

Mg/Mn partitioning as a test for equilibrium between coexisting Fe-Ti oxides

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ABSTRACT

Partitioning of Mg and Mn between titanomagnetite and ferrian ilmenite of volcanic rocks provides a test for equilibrium between coexisting phases. A plot of $\log(\text{Mg/Mn})_{\text{mt}}$ vs. $\log(\text{Mg/Mn})_{\text{il}}$ for 213 homogeneous oxide pairs from volcanic rocks yields a straight line over more than two orders of magnitude variation in Mg/Mn. Analyses that plot within reasonable limits of analytical precision of this line are consistent with preservation of equilibrium compositions. The test appears to be valid for fresh volcanic rocks but may not be applicable to oxides in metamorphic, plutonic, and altered volcanic rocks in which oxide minerals typically have oxidized or exsolved at subsolidus temperatures. It can be used to discriminate between multiple populations of an oxide phase or to evaluate equilibration of inclusions in silicate phenocrysts for Fe-Ti oxide geothermometry and oxygen barometry.

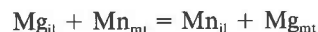
INTRODUCTION

The Fe-Ti oxide geothermometer (Buddington and Lindsley, 1964; Spencer and Lindsley, 1981; Andersen and Lindsley, 1985) has been widely and successfully applied to phenocrysts in volcanic rocks. In some cases both titanomagnetite and ferrian ilmenite (hereafter referred to as "magnetite" and "ilmenite") are homogeneous and clearly record pre-eruption equilibrium (Hildreth, 1977, 1979). In others one or both phases may be exsolved (Haggerty, 1976) or may occur in multiple populations (Carmichael, 1967; Bacon and Metz, 1984). Often, petrographic constraints are ambiguous or unavailable. Consideration of published data has enabled us to present a simple test based on Mg/Mn partitioning that can indicate which phases may represent equilibrium pairs or whether reconstructed analyses of exsolved phases reflect equilibrium with silicate liquid. Satisfaction of this criterion apparently is necessary but not sufficient to prove equilibration.

RATIONALE

A chemical test for equilibration should be useful over a wide compositional range within the normal precision of microprobe analyses. Mg and Mn are present in measurable amounts in most magnetites (mt) and ilmenites (il) of igneous rocks. Our test for equilibrium depends only on the ratios of Mg/Mn in each phase and is not affected by the accuracy of absolute Mg or Mn determinations. We assume that partitioning of Mn^{3+} into Fe-Ti oxides is insignificant at f_{O_2} conditions of crystallization of volcanic rocks.

The exchange reaction



gives the distribution coefficient

$$K_D = (\text{Mg/Mn})_{\text{mt}} / (\text{Mg/Mn})_{\text{il}}$$

A plot of $\log(\text{Mg/Mn})_{\text{mt}}$ vs. $\log(\text{Mg/Mn})_{\text{il}}$ (atomic) for various Fe-Ti oxide pairs thus should yield a simple array of points, within reasonable analytical uncertainties, if the phases did indeed equilibrate. If the partitioning is not strongly dependent on bulk composition, temperature, or pressure, such a plot should be approximately linear. We have found this to be the case for virtually all analyses of homogeneous oxide pairs from volcanic rocks for which equilibration was likely.

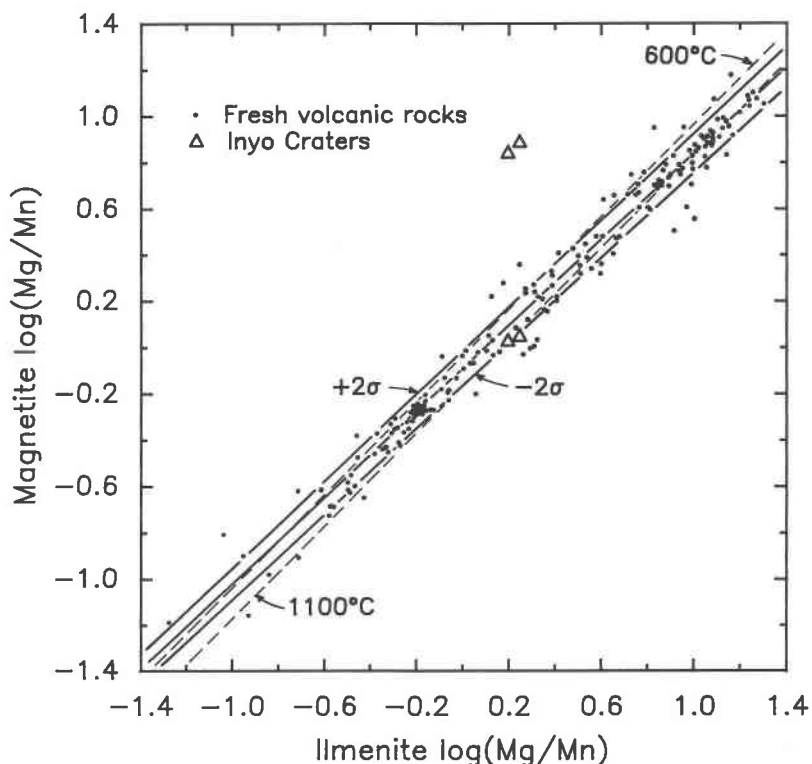
CALIBRATION

Data for 213 homogeneous oxide pairs from fresh volcanic rocks are plotted in Figure 1. It is not possible to discriminate between scatter due to imprecision and scatter due to other factors, but the width of the array in Figure 1 is consistent with precision being responsible for most deviations. When relevant information is available, there generally are petrographic or field-occurrence reasons for suspecting that points that fall far from the regression line reflect disequilibrium. Regression of the entire data set resulted in the equation for the best-fit line,

$$\log(\text{Mg/Mn})_{\text{mt}} = 0.9317 \log(\text{Mg/Mn})_{\text{il}} - 0.0909,$$

for which $r = 0.990$ (Table 1). The plotted data include groundmass and phenocrystic oxides from alkali basalts,

Fig. 1. Mg/Mn (atomic) for 213 ilmenite-magnetite pairs (dots) in fresh volcanic rocks. Linear regression gives $\log(\text{Mg}/\text{Mn})_{\text{m}} = 0.9317 \times \log(\text{Mg}/\text{Mn})_{\text{i}} - 0.0909$, $r = 0.990$ (middle solid line). Error envelope (solid lines labeled $\pm 2\sigma$; Table 1) was determined on the basis of typical microprobe precision ($\pm 2\sigma$). Known precision of equilibrated homogeneous oxide pairs from volcanic rocks should overlap the best-fit equilibrium line, or they should plot near the error envelope when precision is unknown. Data from Carmichael (1967), Lipman (1971), Haggerty (1976), Hildreth (1977, 1983), Bacon and Duffield (1981), Bacon and Carmichael (1973), Eckren et al. (1984), Mahood (1981), Sigurdsson and Sparks (1981), and C. R. Bacon and T. H. Druitt (unpub. data, 1985). Also shown are ilmenite-magnetite pairs from rhyolites of the Inyo Craters with two populations of titanomagnetite (open triangles; Carmichael, 1967); the equilibrium test strongly suggests which titanomagnetite most likely equilibrated with analyzed ilmenite. Dashed lines show partitioning derived from experimental studies of D. H. Lindsley and coworkers (written comm., 1987) calculated at 600 and 1100 °C.



tholeiites, andesites, dacites, rhyolites, and a few differentiated alkalic rocks. Ratios of Mg/Mn range over two orders of magnitude. Three data points from Helz (1973; written comm., 1985), which represent analyzed oxides equilibrated under known conditions, plot close to the best-fit line but were not included in the calibration.

Because of the overall trend of decreasing Mg/Mn with increasing SiO_2 content of magmas, higher-temperature oxide pairs plot at higher values of Mg/Mn. We have not recognized a significant effect of f_{O_2} (determined from the oxide pairs) relative to the best-fit line for the data of Figure 1. If the exchange were truly ideal and independent of temperature, the slope of the best-fit line should be unity. A small temperature dependence would shift the intercept and, coupled with the natural variation in Mg/Mn with differentiation of magmas, would explain the observed slope of the best-fit line. Experimental studies by D. H. Lindsley and coworkers (written comm., 1987) define the temperature dependence and confirm the validity of the empirical best-fit line (Fig. 1).

TEST FOR EQUILIBRIUM

Because most of the scatter about the best-fit line in Figure 1 can be assigned to the combined effects of analytical precision and a small temperature dependence, we have arbitrarily specified conservative error limits beyond which an oxide pair may be said to fail the test for equilibrium. Clearly, use of the test requires knowledge of realistic limits of analytical capability in the concentration range of interest. The envelope shown in Figure 1 represents our estimate of typical microprobe analytical precision based on our experience with replicate analyses of oxide standards. Representative error limits (Table 1) were found by assuming that 1 wt% of MnO and MgO would produce a signal of 2000 counts with an error of $\sigma = \sqrt{n}$ and calculating "worst case" deviations in Mg/Mn as functions of typical MnO and MgO contents of volcanic magnetite and ilmenite over the range of $\log(\text{Mg}/\text{Mn})_{\text{i}} = -1.4$ to 1.4. To accomplish this it was necessary to develop empirical relationships between MgO and MnO contents of both phases in order to realistically vary possible error in Mg/Mn owing to counting statistics. We did not take into account counting errors for standards or errors in background determinations. The error envelope is a compromise that probably does not represent extreme compositions well and may not be appropriate for oxide analyses performed in other laboratories. Because several points in Figure 1 fall just outside the calculated error limits, we suspect that our error estimate is too optimistic when applied to data from different laboratories. The 2σ

TABLE 1. Equations of equilibrium line and representative error limits

	Equilibrium	Upper limit	Lower limit
Slope	0.9317	0.9430	0.9213
Intercept	-0.0909	-0.0124	-0.1696

error lines are merely semiquantitative guidelines for evaluation of oxide pairs when a specific estimate of precision is not available.

To satisfy this empirical test for equilibrium, the oxide pair in question should plot within known analytical precision of the equilibrium line, or near the error envelope (Table 1) if precision cannot be determined. We emphasize that this is not a substitute for petrographic evidence for equilibrium. Oxide pairs obtained from homogeneous populations of discrete microphenocrysts in glassy rocks, from pairs of inclusions in the same glass pool within silicate phenocrysts, or from touching grains can be reasonably assumed to have equilibrated. If such pairs fail the chemical test, either they did not equilibrate or they have suffered postequilibration alteration of some kind. Passage of the Mg/Mn test can be a necessary but not sufficient criterion for assessing equilibrium for oxide pairs where petrographic information is ambiguous or lacking.

APPLICATION

Fresh silicic rocks

Carmichael (1967) presented analyses of oxides in two rhyolites from Inyo Craters, California, in which two populations of titanomagnetite and a single population of ilmenite occur. At that time there was no way to determine which titanomagnetite, if either, equilibrated with the ilmenite. Figure 1 shows that the Mg/Mn test can identify the possible equilibrium pairs in Carmichael's data. Bacon and Metz (1984) faced a similar decision in applying the geothermometer to oxides separated from crystal-poor obsidians and first used the Mg/Mn test. For such rocks, the difficulty in obtaining thin sections that contain several oxide grains necessitates use of crystal concentrates, the preparation of which generally destroys any petrographic evidence of equilibration.

Oxide inclusions in silicate phenocrysts

Ilmenite and (or) magnetite commonly occur only as inclusions in silicate phenocrysts. If the two phases are not in communication via continuous glass the Mg/Mn test may be the only basis for judging whether or not the two phases may represent equilibrium conditions. Bacon and Metz (1984) used the test to eliminate disequilibrium pairs of oxides in silicate xenocrysts in andesitic magmatic inclusions in rhyolites; the pairs that passed the test produced a smooth $T-f_{O_2}$ curve. Commonly, oxide inclusions that are not in the same zone of a host crystal do not satisfy the Mg/Mn partitioning criterion.

Whitney and Stormer (1985) presented analyses of magnetite and ilmenite from the Fish Canyon Tuff. These data are for homogeneous to incipiently oxidized discrete magnetite grains and for ilmenite included in other phases, commonly titanite. When Whitney and Stormer's (1985) stated analytical precision is taken into account, the Mg/Mn test indicates that 13 of their 16 pairs probably are consistent with equilibrium. True magmatic conditions apparently are recorded by at least the 13 pairs

even though the rocks are 28 Ma old and occur as thick sheets of commonly devitrified welded tuff.

Exsolved and oxidized crystals

In many volcanic rocks, the oxide phenocrysts, especially titanomagnetite, have oxidized and exsolved into two phases. This process most likely took place during relatively slow cooling of interiors of lava flows and welded tuffs when a vapor phase was present. Subsolidus exsolution-oxidation also is a common feature of Fe-Ti oxides in plutonic and metamorphic rocks. Various authors have attempted to determine the original compositions of the exsolved phases [generally magnetite (Haggerty, 1976)] by (1) collecting many sets of counts in a grid for each grain (Whitney and Stormer, 1985); (2) analyzing hosts and exsolution lamellae and reconstructing the original composition of the crystal (Bohlen and Essene, 1977); or (3) obtaining bulk analyses of mineral separates (Puffer, 1972). Such oxide compositions commonly do not plot within the error envelope for Mg/Mn distribution (Fig. 2). Many examples of oxide pairs from layered intrusions (Vincent and Phillips, 1954; Elsdon, 1972; Mathison, 1975; Pasteris, 1985) and from other plutonic rocks (Czamanske and Mihalik, 1972; Duchesne, 1972; Puffer, 1972; Neumann, 1974; Haggerty, 1976) plot above the envelope. Mathison (1975) analyzed mineral separates and also reintegrated magnetite with ilmenite lamellae. The two methods produced different results. Reintegrated magnetites yielded higher temperatures; some plot within the error envelope, but most plot above it. Mathison's analyses of mineral separates plot farther above the upper error limit than do most of his reintegrated analyses. Some data for high-grade metamorphic rocks (Bohlen and Essene, 1977; Bohlen et al., 1980) and for pegmatites (Puffer, 1975) scatter both above and below the error envelope. Overall, reintegrated or mineral-separate analyses tend to deviate to the high side of the error envelope.

Oxide-pair analyses of ilmenite lamellae and their magnetite hosts have similar Mg/Mn characteristics to those of reconstructed oxide analyses. Among ~40 analyzed pairs, those from volcanic rocks (Lipman, 1971) plot close to the equilibrium line, and most of those from metamorphic rocks (Bohlen and Essene, 1977; Bohlen et al., 1980), granitoids (Neumann, 1974), and layered intrusions (Mathison, 1975; Pasteris, 1985) plot above the envelope. This may in part reflect the temperature dependence of Mg/Mn partitioning (D. H. Lindsley, written comm., 1987) to the extent that oxide pairs approach equilibrium in Mg and Mn concentration at low temperatures, although this effect is inadequate to explain the range of data from natural rocks (Fig. 2).

The generally positive deviation from the equilibrium line for whole-grain and host-lamellae pairs suggests that the oxidation-exsolution process selectively affects Mg and Mn distribution between the new phases. Moreover, exsolved crystals apparently have not behaved as closed systems. The Mg/Mn partitioning test for equilibrium thus

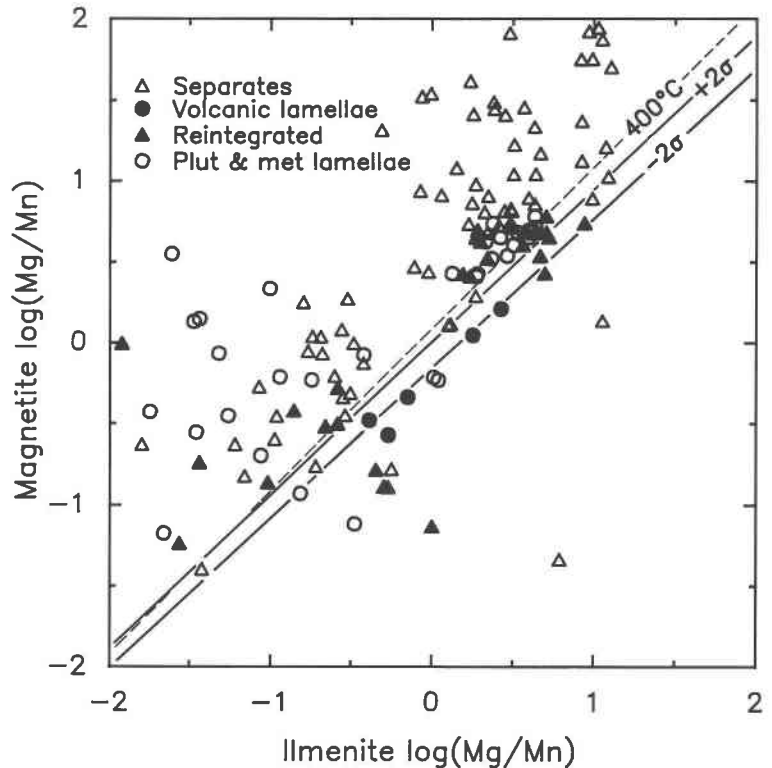


Fig. 2. Mg/Mn (atomic) for oxidized/exsolved ilmenite-magnetite pairs: mineral separates, open triangles [Vincent and Phillips (1954), Duchesne (1972), Elsdon (1972), Puffer (1972), Neumann (1974), Mathison (1975)]; reintegrated host and lamellae, filled triangles [Mathison (1975), Bohlen and Essene (1977), Bohlen et al. (1980)]; lamellae in plutonic and metamorphic rocks, open circles [Neumann (1974), Mathison (1975), Bohlen and Essene (1977), Bohlen et al. (1980)]; and lamellae in volcanic rocks, filled circles [Lipman (1971)]. Error envelope ($\pm 2\sigma$) as in Figure 1. Dashed line shows partitioning at 400 °C calculated from experimental data (D. H. Lindsley, written comm., 1987). Generally positive deviation from equilibrium line suggests increased partitioning of Mn into ilmenite in slowly cooled rocks.

is not applicable to slowly cooled rocks or those with complex cooling histories.

DISCUSSION

The positive deviation from the error envelope for analyzed pairs of plutonic and metamorphic oxides generally seems to be due to high Mn content of ilmenite relative to volcanic ilmenite. The high Mn content of ilmenite does not appear to be related to high whole-rock Mn or high Mn/Fe because oxides from rhyolites with high Mn/Fe plot virtually on the equilibrium line. Rumble (1976) has pointed out that Mn is strongly partitioned into ilmenite relative to magnetite in metamorphic rocks. Buddington and Lindsley (1964), Neumann (1974), and Haggerty (1976) have indicated that Mn contents of ilmenites of igneous rocks increase with decreasing temperature. Because oxidation-exsolution of titanomagnetite occurs at subsolidus temperatures, the tendency for host-lamellae oxide pairs to plot above the equilibrium envelope may be due either to increase in K_D with falling temperature, as found experimentally (D. H. Lindsley, written comm., 1987), or to greater mobility of Mn in ilmenite. Scatter in the data for reconstructed analyses of Adirondack oxides (Bohlen and Essene, 1977; Bohlen et al., 1980) may be a result of open-system behavior of oxide grains. Slow cooling of plutonic rocks, commonly in the presence of an aqueous phase, would be expected to facilitate open-system behavior of Fe-Ti oxides, i.e., migration of Mn (or Mg). The upward deviation from the equilibrium line for oxides in plutonic rocks may be caused by decreased

Mg/Mn in ilmenite if the oxides re-equilibrated during cooling such that the Mn and Mg contents of discrete ilmenite become similar to those of lamellae in magnetite. Similar compositions of discrete and lamellar ilmenite were found by Anderson (1968), Czamanske and Mihalik (1972), and Elsdon (1972). It appears likely that changes in minor-element content beyond original grain boundaries during slow cooling may be more profound than those in Fe or Ti. Because use of the geothermometer involves recalculation of analyses to eliminate effects of minor elements, only preservation of initial Fe and Ti contents is critical to determining temperature and f_{O_2} from oxide pairs that originally equilibrated at high temperature. Grains must not have experienced external re-equilibration with respect to Fe and Ti (Hammond and Taylor, 1982).

CONCLUSION

The Mg/Mn partitioning test for equilibrium can be applied to homogeneous Fe-Ti oxide crystals in fresh volcanic rocks. Volcanic oxide pairs whose measured precision does not overlap the equilibrium line or that fall significantly outside the calculated error envelope probably do not record equilibrium magmatic conditions and therefore should not be used for geothermometry and oxygen barometry. The test may not be valid for reconstructed analyses of exsolved crystals or for host-lamellae pairs because many examples that fail the Mg/Mn test yield reasonable temperature and f_{O_2} results that compare favorably with values derived from other equilibria (e.g.,

Bohlen and Essene, 1977). Thus, failure of carefully re-integrated bulk compositions of oxide grains or analyses of host-lamellae pairs from slowly cooled rocks to fall within the error envelope of Figure 1 does not necessarily invalidate their use for geothermometry and oxygen barometry.

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