Do major oxide tectonic discrimination diagrams work? Evaluating new log-ratio and discriminant-analysis-based diagrams with Indian Ocean mafic volcanics and Asian ophiolites

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ABSTRACT

Many geochemical diagrams exist that classify old volcanic terranes of ambiguous provenance into various modern plate tectonic settings, with variable success. Recently proposed diagrams, based on log-ratios and linear discriminant analysis with large datasets of major oxides, were tested here with data for ocean island, arc and mid-ocean ridge lavas from the Indian Ocean. Success rates are 45–100%, with misclassifications potentially caused by alteration, although alteration demonstrably need not cause misclassification. The diagrams were further applied to some Asian ophiolites, representing Tethyan and Indian ocean crusts, to see if the diagrams confirm their tectonic setting inferred from trace and isotopic data. Lower success rates (30–60%, but 75–100% for specific suites) are not surprising in view of the ubiquitous and complex alteration in ophiolites. Log-ratio transformation and linear discriminant analysis appear to be powerful methods when discrimination diagrams are based on major oxide data alone.

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Introduction

Over the years several igneous geochemists have devised geochemical diagrams that discriminate between volcanic rocks of various plate tectonic settings and which might reveal the original tectonic setting of volcanic terranes that have been transported, deformed and metamorphosed. Early schemes were based on the relatively small datasets on volcanic rocks available then (a few hundred samples) and the boundaries between the various fields were constructed by the eye, and thus subjective (e.g. Pearce and Cann, 1971, 1973). Agrawal (1999) showed the use of probability-based classifier surfaces as boundaries between rock categories, and Agrawal et al. (2004) used them in major oxide plots based on linear discriminant analysis of >1000 samples of volcanics from various tectonic settings. In sync with a fast-growing global database of volcanic rock compositions, there is a current surge of interest and activity in this field, and very recent literature includes extensive evaluations of existing schemes (e.g. Snow, 2006; Vermeesch, 2006a) as well as new ingenious schemes (e.g. Shragge and Snow, 2006; Vermeesch, 2000b; Verma et al., 2006). In this study, I evaluated the discriminating power of diagrams proposed by Verma et al. (2006) (called VGA06 hereafter) and Vermeesch (2006a) (V06a hereafter).

The diagrams, test data and data processing

The VGA06 diagrams (Fig. 2) are based on a large training set (2300 samples) of young (Late Miocene through Recent) basic (SiO$_2 < 52$ wt.%) and some ultrabasic rocks (SiO$_2 < 45$ wt.%) from four tectonic settings (ocean island, island arc, mid-ocean ridge and continental rift). With 400 additional (test) samples, they yielded successful classification rates of 83–97%. The V06a plot (Fig. 3) is based on 738 training samples with SiO$_2$ values between 45% and 53% belonging to OIB, IAB and MORB categories.

Rollinson (1993) has asked whether geochemical diagrams fundamentally can indicate tectonic setting because igneous rock compositions are strongly determined by sources (mantle and crustal) and processes (partial melting, fractionation, contamination) and not directly by tectonic setting. Continental crustal contamination, a not a consideration for oceanic volcanics, can be significant for continental rift basalts. The 52% SiO$_2$ cutoff used by VGA06 does not imply that such rocks are free of crustal contamination (indeed the converse may be true, as more primitive, hotter liquids may assimilate much more crust than evolved liquids, e.g. Huppert and Sparks, 1985). However, basic and ultrabasic rocks would have a vastly larger mantle input than evolved rocks, which may even be continental crustal melts (e.g. Verma, 2000).

Major oxide data in an analysis must add to 100% and are thus subject to closure, and spurious correlations exist in such closed datasets (Chayes, 1960). Aitchison (1982, 1986) proposed log-ratio transformation to ‘free’ the data values to range from $-\infty$ to $+\infty$, and both VGA06 and V06a take advantage of this desirable property. Both use SiO$_2$ (the most abundant oxide) as the denominator to all ratios, and have performed linear discriminant analysis of the log-ratio data to obtain two discriminant functions. The V06a plot is a modification of one by Pearce (1976), who performed linear discriminant analysis but was unaware of closure (Vermeesch, 2006a). The differences between the VGA06 and V06a diagrams are that whereas the former contain discriminant functions including all the oxides, the latter’s functions exclude FeO, Fe$_2$O$_3$ and P$_2$O$_5$. Due conversion of total Fe into Fe$^{2+}$ and Fe$^{3+}$ is an important step in the VGA06
diagrams, for which the proposal of Middlemost (1989) is used. The field boundaries are probability-based surfaces (Agrawal, 1999). LOI-free major oxide data are obtained using the SINCLAS program of Verma et al. (2002).

The VGA06 diagrams are five diagrams, offering all possible combinations of the OIB-CRB-MORB-IAB groups. I tested the VGA06 and V06a diagrams here using 333 samples of mafic volcanics from the Indian Ocean region (Fig. 1). The data come from the archetypal ocean islands of Mauritius and Rodrigues (110 and 10 samples, respectively), the arc volcano Barren Island in the Andaman Sea (45 samples), and the Carlsberg and Southwest Indian ridges (40 and 128 samples respectively). I then applied the diagrams to ophiolites (96 samples) in Iran, Pakistan, Tibet and the Andaman islands that represent remnants of the Tethyan and Indian oceanic crusts. None of these samples is among the >2700 total samples used by VGA06, or the ~1000 samples used by V06a, in their training and testing sets.

The results
Figure 4 is the total alkalis-silica (TAS) diagram (Le Bas et al., 1986) showing the general characteristics of the test samples. Almost all Mauritius and Rodrigues samples are basic, and a few ultrabasic, and most of these alkalic. Several Barren Island samples are basaltic andesite, and two andesite. The Carlsberg Ridge sample suite does not resemble typical N-MORB (which are low-K tholeiites), but are rather alkalic. Most Southwest Indian Ridge samples are true N-MORB. Figures 2 and 3 show the data for them on the VGA06 and V06a diagrams, and Tables 1 and 2 give the number of samples that lie within a particular field in each, along with the overall percentage success rates for each rock suite. The main observations and interpretations follow.

Mauritius and Rodrigues OIB
The raw and adjusted (LOI-free) SiO$_2$ values are all ≤52%. However, the VGA06 diagrams classify almost 60% of the Mauritius samples with CRB, with only 37% with OIB, and 80% of the Rodrigues samples with OIB. This means that OIB and CRB cannot be distinguished by VGA06, something these authors found with their own testing set. There are strong chemical and isotopic similarities between CRB and OIB (e.g. Smith, 1993; Fitton, 2007). OIB-like magmas are abundant in continental rifts, suggesting closely similar mantle sources. Although mantle plumes are often invoked for both OIB and CRB, OIB-type chemistry is no longer considered diagnostic of plumes (Natland and Winterer, 2005; Hofmann and Hart, 2005; Fitton, 2007). CRB and OIB also cannot be distinguished with alteration-resistant trace elements such as Nb and Zr (Fitton, 2007).

The V06a plot correctly classifies 77% of the Mauritius (but only 60% of the Rodrigues) samples, partly because of its different discriminant functions. But it has also an edge over VGA06 by not having a CRB category to which OIBs can be so similar. Indeed, dropping the CRB category dramatically improves the performance of the VGA06 diagrams (Table 3). Whereas the VGA06 diagrams together perform much more poorly than the V06a plot, the VGA06
diagram, without a CRB category, has a much better individual performance, comparable to that of V06a (Table 3). Thus, more categories in such diagrams do not mean improved performance; rather, the opposite can be true. Finally, because an overwhelming majority of ophiolite suites are oceanic (and few, if any, CRB suites would become ophiolites), it may be worthwhile to drop the CRB category from such diagrams.

Barren Island arc volcano

Several of the 45 samples notably have LOI-free SiO₂ > 52%, the upper limit for the VGA06 diagrams, and therefore these should strictly not be tested. Nevertheless, these diagrams show an overall (and minimum) success rate of 72%, and seem to work well for arc rocks. The V06a plot correctly classifies 100% of these, indicating that the degree of differentiation is not a concern over this SiO₂ range.

Carlsberg Ridge

Not too surprisingly, most Carlsberg Ridge MORB samples are not classified with MORB in the five VGA06 diagrams. In fact, overall 72% of these samples are classified as IAB and 26% as MORB. On the V06a plot, only 37.5% of these samples are classified with MORB, and 67.5% are misclassified with OIB. It was noted from the TAS diagram (Fig. 4) that these rocks are not N-MORB. They may be enriched (E)-MORB.

E-MORB are abundant along a very long section of the Southeast Indian Ridge east of ~100°E, without any nearby hotspot (Mahoney et al., 2002a). Trace element data for the Carlsberg Ridge suite here (Banerjee and Iyer, 1991) are limited to Ni, Co, Cr and Cu, and hence the possible E-MORB nature of this suite cannot be ascertained. Part of the problem may be that several major oxides in this study were measured by atomic absorption spectrophotometry, where instrumental calibration with monoelement solutions (as opposed to the multielement natural rocks) is the norm. Alternatively, the alkalic compositions of this suite (and their misclassification in the diagrams) may be because of weathering and alteration (see e.g. Verma, 1981; Jochum and

Fig. 2 (a–e) Data for Indian Ocean volcanics on the discrimination diagrams of Verma et al. (2006). The linear equations for discriminant functions DF1 and DF2 for each of the five plots can be found in Verma et al. (2006). Data sources are: Mauritius Older, Intermediate and Younger Series (Sheth et al., 2003; Nohda et al., 2005; Paul et al., 2005, 2007); Mauritius Older Differentiated Series (Paul et al., 2007); Rodrigues (Baxter et al., 1985); Barren Island (Alam et al., 2004; Luhr and Haldar, 2006; Pal et al., 2007); Carlsberg Ridge MORB (Banerjee and Iyer, 1991); Southwest Indian Ridge MORB (Nakamura et al., 2007).

Fig. 3 Data for the suites shown in Fig. 2, on the Vermesch (2006a) plot.
Table 1 Percentage classifications for volcanic rocks from the Mauritius and Rodrigues ocean islands, Barren Island arc volcano, and Carlsberg and Southwest Indian Ridges on the Verma et al. (2006) diagrams.

<table>
<thead>
<tr>
<th>Fig. no.</th>
<th>OIB (%)</th>
<th>CRB (%)</th>
<th>MORB (%)</th>
<th>IAB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maur (n = 119)</td>
<td>21.5</td>
<td>2.5</td>
<td>96.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Rodrigues (n = 10)</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Barren (n = 45)</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Carls (n = 40)</td>
<td>1.0</td>
<td>1.0</td>
<td>98.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SWIR F-type (n = 20)</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SWIR L-type (n = 61)</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SWIR H-type (n = 47)</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SWIR overall (n = 128)</td>
<td>0.0</td>
<td>0.0</td>
<td>100.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The data are arranged to show the number of samples of a particular rock suite that lie within a specific field (tectonic setting) in each of the diagrams. For example, the number of samples of Mauritius rocks (110 in total) that lie within the fields of OIB, CRB, MORB, and IAB are 21, 89, 0, and 0, respectively (see the '2a' columns under all four categories). The percentage of samples that lies within each of the four fields is calculated as the sum of values in any category divided by five times the number of total samples for that rock suite, multiplied by 100. For example, the number of Mauritius rock samples classified as OIB, in diagrams 2a through 2e, is (21 + 20 + 61 + 47 + 128) / 5 = 0.204. This, divided by 550 (the total number of tries), and multiplied by 100 gives the percentage of Mauritius samples classified as OIB as 37.1%. Zeros in particular cell mean that the particular tectonic field was available in a plot but no samples plotted in it, whereas dashes mean that the particular tectonic field was not present in the plot. Because Fig. 2b-d successively exclude each of the four tectonic fields, any biases and wrong assignments to sample points because of the 'correct' field simply not being available in a plot should mutually cancel out. Percentages close to and above 50% are shown in boldface. F-type SWIR MORB are fresh MORB, L-type are low-degree weathered MORB, and H-type are high-degree weathered MORB (see text).

Case study: Asian ophiolites

Ophiolites are almost always structurally deformed and altered. If not metamorphosed as well. Many ophiolite suites that occur in Asia represent long-subducted Tethyan and Indian oceanic crusts. Because the tectonic setting of several is well documented, they offer an opportunity to apply the study by Nakamura et al. (2006) diagrams to fresh and altered MORB from the same area, and thus to evaluate the role of weathering and alteration in misclassifications. Their 128 samples come from the Southwest Indian Ridge MORB. For the high-temperature altered the V06a plot from fresh and altered MORB from the same area, and thus to evaluate the role of weathering and alteration in misclassifications. Their 128 samples come from the Southwest Indian Ridge MORB. For the high-temperature altered the V06a plot from fresh and altered MORB from the same area, and thus to evaluate the role of weathering and alteration in misclassifications. Their 128 samples come from the Southwest Indian Ridge MORB.
understood, with major and trace element and sometimes Sr-Nd-Pb isotopic determinations, it is tempting to use the current diagrams to see if these can corroborate (and presumably, by themselves reliably indicate) the setting. Figure 5 shows the data for these ophiolites on the Zr–Ti diagram, proposed by Pearce and Cann (1973) and here in its modified form after linear discriminant analysis (Vermeesch, 2006a). Some show affinities with a single tectonic category (e.g. Parh Group with OIB), and others with more than one.

Figures 6 and 7 show the data for these ophiolites on the VGA06 and V06a diagrams, and Tables 4 and 5 summarize the results. The c. 75 Ma Parh Group (Bibaï Volcanics) alkali basalts and basanites are known to have formed as intrusions in shelf-type marine limestones and other sediments, and based on their normalized multielement patterns and isotopic evidence Mahoney et al. (2002b) interpret them as OIBs. The data lie in the CRB and OIB fields in Fig. 5 (and OIB field in Fig. 7) and these plots reaffirm the known great geochemical closeness of CRB to OIB. The V06a plot classifies all samples correctly with OIB. Data for the Muslim Bagh ophiolite cover all fields in the VGA06 diagrams with the MORB field slightly dominating (48.6% MORB followed by 23.8% IAB samples); notably, these were interpreted as of composite tectonic setting (ridge plus arc) based on trace element and other evidence (Khan et al., 2007). They are indeed classified as MORB (52%) and IAB (38%) by the V06a plot, and straddle across all the fields in Fig. 7. The Band-e-Zeyarat/Dar Anar ophiolite of Makran was interpreted as MORB based on elemental and Sr-Nd-Pb isotopic evidence (Ghazi et al., 2004); Table 4 shows 51% of the samples classified as MORB followed by 30% IAB samples, whereas the V06a plot classifies 55% of them with IAB. Here these diagrams perform poorly.

Sr-Nd-Pb isotopic character of the Indus-Zangbo and Eastern Himalayan syntaxis ophiolites indicates their Tethyan MORB provenance (Zhang et al., 2005). 60% samples of both suites are classified as MORB with the VGA06 diagrams, and 65% and 75% respectively with the V06a plot. Finally, the South Andaman ophiolitic basalts do not show a clear preference for any field with either the VGA06 or V06a diagrams, although Srivastava et al. (2004) identified them with MORB with the earlier discrimination diagrams of Agrawal et al. (2004). The performance of the diagrams for ophiolite suites is therefore quite vari-
Table 4 Classification percentages for the Tethyan and Indian oceanic crustal ophiolites with the Verma et al. (2006) diagrams.

<table>
<thead>
<tr>
<th>OIB (%)</th>
<th>MORB (%)</th>
<th>IAB (%)</th>
<th>OIB (%)</th>
<th>MORB (%)</th>
<th>IAB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muslim Bagh (n = 21)</td>
<td>90.00</td>
<td>10.00</td>
<td>0.00</td>
<td>25.00</td>
<td>50.00</td>
</tr>
<tr>
<td>Makran (n = 18)</td>
<td>100.00</td>
<td>0.00</td>
<td>0.00</td>
<td>60.00</td>
<td>10.00</td>
</tr>
<tr>
<td>Indus-Zangbo (n = 26)</td>
<td>90.00</td>
<td>5.90</td>
<td>4.10</td>
<td>26.00</td>
<td>60.00</td>
</tr>
<tr>
<td>E. Himalaya (n = 4)</td>
<td>87.50</td>
<td>12.50</td>
<td>0.00</td>
<td>75.00</td>
<td>12.50</td>
</tr>
</tbody>
</table>

able. It is ‘very good’, with 50–50% OIB + CRB or 100% OIB for the Park Group, through ‘fair’, with 60–75% MORB for the Indus-Zangbo and Eastern Himalayan suites, to ‘poor’ for the Makran and South Andaman suites. Thus these diagrams cannot substitute for trace element and isotopic analyses, which are required and of unquestionable value. Similarly constructed diagrams of only the alteration-resistant major (Ti) and trace (e.g. Nb, Zr, Y) elements should provide still better results.

Conclusions and recommendations

Log-ratio transformation and linear discriminant analysis of large datasets in the VGA06 and V06a diagrams resolve quite well the otherwise subtle major oxide differences between mafic rocks of various tectonic categories, here selected from the Indian Ocean region. The diagrams are quite powerful with OIB, IAB and MORB. The VGA06 diagrams cannot distinguish between CRB and OIB in many cases (though no other existing scheme does). The CRB category may perhaps be dropped from future versions. However, the diagrams have a very variable performance when applied to Tethyan and Indian Ocean ophiolite suites outcropping in Asia, and as clues to the original tectonic setting of ophiolites, these remain quite inferior to trace element and isotopic data.

Table 5 Classification percentages for the Tethyan and Indian oceanic crustal ophiolites with the Vermeesch (2006a) diagram.

<table>
<thead>
<tr>
<th>Fig. no. 7</th>
<th>OIB (%)</th>
<th>MORB (%)</th>
<th>IAB (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Park Group (n = 9)</td>
<td>90.00</td>
<td>10.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Muslim Bagh (n = 21)</td>
<td>100.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Bela (n = 24)</td>
<td>90.00</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Makran (n = 18)</td>
<td>100.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Indus-Zangbo (n = 26)</td>
<td>90.00</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>E. Himalaya (n = 4)</td>
<td>87.50</td>
<td>12.50</td>
<td>0.00</td>
</tr>
<tr>
<td>S. Andaman (n = 16)</td>
<td>87.50</td>
<td>12.50</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Future geochemical schemes might employ large datasets of only the alteration-resistant major (Ti) and trace (e.g. Nb, Zr, Y) elements to acquire maximum possible power and utility (e.g. Vermeesch, 2006a,b).

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References

Fig. 7 The ophiolite data on the Vermeesch (2006a) plot. The Bela ophiolite, missing from Fig. 6 and Table 4, appears here because Vermeesch’s (2006a) functions exclude P2O5.


Verma, S.P., 1981. Seawater alteration effects on $^{87}$Sr/$^{86}$Sr, K, Rb, Cs, Ba and Sr in oceanic igneous rocks. *Chem. Geol.*, 34, 81–89.


Note added: The linear discriminant function equations and coordinates for the VO6a plot used here were wrongly printed in Vermeesch (2006b). The equations and values can be found at: http://pvermeesch.andropov.org/noble/disc/erratum.html.