

# Empirical calibration of the V partitioning between magnetite and ilmenite as an oxybarometer: an amplification

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**ABSTRACT.** Vanadium is measured in magnetite and ilmenite collected in two Fe-Ti ore deposits characterized by different  $fO_2$ . In the Grader ilmenite deposit (Havre-Saint-Pierre anorthosite complex, Québec), the  $fO_2$  has been estimated at  $\Delta NNO$  ca. + 0.6 log units, whereas in the Fedorivka layered intrusion (Korosten anorthosite, Ukraine) a lower  $fO_2$  ranges from  $\Delta FMQ > +0.7$  log units down to -1.4 log units. After correction for subsolidus compositional re-equilibration of the magnetite, the partition coefficient  $D_V^{Mt/Ilm}$  is compared to the  $(Eu^{2+}/Eu^{3+})_{Plag}$  ratio calculated from the Eu distribution between pairs of plagioclase and apatite. Both parameters show a good correlation, the  $(Eu^{2+}/Eu^{3+})_{Plag}$  varying from ca. 30 to ca. 200, and the  $D_V^{Mt/Ilm}$  from ca. 1 to 27. Calibrations of the two oxybarometers are proposed. Though further experiments are needed to ascertain the relationships, comparison with independent data shows that the empirical estimates of  $fO_2$  with  $D_V^{Mt/Ilm}$  are credible.

**KEYWORDS:** vanadium, Eu valence, oxygen fugacity, partition coefficient, Grader deposit, Fedorivka layered intrusion

## INTRODUCTION

Oxygen fugacity ( $fO_2$ ) is a major controlling factor of the evolution of magmatic rocks. Its value can be determined by a number of approaches that mostly derive from the classical work of Buddington and Lindsley (1964) on the Fe-Ti oxides system as a geothermometer and oxybarometer. Thermodynamic modelling (e.g. Andersen et al., 1993; Ghiorso and Sack, 1995; Lindsley and Frost, 1992) or experimental work (e.g. Lattard et al., 2005; Toplis and Carroll, 1995) have been widely used. Systems involving change in the oxidation state of some multivalent elements have also been proposed, such as Eu (Drake, 1975), Fe (Lundgaard and Tegner, 2004) or V (Toplis and Corgne, 2002). The relative proportions of the different  $V^{n+}$  ionic species  $V^{3+}$ ,  $V^{4+}$  and  $V^{5+}$  are indeed sensitive to  $fO_2$  variations and have been used to characterize terrestrial, martian and lunar basalts (e.g. Papike et al., 2005). The  $V^{3+}$  and  $V^{4+}$  contents of titanomagnetites from layered intrusions (e.g. Bushveld and Skaergaard) have been determined (Balan et al., 2006). Though some variations are observed within the same intrusion and between intrusions, it is shown that  $V^{3+}$  is the dominant species (more than 83% of the total  $V^{3+}+V^{4+}$ ). Toplis and Corgne (2002) have developed a theoretical model based on experimental data in which the V content of magnetite varies as a function of the magma  $fO_2$ . The magnetite V content is indeed determined by (1) the  $V^{3+}$  content of the magma which increases with decreasing  $fO_2$ ; and (2) the degree of fractionation attained by the magma when magnetite crystallizes at the liquidus. The lower the  $fO_2$ , the later magnetite crystallizes (e.g. Toplis and Carroll, 1995) and the richer is its V content. This theoretical model, however, does not account for the Ti content of the magma and of magnetite nor for the possible role of ilmenite in controlling the V evolution in the magma. Moreover the V content in magnetite as an oxybarometer relies on the knowledge of the V content of the parental magma.

We show in this work that the issue of the V content of the magma can be avoided by considering the V content in the ilmenite coexisting with magnetite (Duchesne et al. 2007). We use a fully empirical approach in which (1) the partition coefficient of V between magnetite and ilmenite  $D_V^{Mt/Ilm}$  is measured in two layered intrusions characterized by rather extreme  $fO_2$  values; (2) the  $D_V^{Mt/Ilm}$  values are compared with another  $fO_2$  indicator, the  $Eu^{2+}/Eu^{3+}$  ratio in plagioclase, to show that both parameters vary consistently and are quite sensitive to  $fO_2$  variations; (3) we examine the possible influence of subsolidus re-equilibration on the accuracy of the method; and (4) we calibrate the two oxybarometers with the known values of  $fO_2$  in the two layered intrusions.

## ANALYTICAL METHODS

This study focuses on the geochemistry of minerals separated from rock samples. The rocks were crushed to 60-150  $\mu m$ , separated into two fractions by bromoform, and each fraction was then

run through a Frantz magnetic separator at increasing intensities. Concentrates of magnetite and ilmenite were then purified by centrifugation in hot Clerici solution at densities of  $4.8 \text{ gcm}^{-3}$  and  $4.5 \text{ gcm}^{-3}$ , respectively. Concentrates of apatite were purified by centrifugation in bromoform and methylene iodide. Plagioclase separates were further etched by HCl 6N to differentially dissolved traces of apatite forming mixed grains with plagioclase. This operation is crucial due to the high REE concentration of apatite relative to plagioclase.

XRF (ARL 9400 XP) on pressed pellets was used to analyse separated fractions of ilmenite and magnetite for V (Duchesne and Bologne, 2007, 2011). Li-tetraborate glass discs were also used to analyse Fe, Ti, Si, Mg, Mn, Al, and Ca in separated ilmenites. International reference materials (SARM 59 and 12, IGS 31 and 32, GBW 07226), samples 16716 G/91, V4-1, 16717 provided by Titania A/S, as well as synthetic standards and in-house standards, measured by other methods, were used for calibration.

ICP-MS (VG Plasma Quad PQ2) was used to analyse Sr and REE, following the method of Vander Auwera et al. (1998), (1) in plagioclase after alkali fusion, and (2) in apatite after differential open acid digestion. International standards ACE, BEN, GA, GH, GSN, DRN, ANG, FKN and JF1 were used for the calibration of plagioclase, and synthetic solutions were used for apatite. P in the plagioclase was also measured to monitor possible contamination by apatite.

## THE Fe-Ti OXIDE DEPOSITS AND THEIR $fO_2$ CONDITIONS OF FORMATION

### *The Grader layered intrusion*

The Grader ilmenite deposit is a layered intrusion (Charlier et al., 2008) in the Havre-Saint-Pierre massif-type anorthosite (Québec), located close to the world-class ilmenite deposit of Lake Tio (Lister, 1966). It is made up of a series of cumulate rocks starting with hemo-ilmenite+plagioclase cumulate grading upsection into hemo-ilmenite+plagioclase+apatite, then into noritic cumulates to eventually end with gabbro-noritic cumulates. Magnetite is a liquidus phase in the norite and gabbro-norite. The silicate minerals show small but significant cryptic variations: from bottom to top, plagioclase varies from  $An_{49}$  to  $An_{46}$ , orthopyroxene from Mg# 67 to 63.

The hematite content in ilmenite ranges from 32 to 20 mol.% (Table 1); its V content is in the 1164-1683 ppm range. The magnetite is Ti-poor and the V content is in the 2305-2498 ppm range. When the two oxide minerals are in contact, their liquidus compositions have been modified by subsolidus re-equilibration as evidenced by a strong zoning in the hematite exsolutions. The hematite content decreases towards the contact with magnetite, which testifies that the hematite in the ilmenite has reacted with the ulvöspinel dissolved in magnetite to produce magnetite and ilmenite. The net result of this interoxide reaction (Duchesne, 1970, 1972, 1999; Frost and Lindsley, 1992) is a magnetite nearly completely devoid of Ti.

The cumulates of the Grader deposit are crosscut by fine-grained (chilled) dykes of ferrodiorite which can be considered as representing the parental magma of the intrusion (Charlier et al., 2008). On the basis of the experimental work on jotunites of similar compositions (Vander Auwera and Longhi, 1994), we assume a crystallization temperature of ca.  $1100^\circ\text{C}$  for the Grader deposit. At that temperature the calibration curves (Fig. 6 of Lattard et al., 2005) permit determination of  $fO_2$  with a good approximation at ca.  $\Delta\text{NNO} = +0.6 \pm 0.3 \text{ log units}$ , i.e.  $\Delta\text{FMQ} = +1.48 \pm 0.35 \text{ log units}$ .

### *The Fedorivka layered intrusion*

The Fedorivka layered intrusion belongs to the Korosten Pluton, a large anorthositic-rapakivi-granite complex in Ukraine (Duchesne et al., 2006). It can be divided into 4 lithostratigraphic units: a Lower Zone (LZ, 72 m-thick), a Main Zone (MZ, 160 m-thick), and an Upper Border Zone, itself subdivided into 2 sub-zones (UBZ<sub>1</sub>, 50 m-thick; UBZ<sub>2</sub>, 40 m-thick). The dominant cumulus assemblage in MZ and UBZ<sub>2</sub> is andesine ( $An_{39-42}$ ), iron-rich olivine ( $FO_{32-42}$ ), augite ( $En_{29-35}Fs_{24-29}Wo_{42-44}$ ), ilmenite ( $Hem_{1-6}$ ), Ti-magnetite ( $Usp_{52-83}$ ), and apatite. The data reveal a continuous evolution from the floor of the intrusion (LZ) to the top of MZ, due to fractional

crystallization, and an inverse evolution in UBZ, resulting from crystallization downwards from the roof.

The Fedorivka magnetites are particularly rich in TiO<sub>2</sub>, with values up to 27% TiO<sub>2</sub>, equivalent to 83% Usp in the UBZ<sub>2</sub>. Conspicuous ulvöspinel exsolutions, forming a cloth microtexture, are the only Ti phase in magnetites from several layers in MZ and UBZ<sub>2</sub>. This shows that these magnetites have been protected from oxidation during the subsolidus evolution. Moreover, these magnetites show no textural evidence of interoxide subsolidus reaction, spinelliferous ilmenite rims being completely absent at the contact between the two oxides. It is however obvious that some deuteric reactions have occurred between the oxides because their equilibrium temperature and *f*O<sub>2</sub>, following QUIIF (Andersen et al., 1993), are below 400°C and -25 log units, respectively. This re-equilibration seems to have, however, preferentially affected the ilmenite because it is significantly less abundant than magnetite (Frost et al., 1988). Ilmenite has thus lost some Fe<sub>2</sub>O<sub>3</sub> component in the re-equilibration process.

An estimate of the crystallization temperatures in the MZ and UBZ<sub>2</sub> can be obtained using the experimental data on ferrobasic composition of Toplis et al. (1994a, 1994b). At these temperatures, the composition of the magnetite constrains the liquidus *f*O<sub>2</sub> value, following the Spencer and Lindsley (1966) model. These liquidus *f*O<sub>2</sub>-T conditions vary during fractionation from ΔFMQ = 0.7 log units and 1045°C at the base of the MZ (sample #228), to ΔFMQ = 0.4 log units and 1030°C on top of the MZ (sample #113) to ΔFMQ = -1.4 log units and 1020°C in UBZ<sub>2</sub> (sample #69). This estimate has been tested using the QUIIF algorithm which permits calculation of the composition of the olivine in equilibrium with a Ti-magnetite at given T and *f*O<sub>2</sub> values. When applied to the Main Zone samples, the calculated olivine compositions are identical within errors with those observed.

The remarkably low *f*O<sub>2</sub> values observed in Fedorivka are also corroborated by the late appearance in the series of rocks of cumulus magnetite (the olivine which co-exists with the first cumulus magnetite is iron-rich Fo<sub>42</sub>), and by the high V<sup>3+</sup> content of the melt, reflected in the high V content of the first liquidus magnetite (up to 1.85% V) (Duchesne et al., 2006). In conclusion, the Fedorivka layered intrusion appears to have crystallized at low *f*O<sub>2</sub> conditions, down to ΔFMQ = -1.4 log units at 1020°C.

There is a significant variation of D<sub>V<sup>Mt/Ilm</sup></sub> within the intrusion (Table 2) from low values ca. 7 in the LZ and UBZ<sub>1</sub> increasing progressively to ca. 27 in UBZ<sub>2</sub>, the most evolved part of the intrusion (Duchesne et al., 2006). Only one sample (#137.5) appears off the main trend with much higher V content in magnetite than the neighbouring samples. It has been shown that this sample has gone through a drastic process of subsolidus re-equilibration. During the oxidation of the ulvöspinel content, the magnetite has lost ilmenite by external exsolution. The net result of this process is an increase in the magnetite V content and consequently of the measured D<sub>V<sup>Mt/Ilm</sup></sub> (Duchesne et al., 2006).

## REDOX EVALUATION WITH THE EU ANOMALY

The Eu<sup>2+</sup>/Eu<sup>3+</sup> ratio is not directly measurable by analytical methods at the level of concentrations in most rocks and minerals. An approximate method has been suggested by Philpotts (1970) in which Sr with the same charge and ionic radius as Eu<sup>2+</sup> is used as a proxy for Eu<sup>2+</sup> and in which Sr and total Eu are measured in two mineral phases in equilibrium.

We have applied this method to pairs of plagioclase and apatite. Consider the Eu in the two equilibrated phases plagioclase and apatite:

$$Eu_{Plag}^{bulk} = Eu_{Plag}^{2+} + Eu_{Plag}^{3+} \text{ and } Eu_{Ap}^{bulk} = Eu_{Ap}^{2+} + Eu_{Ap}^{3+}$$

hence

$$Eu_{Plag}^{3+} = (Eu_{Ap}^{bulk} - D_{Eu^{2+}}^{Ap/Plag} Eu_{Plag}^{bulk}) / (D_{Eu^{3+}}^{Ap/Plag} - D_{Eu^{2+}}^{Ap/Plag}) \quad (1)$$

$Eu_{Ap}^{bulk}$  and  $Eu_{Plag}^{bulk}$  are determined by chemical analysis. A good value of  $D_{Eu^{3+}}^{Ap/Plag}$  can be obtained by extrapolation between neighbouring REE and becomes  $D_{Eu^{*}}^{Ap/Plag}$ . Moreover  $D_{Sr}^{Ap/Plag}$  can be used as a proxy for  $D_{Eu^{2+}}^{Ap/Plag}$ . Hence, formula (1) becomes:

$$Eu_{Plag}^{3+} = (Eu_{Ap}^{bulk} - D_{Sr}^{Ap/Plag} Eu_{Plag}^{bulk}) / (D_{Eu^{*}}^{Ap/Plag} - D_{Sr}^{Ap/Plag}) \quad (2)$$

$D_{Eu^{*}}^{Ap/Plag}$  and  $Eu_{Ap}^{bulk}$  being much higher than  $D_{Sr}^{Ap/Plag}$  and  $D_{Sr}^{Ap/Plag} Eu_{Plag}^{bulk}$ , formula (2) may be simplified to:

$$Eu_{Plag}^{3+} \approx Eu_{Ap}^{bulk} / D_{Eu^{*}}^{Ap/Plag} = Eu_{Ap}^{bulk} / (Eu_{Ap}^{*} / Eu_{Plag}^{*}) = (Eu^{bulk} / Eu^{*})_{Ap} Eu_{Plag}^{*}$$

This shows that the error on  $Eu^{3+}$  very much depends on the accuracy of the Sm, Eu and Gd determination in apatite and on the Sm and Gd determination in plagioclase. The Sm and Gd contents in plagioclase are of the order of 0.05 to 0.3 ppm, that is close to the quantification limits. It is thus crucial to accurately determine these elements in plagioclase. Reproducibility of the ICP-MS determinations (Vander Auwera et al., 1998) and duplicate runs permit to assess the error on the REE determination in apatite as 3% and in plagioclase as 10%. An error propagation calculation shows that the  $(Eu^{2+}/Eu^{3+})_{Plag}$  ratio is evaluated with an error of 15%.

In the Grader deposit, Sr, Sm, Eu and Gd were determined in plagioclase and apatite pairs from samples coming from various levels in the sequence. The results of the calculations following Philpotts (1970) methods are reported in Table 3. The  $(Eu^{2+}/Eu^{3+})_{Plag}$  ratio varies between ca. 30 at the base of the intrusion and ca. 40 at the top. The average ratio is  $33.6 \pm 1.8$ . The slight variation towards more reducing conditions upsection is in agreement with the small decrease in the pyroxene Mg#.

The analyses of six pairs of apatite and plagioclase separates from the Fedorivka layered intrusion are also presented in Table 3 together with the results of Philpotts equations. The  $Eu^{2+}/Eu^{3+}$  ratio varies from 86 to 216, the lowest values occurring at the base and top of the intrusion and the most evolved in the UBZ<sub>2</sub> in agreement with the model of crystallization from the floor and the roof of the intrusion.

## DISCUSSION

### *Influence of subsolidus reactions on $D_V^{Mt/Ilm}$*

A major drawback of the Fe-Ti oxide thermo-oxybarometer in plutonic rocks is the possible re-equilibration of liquidus compositions during cooling, with the consequence that the measured T- $fO_2$  conditions are those of the last equilibrium attained (see e.g. Duchesne, 1972), at much lower values of T and  $fO_2$  than the primary/liquidus conditions. It is therefore crucial to examine to what extent this re-equilibration has affected the V contents of the oxides and the  $D_V^{Mt/Ilm}$  value.

In the Grader layered intrusion, as shown above, both oxide compositions have been modified but with different intensities. Since the dominant oxide is hemo-ilmenite, it can be anticipated that it has been less affected than magnetite (Frost et al., 1988) and the possible modifications of its V content can be ignored. At the temperature and  $fO_2$  of concern, the composition of the magnetite that would have been in equilibrium with the Grader hemo-ilmenites can be calculated with the QUILF algorithm of Andersen et al. (1993). The values are reported in Table 1. It turns out that the liquidus magnetites were notably richer in Ti than the measured magnetites. The subsolidus reaction has also affected the trace element contents. Indeed the external exsolution of an ilmenite phase has concentrated V in the magnetite because the exsolved ilmenite was poorer in V than magnetite. A maximum enrichment would have occurred if the exsolved ilmenite had been devoid of V, a plausible case because of its low hematite content (Schuiling and Feenstra, 1980). The recalculated magnetite compositions are given in Table 1. The recalculated  $D_V^{Mt/Ilm}$  coefficients are lower by almost a factor 2 than the measured values. The re-equilibration has greatly affected the V content of the magnetite, but the change of the  $D_V^{Mt/Ilm}$  coefficient is small relative to the whole range of observed values (from 1 to 27). This means that the use of the

measured (uncorrected) value of  $D_V^{Mt/Ilm}$  would have led to an estimate of  $\Delta FMQ$  in error of 0.05 log units (see below).

In the Fedorivka layered intrusion, as discussed above, the primary compositions of the magnetite at the base and top of the MZ and in the UBZ2 (where ulvöspinel is preserved in the magnetite) have not been affected by cooling and thus the measured V content can be considered as the original content. The hematite content of the ilmenite on the other hand has been slightly modified in the process but this cannot have significantly affected the V contents. On the other hand, when the magnetite is completely oxidized (with oxy-exsolutions of ilmenite in a trellis microstructure), such as in sample #137.5, the magnetite V content has been significantly changed. If the primary content cannot be recalculated e.g. with the help of QUILF, such samples should be discarded.

In conclusion, though the subsolidus reaction between the two Fe-Ti oxides has affected to various degrees the primary V contents, it is possible to correct this effect through the appropriate use of the QUIIF model, and the remaining uncertainties have little influence on the absolute variation of the  $D_V^{Mt/Ilm}$  values. Thus the proposed use of  $D_V^{Mt/Ilm}$  values as oxybarometer suffers less from the drawbacks of the Fe-Ti system.

### ***Correlation of $D_V^{Mt/Ilm}$ with $(Eu^{2+}/Eu^{3+})_{Plag}$ ratio and $fO_2$***

Fig. 1a shows the relationship between the  $D_V^{Mt/Ilm}$  values and the  $Eu^{2+}/Eu^{3+}$  in plagioclase in logarithmic coordinates. The overall trend is, within errors, continuous and linear, indicating that both parameters are sensitive to variations of  $fO_2$ . A linear function  $\log(Eu^{2+}/Eu^{3+})_{Plag} = 0.539 \log D_V^{Mt/Ilm} + 32.96$  gives the best fit with a correlation factor  $r = 0.98$ .

### ***Calibration of the $D_V^{Mt/Ilm}$ oxybarometer***

Fig. 1b shows the result of the calibration of the  $D_V^{Mt/Ilm}$  oxybarometer. Though more data are needed to better ascertain the calibration, the results are promising. The relationship between the two variables is the following:

$$\Delta FMQ \text{ log units} = -0.003(D_V^{Mt/Ilm})^2 - 0.041 D_V^{Mt/Ilm} + 1.528 \text{ (with } r=1.0) \quad (3).$$

This relationship has been applied to samples from the Lower Zone c of the Skaergaard intrusion, which is characterized by the appearance of magnetite as an abundant cumulus phase. In sample S2 from Balan et al. (2006) which contains a magnetite with  $1.1 \pm 0.1$  atom% V, and an ilmenite with  $0.140 \pm 0.015$  atom%V (Balan, person. comm.), the  $D_V^{Mt/Ilm} = 7.8 \pm 1.6$ , which gives with equation (3) a  $\Delta FMQ = +1.03 \pm 0.13$  log units. Similarly, Vincent and Phillips (1954) have measured 1.74%  $V_2O_3$  in magnetite and 0.32%  $V_2O_3$  in ilmenite from sample 2308, which gives  $D_V^{Mt/Ilm} = 5.4$  and  $\Delta FMQ = +1.21$  log units, close within error to Balan's sample. It thus appears that the appearance of magnetite in the Skaergaard layered intrusion is for  $fO_2$  conditions slightly more oxidized than in the Fedorivka layered intrusion, where the appearance of magnetite is for  $\Delta FMQ = +0.7$  log units. At the appearance of magnetite, the olivine was  $FO_{54-56}$  in the Skaergaard intrusion (McBirney, 1996; Wager and Brown, 1968) compared to  $FO_{42}$  in the Fedorivka intrusion (Duchesne et al. 2006), thus indicating a less evolved magma and a higher  $fO_2$  in the Skaergaard (Toplis and Carroll, 1995).

### ***Calibration of the $(Eu^{2+}/Eu^{3+})_{Plag}$ oxybarometer***

Using Philpotts's approach, Drake (1975) has proposed an experimentally determined relationship between  $fO_2$  and the  $Eu^{2+}/Eu^{3+}$  ratio in plagioclase in a basaltic liquid valid at 1 atm and for a restricted temperature range (1187 -1300°C):

$$\log fO_2 = -4.60 (\pm 0.18) \log (Eu^{2+}/Eu^{3+})_{Plag} - 3.86 (\pm 0.27)$$

We have applied this relationship to our data and the results are 1.7 to 2.7 log units lower than our estimates of the  $fO_2$  values by Fe-Ti thermo-oxybarometry (see above). We thus prefer to calibrate the  $(Eu^{2+}/Eu^{3+})_{Plag}$  variation with the  $\Delta FMQ$  taken from equation (3). The equation is:

$$100\Delta\text{FMQ log units} = -0.008 (\text{Eu}^{2+}/\text{Eu}^{3+})_{\text{Plag}}^2 + 0.340 (\text{Eu}^{2+}/\text{Eu}^{3+})_{\text{Plag}} + 143.481 \quad (r=0.96)$$

Fig. 1c illustrates the relationship. More data are obviously needed to assess quantitatively the relationship but these first results are encouraging.

### **Final remarks**

The present data suggest that  $D_{\text{V}}^{\text{Ilm/Liq}}$  is less dependent on  $f\text{O}_2$  than  $D_{\text{V}}^{\text{Mt/Ilm}}$ . With decreasing  $f\text{O}_2$ , the Ti content of magnetite increases, which increases possible  $\text{Ti}^{4+}$ - $\text{V}^{4+}$  substitutions. In these conditions,  $\text{V}^{3+}$  also increases in the melt and thus concomitantly in magnetite. Both effects are thus combined to increase the  $D_{\text{V}}^{\text{Mt/Ilm}}$ . With decreasing  $f\text{O}_2$ , the hematite content of the primary ilmenite in equilibrium with the magnetite slightly decreases, thus offering less possibilities of substituting  $\text{V}^{3+}$  to  $\text{Fe}^{3+}$ . Here the increasing  $\text{V}^{3+}$  content in the melt is compensated by the lower solubility of  $\text{V}^{3+}$  in the ilmenite. It is also worth noting that ilmenite easily concentrates highly charged cations, such as  $\text{Nb}^{5+}$ . Reported D values are in general  $>2$  and even  $>50$  in rhyolites (Ewart and Griffin, 1994; Stimac and Hickmott, 1994), and, in magnetite at 2-5 kbar experimental pressure, much smaller (from 0.09 to 0.18, Nielsen and Beard, 2000). This seems to indicate that ilmenite is more capable of accommodating highly charged cations than magnetite, thus explaining its relative insensitivity to the various V ionic states.

$D_{\text{V}}^{\text{Mt/Ilm}}$  theoretically varies with temperature and this effect has been neglected here, the values considered being those at liquidus temperatures in the 1020-1100°C range. Further studies, including experiments, are needed to solve this issue. It must be noted, however, that the temperature effect might not be very important. We have shown that, in the case of the Grader magnetites, subsolidus re-equilibration leads to relatively small error in the determination of  $\Delta\text{FMQ}$  (0.05 log units). Moreover experimental determination by Schuiling and Feenstra (1980) at NNO and 550°-600°C (i.e.  $\Delta\text{FMQ}$  ca. 1.2 log units) has given  $D_{\text{V}}^{\text{Mt/Ilm}}$  between 1.2 and 2.6, not far from those observed at similar  $f\text{O}_2$  and high temperature (ca. 5). The possible use of  $D_{\text{V}}^{\text{Mt/Ilm}}$  as an oxybarometer can thus be envisaged in metamorphic rocks.

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## Table captions

**Table 1:** Representative compositions of magnetite and ilmenite pairs in the Grader layered intrusion and evaluation of  $fO_2$  and  $D_V^{Mt/Ilm}$  values.

**Table 2:** Recapitulation of the parameters used in the calibration of the two oxybarometers. The  $\Delta FMQ$  re-calculated values are obtained with equation (1) (see text). The values in italics have been omitted in the calculation of the regressions.

**Table 3:** Sr, Sm, Eu, Gd compositions in plagioclase-apatite pairs in the Grader and the Fedorivka layered intrusions.

## Figure captions

**Figure 1:** A.  $(Eu^{2+}/Eu^{3+})_{Plag}$  vs.  $D_V^{Mt/Ilm}$  in logarithmic coordinates; B.  $\Delta FMQ$  (log units) vs.  $D_V^{Mt/Ilm}$ ; C.  $\Delta FMQ$  (log units) vs.  $(Eu^{2+}/Eu^{3+})_{Plag}$ . The value in bracket (sample #137.5) is not considered in the calculation of the correlation.

Table 1: Representative compositions of magnetite and ilmenite pairs in the Grader deposit and evaluation of D V Mt/Ilm values

Depth (m)	10	30	50	80	110	135
<b>Ilmenite</b>						
SiO <sub>2</sub>	0.34	0.30	0.38	0.28	0.29	0.28
TiO <sub>2</sub>	41.54	40.39	38.58	35.93	37.28	35.68
Al <sub>2</sub> O <sub>3</sub>	0.19	0.24	0.18	0.12	0.15	0.14
Fe <sub>2</sub> O <sub>3</sub> tot	59.21	59.44	61.81	64.04	63.18	65.41
FeO	21.03	23.38	26.77	31.53	29.68	32.82
Fe <sub>2</sub> O <sub>3</sub>	34.36	32.44	31.53	29.26	30.15	29.33
MnO	0.44	0.43	0.34	0.25	0.29	0.26
MgO	1.43	1.93	1.58	1.57	1.73	1.4
Total	99.33	99.11	99.36	98.94	99.57	99.91
Ti/Ti+Fe (atom)	0.418	0.409	0.386	0.358	0.371	0.351
Xhem	0.163	0.183	0.228	0.283	0.258	0.297
<b>V (ppm)</b>	<b>1164</b>	<b>1170</b>	<b>1441</b>	<b>1620</b>	<b>1527</b>	<b>1683</b>
<b>Magnetite</b>						
SiO <sub>2</sub>	0.24	0.19	0.09	0.12	0.08	0.18
TiO <sub>2</sub>	0.37	0.00	0.62	0.56	0.18	2.02
Al <sub>2</sub> O <sub>3</sub>	0.71	0.81	0.63	0.59	0.64	0.6
Fe <sub>2</sub> O <sub>3</sub>	67.64	68.55	66.49	67.08	67.25	63.92
FeO	30.92	30.83	30.95	31.06	30.53	32.17
MgO	0.38	0.33	0.29	0.30	0.28	0.33
Total	100.26	100.71	99.07	99.71	98.96	99.13
Usp	0.011	0.000	0.018	0.016	0.005	0.059
<b>V (ppm)</b>	<b>2327</b>	<b>2305</b>	<b>2498</b>	<b>2428</b>	<b>2494</b>	<b>2409</b>
<b>Ilmenite composition recalculated for QUILF</b>						
Xhem	0.1900	0.2162	0.2532	0.3063	0.2839	0.3171
Xgeik	0.0551	0.0739	0.0604	0.0599	0.0657	0.0529
Xpyr	0.0096	0.0940	0.0074	0.0055	0.0063	0.0056
Xilm	0.7453	0.6159	0.6790	0.6283	0.6441	0.6244
<b>Liquidus magnetite recalculated through QUILF</b>						
N Ti (QUILF)	0.570	0.546	0.514	0.495	0.494	0.517
XFeTiO <sub>3</sub>	0.399	0.3822	0.3598	0.3465	0.3458	0.3619
<b>V recalc. (ppm)</b>	<b>1399</b>	<b>1424</b>	<b>1599</b>	<b>1587</b>	<b>1632</b>	<b>1537</b>
<b>D V meas.</b>	<b>2.0</b>	<b>2.0</b>	<b>1.7</b>	<b>1.5</b>	<b>1.6</b>	<b>1.4</b>
<b>D V recalc.</b>	<b>1.2</b>	<b>1.2</b>	<b>1.1</b>	<b>1.0</b>	<b>1.1</b>	<b>0.9</b>

Table 2: Recapitulation of the parameters used in the calibration of the two oxybarometers. The  $\Delta$ FMQ re-calculated values are obtained with equation (3) (see text). The values in italics have been omitted in the calculation of the regressions.

	sample#	Unit	$(\text{Eu}^{2+}/\text{Eu}^{3+})_{\text{Plag}}$	V Ilm%	V Mt% corr	D V Mt/Ilm	$\Delta$ FMQ	
							estimated	re-calculated
Grader	10		41	0.1164	0.1399	1.2	1.48	1.47
	30		40	0.1170	0.1424	1.2	1.48	1.47
	50		30	0.1441	0.1599	1.1	1.48	1.48
	80		33	0.1620	0.1587	1.0	1.48	1.48
	110		35	0.1527	0.1632	1.1	1.48	1.48
	135		30	0.1683	0.1537	0.9	1.48	1.49
Fedorivka	13	UBZ1	97	0.2351	1.85	7.9		1.02
	37	UBZ1	149	0.0482	0.51	10.6		0.76
	69	UBZ2	216	0.0109	0.29	26.7	-1.40	-1.70
	113	MZ	103	0.0251	0.35	13.9	0.44	0.38
	137.5	MZ	<i>185</i>	0.0476	1.15	<i>24.2</i>	0.44	<i>-1.22</i>
	180	MZ		0.0679	0.66	9.7		0.85
	204	MZ		0.1019	1.02	10.0		0.82
	228	MZ		0.0815	0.96	11.8	0.70	0.63
289	LZ	86	0.2242	1.51	6.7		1.12	

Table 3: Sr, Sm, Eu, and Gd compositions in plagioclase-apatite pairs in the Grader deposit and the Fedorivka layered intrusions

Lithological unit Sample number (#)	Grader deposit								Fedorivka layered intrusion					
	Gabbronorite 10	Gabbronorite 30	Gabbronorite 50	Gabbronorite 80	Norite 110	Norite 135	Nelsonite 140	Nelsonite 160	UBZ1 13	UBZ1 37	UBZ2 69	MZ 113	MZ 137.5	LZ 289
<b>Plagioclase</b>														
Sr ppm (§)	1357	1297	1378	1458	1304	1336	1347	1434	892	963	859	927	936	828
Sm ppm	0.21	0.16	0.28	0.20	0.23	0.35	0.30	0.28	0.36	0.21	0.08	0.16	0.11	0.14
Eu ppm	1.50	1.37	1.61	1.68	1.39	1.51	1.38	1.49	2.90	3.12	2.23	2.50	2.50	1.64
Gd ppm	0.13	0.12	0.15	0.11	0.11	0.11	0.15	0.15	0.18	0.10	0.05	0.13	0.06	0.08
Eu norm (§)	25.9	23.5	27.7	29.0	24.0	26.0	23.9	25.679	49.9	53.8	38.4	43.0	43.0	28.3
Eu*	0.95	0.79	1.16	1.16	0.91	1.11	1.19	1.16	1.44	0.80	0.35	0.81	0.45	0.60
Eu/Eu*	27.3	29.8	24.4	24.4	26.4	23.5	20.1	22.2	34.6	67.7	109.1	53.0	95.3	47.4
<b>Apatite</b>														
Sr ppm (§)	505	522	502	495	521	501	481	472	303	324	305	339	315	302
Sm ppm (§)	107	115	119	112	114	101	101	76	138	127	93	101	91	85
Eu ppm (§)	23.0	28.0	29.41	27.0	27.3	25.1	23.5	18.3	15.9	19.6	16.0	17.1	15.7	15.3
Gd ppm (§)	104	113	113	109	108	98	93	75	122	124	92	94	86	80
Eu norm (+)	397	483	507	466	471	433	405	316	275	338	275	296	271	263
Eu*	595	643	652	623	626	562	547	426	729	708	521	551	501	463
Eu/Eu*	0.67	0.75	0.78	0.75	0.75	0.77	0.74	0.742	0.38	0.48	0.53	0.54	0.54	0.57
D Sr ap/plag	0.37	0.40	0.36	0.34	0.40	0.38	0.36	0.33	0.34	0.34	0.35	0.37	0.34	0.36
D Eu* ap/plag	628	814	560	535	687	507	461	367	505	890	1482	679	1109	777
Eu <sup>3+</sup> plag (*)	0.62	0.58	0.89	0.85	0.67	0.83	0.86	0.84	0.51	0.36	0.18	0.41	0.23	0.33
Eu <sup>2+</sup> plag	25.25	22.96	26.85	28.11	23.36	25.14	23.01	24.84	49.40	53.43	38.19	42.61	42.79	27.95
(Eu <sup>2+</sup> /Eu <sup>3+</sup> )plag	40.9	39.5	30.2	33.0	34.8	30.1	26.7	29.7	96.8	148.7	216.3	103.4	184.7	85.8

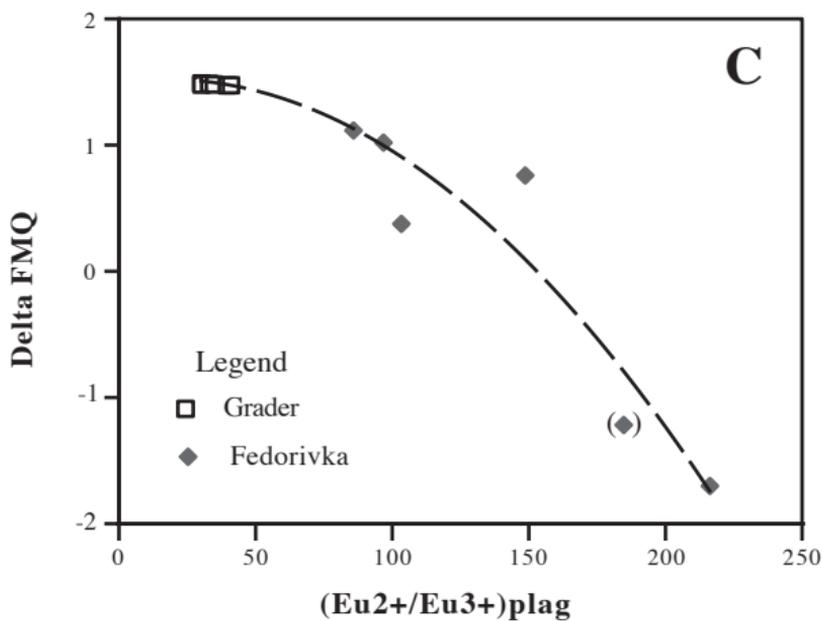
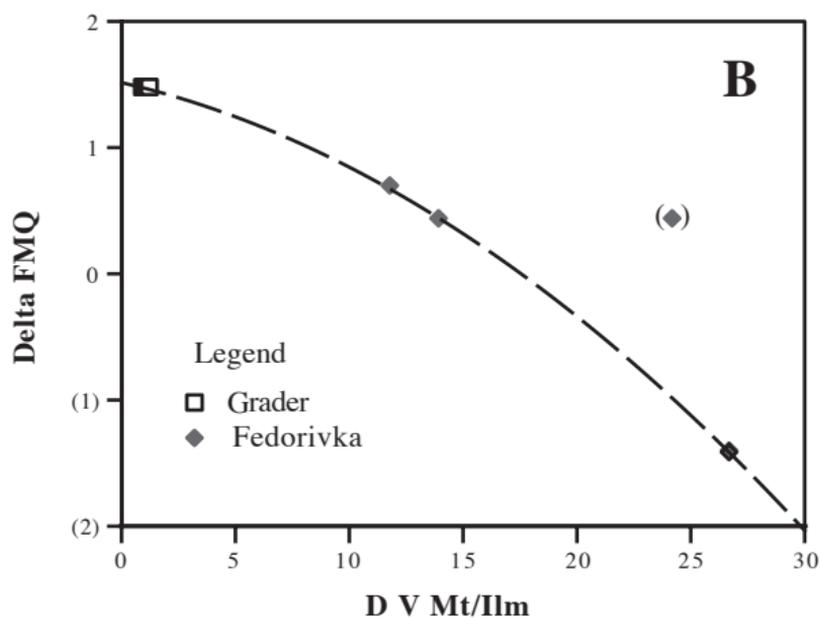
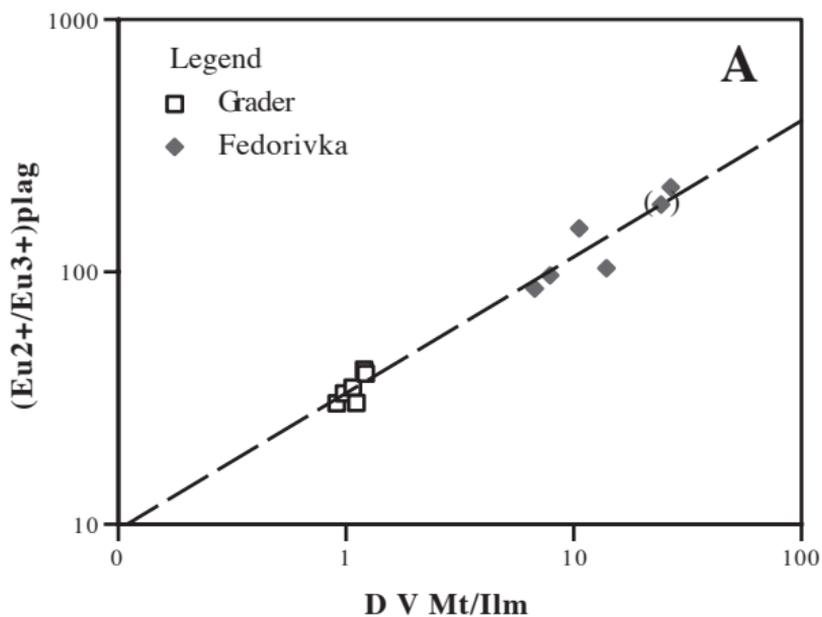
Notes:

(#) sample # is the depth in m in borehole 02-03 in the Grader deposit, and in borehole 581 in the Fedorivka layered intrusion

(§) data from Charlier et al, 2008.

(+) REE normalizing values (after Sun & McDonough, 1989): Sm: 0.153; Eu: 0.058; Gd: 0.2055

(\*) calculated from formula (2) (see text)



**Fig. 1**