XRF MAJOR AND TRACE ELEMENT DETERMINATION IN FE-TI OXIDE MINERALS

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(1 figure and 8 tables)

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ABSTRACT. An XRF method describes the bulk composition (host + exsolved phases) analysis of magnetite and ilmenite grains obtained by physical methods of separation. Fe, Ti, Mn, Mg, Al, Ca, and Si are measured on glass discs (1:20 dilution in Li borate) and V, Cr, Ni, Co, Cu, Zn, S are determined on pressed pellets of *ca.* 1.5 g of magnetite, and the same elements plus Zr and Nb on ilmenite 1.5 g-pressed pellets. When necessary, matrix effects are corrected with the Compton line (absorption) or by measuring the effect of Ti on V and Cr intensities (enhancement). A variety of reference samples are used to assess the accuracy of the method. For Fe, Ti and Mg the accuracy ranges between 0.6% and 3.2%, and for V and Cr between 5.6 and 7.6%. Detection limits and reproducibility are acceptable for most geochemical studies. The method meets the current needs of the geochemical interpretation of Fe-Ti oxide minerals and deposits.

KEYWORDS: ilmenite, magnetite, titanomagnetite, trace element geochemistry, Fe-Ti deposits

Introduction

XRF (X-ray fluorescence spectrometry) is a widely used technique for the analysis of geological material (Potts, 1987). Since Norrish & Hutton (1969), major elements in silicate rocks are commonly determined by analysis on glass discs made up by melting and dissolving the sample powder in borate flux. This method of sample preparation permits to overcome particle size and mineralogical effects, and allows careful matrix corrections due to inter-element absorption and enhancement. This method has been used in our laboratory for more than 30 years (Bologne & Duchesne, 1991). On the other hand, trace elements in silicate rocks are preferably measured on compressed powder pellets, particularly for heavy elements (Z>26) whose matrix corrections are monitored by the Compton scattered tube line (Reynolds, 1967). Glass discs can also be used for trace elements but due to the dilution of the sample in the glass the method is less sensitive than on crude powder pellets (Enzweiler & Webb, 1996). The large number of reference samples now available (e.g. Govindaraju, 1994) permits to ascertain the accuracy of the results and the technological developments of modern instruments bring the precision and reproducibility of the determination far beyond the required ranges for usual petrogenetic interpretations.

The XRF analysis of minerals can in principle be performed by the same approach on glass disc and powder pellets. In practice these methods are, however, more difficult to implement because of: (1) the amplitude of the inter-element effects due to the large variation of element contents; indeed most minerals are solid solutions in which some elements can vary from zero to several tens percents; (2) the lesser number- if not the lack- of reference samples of good quality, covering the number of interesting elements and the range of possible major and trace element variations, the latter varying frequently over several orders of magnitude; (3) the high accuracy needed for stoechiometric consideration and/or for industrial purposes; (4) the small quantities generally available for analysis, particularly when the minerals are obtained by physical methods of separation from rock samples.

We present in this work the analysis methods for Fe-Ti oxide minerals that we have implemented to study the petrology and geochemistry of these minerals. Ilmenite is a solid solution between Fe_2O_3 (hematite), $FeTiO_3$ (ilmenite *sensu stricto*) and $MgAl_2O_4$ (spinel). The major elements vary up to 62%TiO_2 (on altered grains); MgO from 0 to 4.5% or more (e.g. Charlier et al., 2008). Magnetite is built up with a mixture of Fe_3O_4 (magnetite sensu stricto), Fe_2TiO_4 (ulvöspinel), $FeTiO_3$ (ilmenite) and $MgAl_2O_4$ (spinel) in various proportions. TiO_2 can vary from say 0.5% up to 28% (see e.g. Duchesne et al., 2006), the V content from a few ppm to the percent level (Charlier et al., 2007; Duchesne et al., 2006)

For logistical consideration we try to achieve the highest accuracy in a minimum time which is adapted for each element to its geochemical interest or industrial value. In other words we focus on the accuracy of major element determination because they are crucial in determining the fO_2-T conditions of equilibrium following e.g. the QUILF method (Andersen et al., 1993) or Lattard's approach (Lattard et al., 2005; Sauerzapf et al., 2008). These elements are also important in assessing the economic value of an ilmenite ore. Some elements, such as Mg, Ca, Al and Cr, are polluting elements in the industrial processing of ilmenite (e.g. Nair et al., 2002). For the trace elements, Cr and V are excellent tracers of petrogenetic processes and are thus worth being more accurately determined (Duchesne et al., 2007; Charlier et al., 2008).

Experimental

Equipment

Analysis was performed on an ARL 9400XP equipped with a Rh anode, end window X-ray tube. The analysis conditions are given in Table 1. Overlap corrections were applied to account for the overlap of TiKβ on VKα, VKβ on CrKα, and SrKβ on ZrKα (Table 1), either by measuring the contribution of the interfering element (Sr, Cr) or by choosing an appropriate background (V), assuming the symmetry of the TiKβ peak profile. Ti and Mn are determined on glass discs and pellets. This permits to run the two methods independently if necessary. Ti-contents measured on magnetite pellets are used to correct matrix effects on V and Cr (see below) without necessarily measuring major elements on glass discs.

Sample preparation

Glass discs
The powdered samples are heated in a porcelaine crucible at 1000°C in a muffle furnace for 2 hours. 0.2 g of oxidized powdered sample and 4 g of X-Ray flux (50% Lithium tetraborate and 50% Lithium metaborate (Socachim) are

mixed in a Pt-5%Au alloy (Claisse Bis!) crucible and fused in a Claisse fluxer apparatus with continuous swirling at *ca.* 1000°C for 15 min. The melt is poured into a platinum mould (28 mm in diameter) and, on cooling, the disc spontaneously separates from it. The glass disc is 2 mm thick and shows a shiny surface. It is important to note that the disc cannot be indefinitely used; after a few weeks a change in count rate for iron is indicative of segregation (Norrish & Hutton, 1969).

Pressed pellets

The powdered sample (*ca.* 1.5 g) is mixed with a few drops of Elvacite (dissolved in toluene) and pressed as 20 mm-diameter pellets under 4.8 tcm^{-2}. The critical thickness of the sample for the NbKα line and densities of the Fe-Ti oxides (4.7 to 5.2) being *ca.* 0.65 mm (Potts, 1987), the minimum weight of sample is 1 g. For easier handling, the pellet is stuck on a cellulose disc of the same diameter.

Reference samples

A major concern in the analyses of Fe-Ti oxide minerals is the paucity of reference material covering the range of investigated contents for all elements. The list of the

Element	X-ray line	Count time (s)		Collimator	Diffracting crystal	Measuring angle		Detector
		glass disc	pellet			peak	background	
Mg	Kα1,2	15		0,60	AX06	19,92	21.32, 18.50	FPC
Al	Kα1,2	15		0,60	PET	144,63		FPC
Si	Kα1,2	15		0,60	PET	109,02		FPC
Ca	Kα1,2	15		0,60	LiF200	113,11		FPC
Ti	Kα1,2	15	10°°	0,25	LiF200	86,14	85,00	FPC
Mn	Kα1,2	15		0,25	LiF200	62,96	63,36	FPC
Fe	Kα1,2	15		0,25	LiF220	57,51	58,21	FPC
V	Kα1		150	0,25	LiF220	123,06	124,82	FPC
Cr §	Kα1		150	0,25	LiF220	107,06	108,59	FPC
S	Kα1,2		15	0,25	Ge111	110,67	108,77	FPC
Co	Kα1		15	0,15	LiF220	77,83	78.43, 77.23	FPC
Ni*	Kα1		20	0,25	LiF220	70,22	71,20	SC
Cu*	Kα1		20	0,25	LiF220	65,49	66,20	SC
Zn	Kα1		15	0,15	LiF220	60,52	59,90	SC
Zr**	Kα1		15°	0,15	LiF220	32,04	31,53	SC
Nb	Kα1		15°	0,15	LiF220	30,38	29,86	SC
Rh***	Kα1		15	0,15	LiF220	26,51		SC

The tube is operated at 50 kV and 50 mA on pellets and at 30 kV and 80 mA on glass discs.
Pulse height discrimination applied.
* measured with Fe filter   °° measured on magnetite for correction's needs   ° on ilmenite only
** ZrKα = ZrKα1 - (ZrBG*0.9878) - 0.0480*(SrKα1-SrBG)
§ CrKα = CrKα1 - CrBG - 0.0413*(VKα1-VBG)
*** Compton scattered tube line

Table 1: Conditions for major and trace element determination by XRF

Ilmenite

SARM-59 South African Bureau of Standards, Ilmenite (RBM)
ILM-6703: AG Der Dillinger Hüttenwerke, Ilmenite X6703181002-1
ILM-88: Titania AS Standard n°88 (ilmenite 16716)
ILM-144: Titania AS Tellness standard ilmenite- average production 1990 (16716 G/91)
GP3-8: Synthetic ilmenite made up by G. Pouliot and M. Bergeron in 1979 at QIT (Sorel, Quebec)
S-104: GBW 07226 Ore concentrate, Panzhihua Iron & Steel research Institute, China
S-102: GBW 07221 Crude ore, Panzhihua Iron & Steel research Institute, China
I66-16: Ilmenite separated from the Rödemyr deposit (Rogaland anorthosite province, Norway), analysed by XRF at the University of Liège

Magnetite

SARM-12 and 46: South African Bureau of Standards Phalaborwa magnetite and stream sediment, respectively
STD-65: Titania AS Standard n°65 (magnetite V4 1)
STD-89: Titania AS Standard n°89 (magnetite 16717)
S-104: GBW 07226 Ore concentrate, Panzhihua Iron & Steel research Institute, China
S-102: GBW 07221 Crude ore, Panzhihua Iron & Steel research Institute, China
M146: Magnetite separated from the Storgangen deposit (Rogaland anorthosite province, Norway), analysed by XRF at the University of Liège
M64-96: Magnetite separated from the Kydlandsvatn deposit (Rogaland anorthosite province, Norway), analysed by AES and XRF at the University of Liège
M66-33: Magnetite separated from the Hesnes deposit (Rogaland anorthosite province, Norway), analysed by XRF at the University of Liège
M66-16: Magnetite separated from the Rödemyr deposit (Rogaland anorthosite province, Norway), analysed by XRF at the University of Liège

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Table 2: Reference material provenance

samples that are used is given Table 2. A few international reference samples do exist such as SARM 12 (magnetite), SARM 59 (ilmenite), and SARM 46 (stream sediment). Some samples, used for industrial purposes and validated by several industrial analytical laboratories, were provided by Titania AS (magnetites STD-65 and -89, ilmenites ILM-88 and -144), by a commercial company (ilmenite ILM-6703), and by the Panzhihua Iron and Steel company (magnetite S-102 and a crude magnetite ore S-104). A series of synthetic ilmenite samples (GP) were melted, ground and doped with various elements at the Quebec Iron & Titanium Corporation laboratory at Sorel. Finally three "in house" magnetite standards (M146, 64-96; 66-33) and an ilmenite (I66-16) were determined for some specific elements by a variety of methods, including ES and XRF.

Matrix corrections

For the major element analysis on glass disc, we have observed that diluting and fusing the sample in Li-borate in the proportion 1:20 give a homogeneous and translucent glass disc, and is sufficient to overcome matrix corrections. This method also cancels mineralogical effects and thus permits the use of synthetic standard samples made up of pure Fe_2O_3 and TiO_2 chemicals to calibrate Fe and Ti determinations. For the minor element analysis on pressed pellets, we account for mass absorption effects with the Compton scattered tube line for Nb, Zr, Ni and Zn. No

corrections were applied to Co. For V and Cr, we account for absorption and enhancement effects due to Fe and Ti contents. The matrix corrections are different between the two elements. Indeed, the absorption edge of the Ti K-lines is at 2.4970 Å, thus shorter than the VKα line (2.5036 Å), but larger than the CrKα line (2.2897 Å). The matrix effect on Cr thus includes intensity enhancement due to Fe and absorption due to Ti, while on V only the enhancement of Fe has to be corrected. Fig. 1 illustrates the matrix effects due to Ti and Fe on the V and Cr peak intensities.

Results

Accuracy

The accuracy of a particular element determination depends on the preparation method and on the reference samples used for calibration.

Glass discs

For Fe and Ti, two synthetic samples made up of pure Fe_2O_3 and TiO_2 and a 1:1 mixture of Fe_2O_3 and TiO_2 are used to calibrate the determinations. A series of reference samples have been measured by that method. The relative average deviations to the 'recommended' values (Tables 3 and 4) are 1.2% and 0.6% for Fe_2O_3 in ilmenite and magnetite, respectively, and 1.8% and 3.2% and for TiO_2
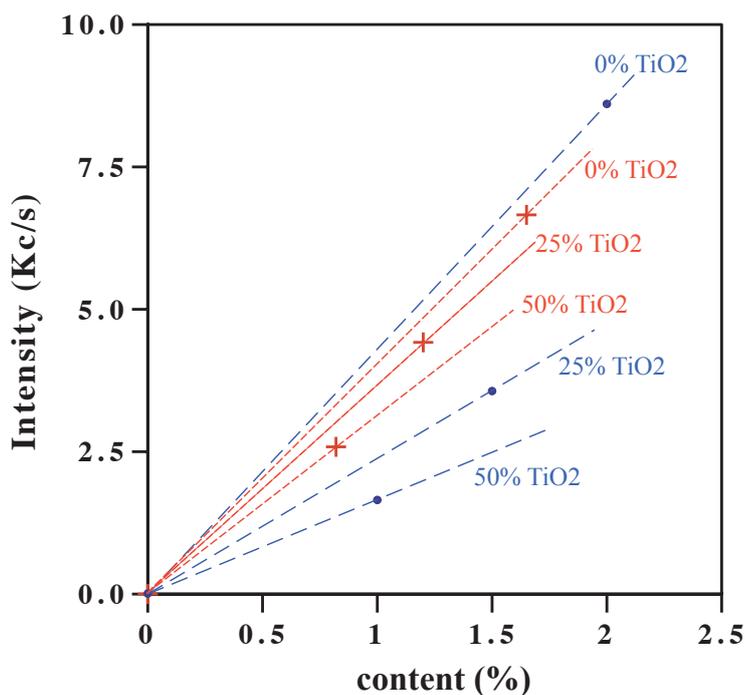
Figure 1: Peak intensity (Kc/s) vs Element content (%). In blue calibration curves for Cr_2O_3 for various amounts of TiO_2. In red, same for V_2O_3. Note that the influence of the absorption of Ti is more significant for Cr than for V (see text). Linear interpolation permits a correction as a function of the TiO_2 content of the sample.

Name	Nature	Fe_2O_3	TiO_2	MgO	MnO	CaO	Al_2O_3	SiO_2
Fe_2O_3	synthetic	100,00	0,00	0,00	0,00	0,00	0,00	0,00
$50Fe_2O_3$-$50TiO_2$	synthetic	50,30	47,70	0,00	0,00	0,00	0,00	0,00
TiO_2	synthetic		100,00	0,00	0,00	0,00	0,00	0,00
SARM-59	int. ref. sample	*50,30*	*48,80*	0,56	1,05	0,05	0,61	0,75
ILM-88	ref. sample	*50,18*	*44,30*	4,20	0,29	0,30	0,65	2,60
ILM-6703	ref. sample	*58,51*	*28,74*	2,47	0,20	0,99	3,40	5,67
S-104	ref. sample	*72,66*	*12,34*	3,49	0,34	1,48	5,11	5,55
S-102	ref. sample		*10,63*	6,16	0,29	6,38	8,26	20,33
average dev. (%)		1,2	1,8	1,7	6,0	8,4	7,1	2,6

in italics, recommended value of the reference sample which is measured as an ordinary sample to estimate the accuracy (average deviation)

Table 3: Calibration samples for major-element determination of ilmenite (glass discs)

Name	Nature	Fe_2O_3	TiO_2	MgO	MnO	CaO	Al_2O_3	SiO_2
Fe_2O_3	synthetic	100,00	0,00	0,00	0,00	0,00	0,00	0,00
$50Fe_2O_3$-$50TiO_2$	synthetic	50,30	47,70	0,00	0,00	0,00	0,00	0,00
SARM-12	int. ref. sample	*95,22*	*0,72*	2,80	0,220	1,09	0,77	0,34
STD-65	ref. sample	*85,80*	*3,46*	2,90	0,031	0,40	2,00	4,30
STD-89	ref. sample	*86,09*	*4,50*	2,60	0,036	0,45	2,20	4,11
S-104	ref. sample	*72,66*	*12,34*	3,49	0,336	1,48	5,11	5,55
S-102	ref. sample		*10,63*	6,16	0,288	6,38	8,26	20,33
average dev. (%)		0,6	3,2	1,7	6,4	2,6	12,3	5,4

in italics, recommended value of the reference sample which is measured as an ordinary sample to estimate the accuracy (average deviation)

Table 4: Calibration samples for major-element determination of titanomagnetite (glass discs)

in ilmenite and magnetite, respectively. The other elements (Mg, Mn, Ca, Al and Si) were calibrated with several reference samples and the obtained accuracies range from 1.7% to 12.3% (Tables 3 and 4). We prefer using "natural" samples for calibration because in our experience it is a more reliable method than using "synthetic" mixtures of chemical compounds.

The overall accuracy of the glass disc determinations is very satisfactory. The best accuracy is obtained for Fe, Ti and Mg, elements that are crucial to assess the solid solution stoechiometry of the minerals.

Pressed pellets

Tables 5 and 6 show the reference sample values that are used to calibrate the trace element determinations. Estimates of the accuracy of the determination are obtained by averaging the relative deviations to the "recommended" values. V and Cr are calibrated with

Name	Nature	V	Cr	Ni	Co	Nb	Zr	Cu	Zn	S
Fe_2O_3+C	synthetic	0,5571	0,6842							
Fe_2O_3	synthetic	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000	0,0000
GP3	synthetic	0,4416	0,4048					0,0260		
GP4	synthetic	0,5448	0,5338					0,0097		
GP5	synthetic	0,0719			0,0262					
GP8	synthetic	0,5188	0,5084	0,0093	0,0096			0,0092		
SARM-59	int. ref. sample	0,1399	0,0684			0.0505*	0.0660*			
ILM-88	ref. sample	0,1156	0,0534	0,0180	0,0115	0,0058	0,0203	0,0037	0,0200	0,0550
ILM-6703	ref. sample	0,1399		0,0424	0,0125	0.0031*	0.0283*	0,0160	0,0153	0,2600
ILM-144	ref. sample	0,1155	0,0513	0,0140	0,0110	0,0058	0,0150	0,0019	0,0150	0,0480
I66-16	in house								0,0434	
average dev. (%)		7,0	5,4	6,8	14,7	10,1	16,8	16,3	17,3	13,9

* determined by XRF with international reference samples of silicate rocks

Table 5: Calibration samples for trace-element determination of ilmenites (pellets)

Name	Nature	V	Cr	Ni	Co	Cu	Zn	S	TiO₂
Fe_2O_3+A	synthetic	1,1209							
Fe_2O_3+C	synthetic		1,3685			0,0000			50,00
Fe_2O_3+B	synthetic								25,03
Fe_2O_3	synthetic	0,0000		0,0000	0,0000			0,0000	0,00
SARM-46	int. ref. sample	*0,0225*	*0,0559*		0,0056	0,0566	0,5900	0.17*	0,60
SARM-12	int. ref. sample	*0,0520*	*0,0021*	0,0281	0,0223	0,0502	0,0141	0,0695	0,72
S-104	ref. sample	*0,3124*	*0,0240*	0,0140	0,0200	0,0210			12,34
STD-65	ref. sample	0,3533	*0,7458*	0,0800	0,0106	0,0100	*0,1500*	0,6600	3,46
STD-89	ref. sample	0,3601	*0,6760*	0,0826	0,0115	0,0090	*0,1340*	0,4100	4,50
M146	in house	*0,5299*	0,5953						0,50
M64-96	in house	*0,7337*	0,2668						1,00
M66-16	in house								0,50
M66-33	in house								7,00
average dev. (%)		7,4	6,2	9,3	8,1	8,9	8,7	28,8	14,3

in italics, recommended value of the reference sample which is measured as an ordinary sample to estimate the accuracy (average deviation)

Table 6: Calibration samples for trace-element determination of titanomagnetite (pellets)

Element	Ilmenite		Magnetite	
	pellet	glass disc	pellet	glass disc
Nb	2,0			
Zr	8,1			
Zn	8,3			
Cu	7,1			
Ni	12		21	
Co	60		120	
MnO	19	50	18	50
Cr	9		5	
V	21		5	
TiO_2		0,007%	21	0,01%
CaO		0,01%		0,01%
S	15		17	
SiO_2		0,038%		0,03%
Al_2O_3		0,026%		0,02%
MgO		0,05%		0,05%

Table 7: Detection limits for major and trace elements (ppm or %) on pellets and glass discs

relatively large numbers of samples and the method gives accuracies of 5.6-7.6%, which is satisfactory inasmuch as the recommended values are far from 'perfect'. The other elements are calibrated with a lower number of samples and consequently the accuracies are more difficult to estimate and thus less reliable. It should be noted that parts of the Ni, Co, and Cu contents may possibly be brought by traces of sulphides (S) which might be heterogeneously dispersed in the samples. This can explain the lower accuracy of the determination and consequently the lower geochemical interest of these elements as petrogenetic indicators than V and Cr. Note that a less accurate determination of Ti is obtained on pressed pellets of magnetite than on glass discs. This value is nevertheless sufficiently accurate to correct the matrix effects on V and Cr in case a glass disc determination is not performed/available.

We have noted that in the determination of low contents of V and Cr in ilmenite we sometimes obtain negative values, which means that the background intensity is higher than the blank intensity. To measure contents close to the detection limit, it is thus crucial to use a blank of "spec pure" ilmenite, specially synthetized for this purpose (Duchesne & Bologne, work in progress).

Magnetite

	Range	Average	s	s%	LD (ppm)
TiO_2	0.2-25 %	11,50	0,10	0,85	21
MnO	0.003-0.38 %	0,18	0,002	0,98	18
V	0.27-2.30 %	0,57	0,01	1,2	5
Zn	500-1500 ppm	827	66	7,9	18
Cu	20-700 ppm	179	20	11,4	12
S	0.17-4.8 %	2,7	0,3	12,2	17
Cr	60-1600 ppm	234	30	12,8	5
Co	110-390 ppm	181	34	18,1	120
Ni	10-500 ppm	125	40	31,4	27

Ilmenite

	Range	Average	s	s%	LD (ppm)
MnO	0.3-0.5 %	0,47	0,002	0,5	19
S	0.02-2 %	0,22	0,002	1,0	15
Nb	16-22 ppm	19	0,28	1,4	2
V	0.01-0.32 %	0,1070	0,0026	2,4	21
Zr	40-650 ppm	178	7	3,7	8
Zn	20-190 ppm	78	6,2	6,4	6
Cu	10-220 ppm	33	6	19,4	7
Co	<LD-150 ppm	59	21	36,0	60
Ni	<LD-86 ppm	33	8	25,8	12
Cr	<LD-220 ppm	47	17	35,6	9

Table 8: Reproducibility of major and trace element determinations on pellets

Detection limit

The instrumental detection limit LD for trace elements measured on pellets is calculated from the background count rate using: $LD = (3\sqrt{2B/T})/S$ where B = background count rate (in c/sec), T is the count time and S is the sensitivity net c/sec/concentration units. For elements involving ratios of line intensity to Compton scattered tube line intensity, the LD includes the error of this contribution. The results are given in Table 7. They meet the aims of the method and are thus satisfying. Note the relatively low LD of V and Cr due to the longer counting times (150 s *vs*. 15 s). Co, however, has an LD far larger than the other elements in both minerals. This is due to the proximity of the analytical line CoKα to the relatively very intense FeKß line, which increases the background intensity and reduces the peak/background ratio.

Precision

The precisions *s* of the element determination on pressed pellets have been evaluated on two series of samples measured at different days, and using $s = \sqrt{(\Sigma w^2/2k)}$ where *w* is the range, or difference between duplicates, and *k* the number of samples (Table 8). This method covers the whole interval of concentrations and is sufficient to give a good estimate of the standard deviation (Davies & Goldsmith, 1986). Excellent reproducibilities (<1.5%) are obtained for Ti, Mn and V in magnetite and Mn, S and Nb in ilmenite. Zn in both minerals and V and Zr in ilmenite are measured with *s* <10%. The reproducibility increases rapidly when the average content approaches the detection limit (see e.g. Ramsey et al., 1995), as observed in the present case for Co and Ni in both minerals and Cr in ilmenite.

Discussion

The principal aim of the present work is to show the strengths and weaknesses of a simple method of mineral analysis. The major strength of the method is to permit the analysis of relatively small quantities of the whole mineral, that is the host mineral and its various exsolved phases, an objective that cannot be easily attained with an electron microprobe, even with a defocused beam. This method can be highly recommended for the analysis of major elements and particularly for Fe and Ti. Moreover, the method is easy to implement with few synthetic reference samples and a few natural reference samples. This is very convenient to overcome the limited life of the glass discs.

For trace elements, whether determined on glass discs or on pellets, the weakness of the method is that the accuracy strongly depends on the availability of reference samples. For elements such as e.g. S it suffers from the small number of reference samples and of their relatively low quality. However, for V and Cr, the method provides low detection limits and excellent accuracy and precision that meet the needs of most geochemical interpretation.

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