainties in (a) the experimental
data, (b) the estimated spinel/liquid partition coefficients, (c) the assumed refractory assemblages, and (d) the actual values of $f_O^2$ during partial melting in the upper mantle, these calculated values were used as guidelines in constructing Fig. 1, rather than exact values. The $D_v$ values used to construct Fig. 1 ($D_v = 0.15, 0.45, 0.75, 1.0, 1.15$) were chosen to span the range of calculated values but with the melting curves sufficiently spaced to be viewed clearly. Melting curves were calculated from the batch melting equation:

$$C_i^f = C_i^0 / \left[ D_i^0 + (1 - D_i^0) F \right]$$

where $C_i^f$ = concentration of element $i$ in the liquid; $C_i^0$ = initial concentration of $i$ in the source; $D_i^0$ = bulk partition coefficient for $i$ in the refractory residue, and $F$ = % partial melt. Strictly speaking, this equation applies to modal melting and thus represents a grossly oversimplified model. However, in view of the other uncertainties involved, the use of more complex models is unwarranted and for a first approximation, unnecessary. Fractionation paths are based on Rayleigh fractionation:

$$C_i^f = C_i^0 f_i (1 - D_i^0)^{-1}$$

where $C_i^f$ = concentration of element $i$ in the liquid, $C_i^0$ = the initial concentration of $i$ in the magma, and $f$ = fraction of melt remaining.

**Appendix B**


References

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