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INTRODUCTION

For kimberlites and petrogenetically similar rocks, data on the total concentration of iron in ilmenites and chromites, its crystallographic site distribution, and the ferrous/ferric ratio may be useful in identifying potentially diamondiferous lithologies and distinguishing them from other igneous suites. Conventional chemical analytical methods permit the accurate determination of total iron in these minerals, but distribution data depend heavily on the analytical method used and the assumptions adopted. The resulting lack of reproducibility within and between laboratories is unacceptable if the value of the analyses to exploration is to be fully realised.

In this study, ilmenite and chromite grains are used to compare various analytical procedures. The accuracy of each procedure is evaluated by comparing the indirectly obtained ferrous/ferric ratio data with data obtained by Mössbauer spectroscopy. Mössbauer spectroscopy enables the direct determination of the ferrous/ferric ratio for each crystallographic site and the discrimination of any secondary ferruginous phases incorporated in the mineral examined and, because it uses the solid mineral grains, there is no risk of altering the oxidation state of the iron during chemical dissolution. The spectra obtained by Mössbauer analysis are a direct response to the number of iron atoms in each electronic configuration and hence, determinations of site occupancies and oxidation states do not depend on assumptions such as mineral stoichiometry and the absence of lattice defects.

Ilmenite and chromite grains were selected for analysis, on the basis of their apparent freedom from inclusions and alteration rims, using a binocular microscope. The selected grains were boiled in 40% HF for 1 hr and subsequently in acid oxalate to remove surface contaminants. Each selected grain was then sectioned and analysed with an electron microprobe using wavelength dispersion procedures (EPMA), with a scanning electron microscope using energy dispersion procedures (SEM), and by Mössbauer spectroscopy; the FeO and Fe₂O₃ content of large grains were also analysed by standard wet chemical methods. For both EPMA and SEM analyses, determination of the ferrous/ferric ratio was made for ilmenite using the Boyd molecular proportions method (Boyd, 1971), and for chromite using the method of Finner (1972).

PRELIMINARY RESULTS AND DISCUSSION

For ilmenites and chromites, agreement between EPMA and SEM analytical data for major components is generally reasonable (e.g., Table 1) although some MgO determinations for ilmenites reveal differences between the methods as high as 20%. However, agreement between EPMA and SEM methods on the ferrous/ferric ratio is usually poor with differences of the order of 50% being common. The disagreement arises because although the difference between the total iron contents determined by each method is small, partitioning of the iron between divalent and trivalent forms by any indirect method

(e.g., the method of Boyd, 1971) will reflect the cumulative errors in determinations of all components used in the calculation.

TABLE 1

Comparison of EPMA and SEM analytical data
for representative ilmenite and chromite grains **

COMPONENT	ILMENITE		CHROMITE	
	EPMA	SEM	EPMA	SEM
SiO ₂	0.00	0.00	0.02	0.00
TiO ₂	49.90	52.29	1.09	1.17
Al ₂ O ₃	0.22	0.00	6.18	6.11
V ₂ O ₃	0.00	0.32	0.17	0.15
Cr ₂ O ₃	1.33	1.42	61.29	61.00
Fe ₂ O ₃	10.25	6.63	2.59	3.09
FeO	27.98	33.23	14.61	15.09
MnO	0.29	0.36	0.33	0.55
MgO	9.28	7.53	12.05	11.82
CaO	0.06	0.00	0.00	0.00
NiO	0.00	0.00	0.13	0.00
*Total Fe	37.20	39.44	16.94	17.87
#FeO/Fe ₂ O ₃	2.73	5.01	5.64	4.88

* Total Fe is expressed as %FeO

The direct ferrous/ferric ratio determined by Mössbauer spectroscopy is 2.70 for the ilmenite and 4.26 for the chromite

**Ilmenite compositions are means of 4 (SEM) and 2 (EPMA) analyses
Chromite compositions are means of 4 (SEM) and 3 (EPMA) analyses

Thus for the ilmenite in Table 1, the difference between the ferrous/ferric ratios calculated from each analysis is largely a reflection of the cumulative differences between the MgO and TiO₂ contents determined by each method.

Mössbauer data for the ilmenite show a ferrous/ferric ratio which is in excellent agreement with the ratio obtained using EPMA. Wet chemical analysis of the ilmenite yields a ferrous/ferric ratio (1.55) which agrees with neither the EPMA data nor the SEM data although the wet chemically determined total iron concentration (37.78) agrees well with both. The ferrous/ferric ratio determined by wet chemical analysis is lower than that determined by EPMA or SEM methods possibly because difficulties in dissolving many rock materials cause wet chemical determinations of ferrous/ferric ratios to err in favour of Fe₂O₃ (e.g., Bancroft et al., 1977) no matter how careful the analyst. However, despite the possible bias in wet chemical determinations of ferrous/ferric ratios, the results obtained to date are in better agreement with the EPMA and Mössbauer data than are determinations based on SEM analyses.

For the chromite, ferrous/ferric ratios determined by EPMA and by SEM frequently disagree with each other and in some grains both differ from the Mössbauer data. Where the Fe₂O₃ concentration is much lower than the FeO concentration, slight differences in the Fe₂O₃ content determined by each procedure will be magnified in the calculated ferrous/ferric ratio, but this observation cannot explain the difference in the first place. There are three possible explanations for the disagreement between the procedures:-

1. Two of the three procedures are inaccurate. This explanation is unlikely in view of the data for ilmenites.

2. Finger's calculation method is unsatisfactory. This explanation is also unlikely because no assumption used in the method appears to be sufficiently erroneous to account for the discrepancies.
3. The differences between the EPMA and SEM data reflect the same cumulative errors that affect the ilmenite analyses and data from both differ from Mössbauer data because the Mössbauer examines whole grains including inclusions which are usually avoided during electron beam point analyses. This explanation is supported by a) high standard deviations between individual point analyses, b) the presence of unidentified platy contaminants noted during crushing, and c) the presence of traces of hematite in the Mössbauer spectra of some chromites. Calculations show that because the ferric iron content of the chromites is so low, as little as 1.5% contaminant hematite could fully account for the difference between the Mössbauer data and data derived by electron beam methods.

CONCLUSIONS

Compositional data for chromites and ilmenites have been used by several authors (e.g., Boyd and Nixon, 1973; Singhvi et al., 1974; Haggerty, 1975; Sobolev et al., 1975) to provide an insight into the origin of kimberlite pipes and to distinguish kimberlitic ilmenites and chromites from those with other origins.

Almost all these studies require knowledge of ferrous/ferric ratios but this study raises some major questions as to the usefulness of some analytical techniques. SEM data appear to be good for overall comparisons but cumulative errors encountered in assessing ferrous/ferric ratios may make this method unsatisfactory for more complex studies. Wet chemical analyses are probably unsuitable due to their tendency for bias in favour of trivalent iron, and although Mössbauer probably gives the best ferrous/ferric ratios it is not suited to routine analyses. Probably the best routine analytical method is EPMA, but its use raises the question of whether bulk grain compositions (including alteration rims zones and inclusions) are more useful or less useful in petrogenetic analysis than the composition of the most alteration and inclusion free part of the grain. Either approach involves assumptions which require careful consideration in relation to both what to analyse and how.

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