Proportionality factors for thin film TEM/EDS microanalysis of silicate minerals

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ABSTRACT. — Chemical compositions can be obtained by energy dispersive spectrometry in a transmission electron microscope by the use of Cliff and Lorimer's ratio method when the appropriate proportionality factors are known.

The experimental values of these factors have been determined for ten geochemically important elements at acceleration voltages of 20, 40, 100, 120 kV. Comparison is made with literature data and conversion factors are given in order to compare differently defined quantities. Finally, examples of quantitative thin film analysis of silicate minerals requiring high spatial resolution (better than 1000 Å) are given.

Key words: TEM, microanalysis, silicates.

RIASSUNTO. — Composizioni chimiche quantitative, con risoluzione spaziale dell'ordine delle centinaia di Å, possono essere rapidamente ottenute con un microscopio elettronico a trasmissione corredato di rivelatore Si(Li). Infatti, operando su campione sottile, la correzione dei dati può essere effettuata col metodo del rapporto di Cliff e Lorimer, applicando opportuni coefficienti di proporzionalità tra intensità X e concentrazione elementare.

Sono stati misurati i valori di questi coefficienti per dieci elementi di importanza geochimica, a tensioni di accelerazione di 20, 40, 100 e 120 kV. I risultati sono confrontati con i dati disponibili in letteratura; vengono altresì forniti i fattori di conversione da impiegare nell'uso di coefficienti definiti in modo diverso.

Vengono infine dati esempi di analisi, con risoluzione spaziale migliore di 1000 Å, di minerali silicatici preparati in campione sottile.

Parole chiave: TEM, microanalisi, silicati.

Introduction

High resolution transmission electron microscopy (HRTEM) has disclosed challenging perspectives in the study of the real structure, of minerals and this technique constitutes now a valuable source of mineralogical, petrological and geological information (BUSECK and COWLEY, 1983; MEL-LINI, 1981). Technical improvement has produced HR microscopes able to gather also chemical data, usually by energy dispersive spectrometry (EDS), from areas as small as a few hundreds Å in diameter. As a results, correlation between microstructural features and defect chemistry is often possible (MORIMOTO and KITAMURA, 1981). Sometimes just a look at the X-ray energy spectrum is sufficient for a correct identification but, in other cases, data processing is required to obtain a quantitative estimate of the actual chemical composition.

The best approach to the quantitative analysis of thin films in a TEM/EDS system still remains the simple Cliff and Lorimer's ratio method (CLIFF and LORIMER, 1972 and 1975; CHAMPNESS et al., 1981). In fact, the method assures satisfactory quantitative results, still requiring just a cheap pocket calculator as computing facility. As absorption and fluorescence effects can be largely disregarded in a thin film, these authors related the intensity ratio of the X-ray lines from elements A and B with the concentration ratio, by the following linear equation

$$\frac{C_{\rm A}}{C_{\rm B}} = K_{\rm AB} \frac{I_{\rm A}}{I_{\rm B}} \tag{1}$$

The K_{AB} factors depend only on the atomic number Z of the elements A and B, and on

the accelerating voltage of the microscope. When normalization is imposed (e.g., 100 wt% as oxide sum or fixed number of ions per formula unit) (n-1) equations in the form (1) describe a n-component system. These relations can be obtained in a few minutes also in a simple, non computer controlled system and easily solved to produce the chemical data. Raw data correction requires the knowledge of the KAB factors only. These factors can be either theoretically computed starting from the very basic physics of the electron-matter interactions (GOLDSTEIN et al., 1977; HRUN et al., 1979) or empirically measured on standard materials. This latter approach, although troublesome and time consuming, seems to assure better accuracy (WILLIAMS, 1982). Unfortunately, limited work has been done in this field. In what follows, proportionality factors for geochemical important elements of our interest are reported in comparison with literature data. Working examples are given to stress the advantages and the limits of this microanalytical approach. Extensive references to the theoretical foundations and experimental approach can be found elsewhere (WILLIAMS, 1982).

Concentration units and K_{AB} numerical values

Direct comparison of data from different sources, all of them defined as the Cliff and Lorimer « K_{AB} » values, may yield amazing differences. For instance, « K_{MgSl} » may range from 0.33 (ISAACS et al., 1981) to 1.59 (CHAMPNESS et al., 1981). However, these large discrepancies are not real and depend on the different concentration units and/or the different form of the basic equation (1).

a) Concentrations may be expressed in several ways, as atomic weight percent (henceforth C), oxide weight percent (C') and atomic percent (N). Depending on which units are used, the Cliff and Lorimer's equation specializes to

$$\frac{C_{\rm A}}{C_{\rm B}} = K_{\rm AB} \frac{I_{\rm A}}{I_{\rm B}} \tag{1}$$

$$\frac{C'_{\rm A}}{C'_{\rm B}} = H_{\rm AB} \frac{I_{\rm A}}{I_{\rm B}}$$
(2)

$$\frac{N_{\rm A}}{N_{\rm B}} = J_{\rm AB} \frac{I_{\rm A}}{I_{\rm B}} \tag{3}$$

Obviously, the choice is a matter of personal opinion, although each of them may simplify the current calculations. Nevertheless, as the numerical values of K_{AB} , H_{AB} and J_{AB} for the same A and B pair are different, a clear statement and a word of warning seemed necessary. Henceforth, J_{AB} values from eq. 3 will be given. The conversion between K_{AB} , H_{AB} and J_{AB} can be obtained by stoichiometry and its general form, in terms of atomic weight, oxide formula weight and stoichiometric coefficients, is given in table 1.

TABLE 1

Conversion factors relating the different numerical values of the proportionality factors obtained by a different choice of concentration units

	From J _{AB}	KAB	HAB
To			
J _{AB}	1	(AW)B	(FW) BPA
		(WA) _A	(FW) _A P _B
ĸ _{ab}	(AW) _A	í.	(AW) _A (FW) _B P _A
	(AW) _B		(AW) _B (FW) _A P _B
H _{AB}	(FW) _A P _B	(AW) _B (FW) _A P _B	1
	(FW) _B P _A	(AW) _A (FW) _B P _A	

 $(AW)_{A} =$ atomic weight of the element A; $(FW)_{A} =$ oxide formula weight; $P_{A} =$ stoichiometric coefficient of the element A in its oxide (e.g. P_{A1} is 2 for Al₂O₃).

b) Whereas eq. (1) (or the equivalent eqs. (2) and (3)) is the most common choice, some authors (ISAACS et al., 1981; GORDON et al., 1981; WHITE et al., 1982) utilize equations of the form

$$\frac{I_{\rm A}}{I_{\rm B}} = K_{\rm AB} \frac{C_{\rm A}}{C_{\rm B}}$$

PROPORTIONALITY FACTORS FOR THIN FILM TEM/EDS ETC.

Apart from the choice of concentration units these « K_{AB} » values are the reciprocal values of the K_{AB} when compared with eq. (1).

Experimental

The analytical system we used consists of a Philips 400T electron microscope (nominal take-off angle 20°), equipped with an EDAX Si(Li) detector (30 mm² sensitive area, FWHM resolution 154 eV for MnKa, nominal thickness of the Be window 7.5 µ and nominal thickness of the Au contact laver 100 Å), 183 A amplifier and 707 A multichannel analyzer. The specimens were tilted 30° towards the detector. Electron illumination was chosen to assure irradiation of the thinnest regions (say thinner than 1000 Å), and count rate over the whole energy spectrum lower than 3000 cps. Spot size during standardization was usually in the thousands Å range. Collection of spectra from the same area was repeated at 20, 40, 100, 120 kV acceleration voltages and, tipically, four-six areas were analyzed per each standard material. For each peak background was measured on the two sides (higher and lower energy) and subtracted from the peak integral. Proportionality factors were determined as JASI values from individual measurements and subsequently averaged to produce the final JASI coefficients. Several colleagues helped us by supplying standard materials analyzed in bulk or by electron microprobe.

Results and discussion

Proportionality factors are reported as J_{ASI} values of eq. (3) in tables 2-4. Table 2 lists also the different minerals we used as reference materials during standardization. When available (120 and 100 kV), also experimental values from other authors are reported in these tables. Owing to peak overlap, proportionality factors we determined refer to the whole (K α + K β) envelope for Z < 15 and only to K α lines for Z > 15.

The general trend of J_{ASI} values versus the atomic number is quite consistent when data from the different sources, but based on the same equation and the same concentra-

TABLE 2

J_{AB} proportionality factors at 120 kV accelerating voltage

			++	
	Present	Wood et	Morimoto and	Standards used in this work
	work.	#1.(1982)	Kitanura(1981)	
Na	3.52(28)	4.56	7.7	Albite,guarinite.
Mg	1.830 53	1.72	2.15	Clinopyroxene.syn-diopside.
AT	1.20(11)	4.17	1.15	Orthose, albite, topaz, wicro+
				cline,jadeite.
p .	1.1	0.90	1	
s	1	8.95	1.	
£	8.93(12)	0.80	0.82	Orthose,mfcrocline.
Ca.	8,846 53	2.81	0.85	Clinopyroxene,sys-diopside.
				wallastonite,miocalitm.guarinite.
				wohlerite, titanite.
τ.	8-82(10)	0.00	2.50	Titanite.guarinite.wohlerite.
Cr.	1	8.75	8.55	
Me	5.72(15)	0.58	0.50	Niocalite, guarinite, wohlerite.
				levenite.
Fe.	0.72(14)	0.45	0.50	Oliving, clinapyrosene, miocalite.
				garnet,wohlerite,lavenite.guari-
				nite.
81	1	0.80	0.77	
Cu.	1	0.70	1	
Zr	1.47(123	1	1	Guarinite,wohlerite.
ND	1.44(30)	1	1	Guartnite.wohlerite.
	Transformed	from the orts	inal Kasy values	to J _{AS1} values.according to Table 1.
		· ····································	in the discourse of	Fig. 7 in the original paper.

Data from MORIMOTO and KITAMURA (1981) refer to 200 kV. Standard deviations in parentheses.

tion units, are compared, although discrepant values also occur. For instance, the 120 kV J_{ASi} factors we determined do not differ by more than 10 % relative with respect to the other available set (Wood et al., 1982), apart from sodium, potassium and titanium. In the case of 100 kV J_{ASi} values, the best agreement occurs when our data are compared with the values given by LORIMER et al. (1977), and by CHAMPNESS et al. (1981). As regards the occurrence of discrepant values, they may be due to several factors, the most important ones being:

- a) different absorption coefficients in the different detectors (however, this parameter should be effective only for the lower energy lines, up to 2.0 keV);
- b) unsuitable standards (bulk composition not accurately known, heterogeneity on the TEM scale, instability under the beam);
- c) invalid thin film approximation and necessity of more accurate correction procedures.

At this stage, it is impossible for us to state which results are less accurate and

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JAB proportionality factors at 100 kV accelerating voltage

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	Present	Lorimer et	Champness et	Schreiber and	Gordon et	Isaacs et
	work	a1.(1977)	a1.(1981)	Wims (1981)	#1.(1981)	al.(1981)
Na	3.75(34)	3.91	3.92	2.66	1	3.03
Mg	1.74(1)	1.85	1.84	1.66	2.14	1.59
A1	1.19(6)	1.25	1.31	1	1	1
5	1	1	1	0.80	1	1
C1	1	1	1	0.72	/	1
ĸ	0.94(16)	0.74	0.72	/	1	0.63
Ca	0.85(3)	0.74	0.70	1	0.86	0.62
Ti	0.81(12)	0.66	0.63	1	1	0.53
v	1	/	0.62	1	1	1
Cr	1	1	0.63	1	1	0.50
Mn	0.73(15)	0.60	0.62	1	0.71	0.49
Fe	0.75(17)	0.62	0.64	1	1	0.45
Co	1	1	0.65	1	1	1
Ni	1	0.62	0.70	1	1	1
Cu	1	0.80	0.70	0.75	1	1
Zn	1	0.68	0.72	0.75	1	1
Ge	1	1	0.75	1	1	1
Zr	1.61(12)	1	1	1	1	1
Nb	1.60(38)	1	1	1	1	1
	Transformed	to J from 1	the original K			

++ Originally given as 1/Jasi

which are the actual reasons for the different accuracy. Assuming our results are correct, we expect 10 % as the typical relative error in later determinations. However, we would like to stress that the power of this microanalytical method does not lie, at present, in its accuracy but in its high spatial resolution. In fact, as previously stated, analytical data can be collected from areas as small as a few hundreds Å in diameter.

Applications

The analytical system we developed is now successfully applied in the current TEM work of this laboratory. Several topics have been investigated, and they range from particle identification to quantitative chemical determination of small scale intergrowth phenomena, using spot sizes down to 300 Å in diameter.

For instance, the study of the complex mineralogical association occurring within the corona structures of the anorthosite rock from Bergen and Sognefjord (MELLINI et al., 1983) was largely facilitated by the combined high resolution and analytical microscopy approach. As an example, clinopyroxene from corona 2E, when analyzed by a wide beam (2μ) spot, produces chemical data not different with respect to microprobe

TABLE 4

JAB proportionality factors at 20 and 40 kV accelerating voltage

	20 k V	40kV
	present work	present work
a	2.84(35)	3.20(20)
Ig	1.73(3)	1.80(5)
1	1.16(7)	1.19(8)
1	1	1
2	1.14(14)	0.99(12)
a	1.09(5)	0.94(8)
1	1.15(8)	0.94(6)
In	1.18(23)	0.92(26)
e	1.28(30)	0.89(18)
r	1	3.12(12)
ю	1	2.79(30)

TABLE 5

Chemical compositions (atomic ratios)

	a	b	С	đ
Na	0.15	0.08	0.12	0.13
Mg	0.71	0.70	0.66	0.62
A1	0.33	0.39	0.30	0.60
Si	1.89	1.78	1.86	1.72
Ca	0.78	0.85	0.88	0.57
Fe	0.15	0.20	0.17	0.21

for: a) clinopyroxene II from corona 2E, electron microprobe (GRIFFIN, 1972); b) wide beam (2 µm diameter) TEM/EDS analysis of the clinopyroxene + amphibole intergrowth; c) narrow beam (700 Å diameter) TEM/EDS analysis of clinopyroxene II; d) narrow beam (700 Å diameter) TEM/EDS analysis of amphibole



Fig. 1. — Lamellar intergrowth between clinopiroxene (c) and amphibole (a) in the so called « clinopyroxene II » from corona 2E.



Fig. 2. — Fibrous intergrowth between [010] carlosturanite (s) and chrysotile fibers (ch).

data (table 5, columns a and b). However, this specimen comes out to be far from homogeneous by lattice imaging observations, as (010) clinopyroxene lamellae alternate with (010) amphibole lamellae (fig. 1). When the individual phases are analyzed separately, by a 700 Å electron spot, largely different chemical compositions result (table 5, columns c and d), the amphibole being constantly characterized by higher aluminium and iron contents and a lower calcium content. Carlosturanite is a new fibrous mineral (COMPAGNONI et al., 1985), which can be roughly defined as a highly hydrated, high-magnesium, low-silicon serpentine-like mineral. The combined HRTEM/AEM

study shows many interesting and relevant microstructural features, as intergrowth of carlosturanite with diopside and chrysotile or as inclusions of brucite and chromian magnetite. Fig. 2 shows the typical intergrowth between carlosturanite and chrysotile: [010] carlosturanite fibers, 1000 Å as average cross section, run parallel with chrysotile fibers, whose average cross section is 300 Å. The anhydrous composition of the chrysotile fibers, determined by TEM/EDS analysis, is

(Mg2.5Fe0.5) (Si1.7AltrFe0.3)O7

and closely compares with the ideal formula (Mg,Fe)₃ (Si,Al,Fe)₂O₇. Moreover, no titanium or manganese was detected within the chrysotile fibers, although these elements are always present in the closely associated paragenetic carlosturanite.

Generally speaking, the combination of EDS and HRTEM techniques thus consti-

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tutes a powerful tool in the study of the complex mineralogical associations, as the observed microstructural features can be easily associated with sufficiently accurate (approximately \pm 10 % relative) chemical data.