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Electron microprobe analysis of geological carbonates

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ABSTRACT

Electron microprobe analysis (EMPA) of geological materials is often carried out assuming stoichiometry for one unanalyzed element to calculate matrix correction (ZAF) factors. Stoichiometric ZAF routines for multielement groups such as carbonate (CO_3^{2-}) are not commonly available. Consequently, carbonates are commonly analyzed by means of the O stoichiometry techniques applied to silicate and oxide minerals. Using real and simulated analytical data, we show that errors of up to 20% occur if ZAF corrections are made with the assumption of metal valence and stoichiometric O. Two techniques that allow the input of complete compositional data from CO_3^{2-} analyses to ZAF factor calculations and that give accurate results are discussed. First, a new technique uses carbonate standards with compositions represented by the metal oxide MO_4. The results are then recalculated as metal carbonate. The second method assigns incorrect valences to the elements, C is assumed to be stoichiometric, and O is analyzed directly. We show that an analytical total of 100% ± $\sqrt{N}$, where $\sqrt{N}$ represents errors due to X-ray generation statistics, provides a powerful indication of analysis quality. The use of normalized and difference analysis methods, which necessarily assume totals of 100%, are to be avoided for this reason.

INTRODUCTION

Quantitative electron microprobe analysis (EMPA) techniques use ratios of X-ray counts from samples to counts from standards in the equation $C_{spl} = C_{std}k/ZAF$, where C_{spl} and C_{std} are element weight percent in sample and in standard, respectively, and k is the ratio (N_{spl}/N_{std}) of sample to standard X-ray counts at the peak of interest. The factor $C_{std}k$ is the apparent concentration. ZAF is a matrix correction factor, required if sample and standard compositions are significantly different (Reed, 1993).

Essene (1983) outlined the following problems associated with EMPA of carbonates: (1) apparent concentrations for all elements present in significant concentration, including C, must be made available to the ZAF calculations, otherwise ZAF factors will be in error (Albee and Ray, 1970; Reed, 1993); (2) tests must be conducted to establish whether the electron beam is damaging the carbonate sample or standard.

Geological EMPA is often carried out by means of O stoichiometry. The valences of most geological cations are well known, and O is commonly the only anion present. The substitution of other ions for O, e.g., C, F, or S, might not alter the valence of the cation but will change the X-ray absorption/fluorescence spectrum of the sample. This generates erroneous ZAF factors because O stoichiometry was assumed. Analyses made by stoichiometric means are only valid if correct compositional data for unanalyzed elements are included in the ZAF calculations. The valences assigned to analyzed elements do not have to be correct to satisfy this criterion.

Carbonate EMPA is hindered by the lack of ZAF calculation routines in which one assumes CO_3^{2-} stoichiometry. Unfortunately, accurate analysis for C by EMPA of C-coated insulating samples, often in the presence of C-based vacuum-pump oils, polishing abrasives, and lubricants, is problematic. Direct analysis for O combined stoichiometrically with C is an option, but it requires O standards close in composition to the sample to avoid large ZAF factors for O (McGuire et al., 1992; Nash, 1992).

Common shortcomings in reporting EMPA data for carbonates include (1) little or no data on the energy, current, and diameter of the electron beam, (2) lack of inclusion of CO_2 in the ZAF calculation, (3) normalization of data to a 100% total, (4) no data on standards used, (5) no data on the matrix correction routine, and (6) no documentation of beam damage tests. The aim of this study is to assess critically an existing technique of carbonate EMPA analysis and to present two new techniques that give accurate results.

ANALYTICAL TECHNIQUE AND RESULTS

Quantitative assessment of the errors generated by using various EMPA methods for carbonate analyses has been carried out by analysis of carbonates and by computer simulation.

Analysis of carbonates

Optically homogeneous samples of magnesite, calcite, dolomite, siderite, and rhodochrosite were polished and

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Table 1. Analyses of carbonates by methods 1–3

	Magnesite BM1984,547				Calcite Bristol collection				Dolomite BM1933,448				Siderite BM1968,649	
Method	A wt%	ZAF	ELMT	Total	A wt%	ZAF	ELMT	Total	A wt%	ZAF	ELMT	Total	A wt%	ZAF
Mg AAS	(13,10)		28.48(24)	100.06	(2,1)		0.034(1)	99.98	(4,8)		12.57(15)	100.00	(3,9)	
1	24.00	0.841	28.53	100.07	0.03	0.791	0.04	99.92	10.16	0.812	12.52	99.92	11.11	0.732
2	24.00	0.990	24.24	40.95	0.03	0.812	0.04	51.95	10.16	0.872	11.65	49.12	11.11	0.725
3	27.19	1.000	27.18	100.06	0.03	0.951	0.03	99.89	11.51	0.971	11.85	99.37	12.59	0.881
3 recalc			28.47	100.06			0.03	99.89			12.36	99.37		
Ca AAS	(1,1)		0.185(5)		(15,24)		39.83(40)		(17,13)		21.54(25)		(1,1)	
1	0.16	0.900	0.18		39.90	1.005	39.71		20.75	0.963	21.56		0.03	0.978
2	0.16	0.925	0.17		39.90	1.080	36.95		20.75	1.023	20.28		0.03	1.036
3	0.15	0.902	0.17		38.31	1.000	38.31		19.92	0.971	20.74		0.03	0.976
3 recalc			0.17				39.84				21.66			
Mn AAS	(2,1)		0.055(1)		(3,1)		0.126(2)		(2,1)		0.173(2)		(7,2)	
1	0.05	0.827	0.06		0.10	0.876	0.11		0.11	0.859	0.13		0.47	0.883
2	0.05	0.862	0.06		0.10	0.918	0.11		0.11	0.903	0.12		0.47	0.942
3	0.05	0.898	0.06		0.10	0.948	0.11		0.11	0.931	0.12		0.49	0.956
3 recalc			0.06				0.11				0.12			
Fe AAS	(4,2)		0.341(4)		(3,1)		0.05(1)		(4,2)		1.096(12)		(50,54)	
1	0.30	0.835	0.36		0.03	0.890	0.03		0.91	0.870	1.05		20.00	0.891
2	0.30	0.871	0.34		0.03	0.937	0.03		0.91	0.917	0.99		20.00	0.951
3	0.33	0.942	0.35		0.03	0.998	0.03		1.00	0.978	1.02		21.89	1.000
3 recalc			0.37				0.03				1.07			
O AAS			56.79				47.94				51.69			
1	56.79	1.001	56.75		47.94	0.999	48.01		51.69	0.999	51.73		49.46	1.002
2		0.000	16.14			0.000	14.82			0.000	16.08			0.000
3		0.000	72.30			0.000	61.41			0.000	65.63			0.000
3 recalc			56.78				47.89				51.32			
C AAS			14.21				12.00				12.93			
1		0.000	14.20			0.000	12.01			0.000	12.94			0.000
3 recalc			14.20				11.98				12.84			

Note: column headings are apparent element weight percent (A wt%), with estimated standard deviations from 25 analyses and the X-ray generation statistics (1s, $\sqrt{N}$), matrix correction factor (ZAF), corrected element weight percent (ELMT), and the analytical total. AAS data appear under ELMT.

examined by BSE imaging within a JEOL JXA-8600 Superprobe using a 15-kV, 5-nA beam. Contrast was not detectable at maximum amplifier gain, indicating that variations in atomic number were <0.1. The samples were analyzed for Mg, Ca, Mn, and Fe by atomic absorption spectroscopy (AAS) after the digestion of 0.500 g of sample in HF-$HClO_4$. The solutions were diluted 10^3 and 10^4 times for trace- and major-element detection, respectively. The results for each solution are the mean of three analyses, with two major- and trace-element solutions for each sample. A synthetic standard with 50 ppm Mg, Ca, Mn, and Fe was used to calibrate the AAS. Rock standards NBS1c and MESS 1 were analyzed to test the calibration. The AAS data were taken as the true carbonate compositions and are given in Table 1.

The samples were analyzed by wavelength-dispersive EMPA using a JEOL JXA-8600 with Link analytical AN10/85s analyzer and LEMAS automation. Beam conditions were 15 kV, 5 nA, and 25 μm for energy, current, and diameter, respectively. Data were processed using a ZAF program, with $\phi\rho Z$ calculation of the absorption factor (Love, 1983). Samples were analyzed using a grid of 25 points. Standard and sample X-ray counting times and counts were 100 s and 100 000 counts, respectively, on the peak and 50 and 1000 on the background. The standards used were periclase (Mg), wollastonite (Ca), MnO (Mn), Fe_2O_3 (Fe), magnesite (Mg), calcite (Ca), rhodochrosite (Mn), and siderite (Fe). The analytical k ratios were processed by three different matrix correction methods. The results are presented in Table 1. Figure 1 is a plot of X-ray energy vs. element concentration ratios (AAS/EMPA) from Table 1 for the analyses of the five carbonate samples by methods 1–3.

Method 1. Oxide standards were used for the metals. O was standardized from the samples, whose compositions were given by AAS (Table 1). ZAF factor calculations were carried out by means of C stoichiometry with false valencies of 0 for the metal atoms, 2 for O, and 6 for C. Alternatively, the metals could be assigned a valence equal to that of C, and O could be assigned a valence of 0. No data on carbonates analyzed by this method could be found in the literature.

Method 2. Oxide or carbonate standards were used. ZAF calculations were carried out by means of O stoichiometry using the true valencies for O and the metals analyzed for. This method is successfully used for silicate and oxide minerals where the assumption of stoichiometric O with each analyzed element can frequently account for all unanalyzed mass. This technique is commonly used for the EMPA of carbonates, but the mass and X-ray absorption-fluorescence behavior of the additional CO_2 is not provided by the O stoichiometry routine.

Method 3. This new method required the use of carbonate standards, whose compositions were inputted as MO_4 instead of MCO_3. ZAF calculations by means of O stoichiometry with metals of false valence 8 yielded com-

Table 1—*Continued*

Siderite BM1968,649		Rhodochrosite BM1907,640			
ELMT	Total	A wt%	ZAF	ELMT	Total
14.92(18)	100.00	(2,1)		0.100(5)	100.00
15.17	100.11	0.07	0.663	0.11	99.97
15.33	53.17	0.07	0.611	0.12	57.11
14.29	100.05	0.08	0.807	0.10	100.03
14.87	100.05			0.10	100.03
0.118(3)		(3,2)		0.337(5)	
0.03		0.39	1.056	0.37	
0.03		0.39	1.139	0.34	
0.03		0.37	1.048	0.35	
0.03				0.37	
0.323(5)		(40,27)		44.98(45)	
0.53		41.61	0.926	44.92	
0.50		41.61	0.999	41.67	
0.51		43.46	1.000	43.46	
0.53				44.97	
22.80(21)		(7,5)		2.27(3)	
22.45		2.07	0.934	2.22	
21.04		2.07	1.007	2.06	
21.88		2.27	1.046	2.17	
22.78				2.25	
49.46				41.84	
49.36		41.84	0.999	41.88	
16.27			0.000	12.94	
63.33			0.000	53.94	
49.45				41.86	
12.38				10.47	
12.39			0.000	10.48	
12.37				10.48	

positions as weight percent oxide (MO_4), which were recalculated to yield the weight percents of elements in the carbonate. No data on carbonates analyzed by this method could be found in the literature.

Beam damage considerations

Beam damage to carbonates was investigated by repeat analyses of a single point using the beam parameters previously described. We observed insignificant composition changes over five analyses. However, at higher beam currents and smaller beam sizes, compositional or visible damage was observed. Under the reflection optical microscope, calcite showed damage from a beam current of 15 nA and a size of 10 μm in diameter and showed significant compositional changes between analyses from a current of 10 nA and a size of 20 μm. The carbonates containing little Ca were stable under beams of 15 nA and current 10 μm in size, but dolomite was damaged by beams with currents >10 nA and with diameters <10 μm. Small experimental dolomite crystals have been analyzed using an energy-dispersive detector at 15 kV, 0.5 nA, and a point beam (Dalton and Wood, 1993).

Simulation of carbonate analyses

The stoichiometric compositions of $MgCO_3$, $SrCO_3$, $CaCO_3$, $BaCO_3$, $MnCO_3$, $FeCO_3$, and $MgCa(CO_3)_2$ were calculated and processed by means of methods 2 and 3. Samples and standards had the same compositions for this simulation. The ZAF factors should always be at unity if correct data on sample composition, which include elements determined by stoichiometry, were input to the iterative ZAF calculations.

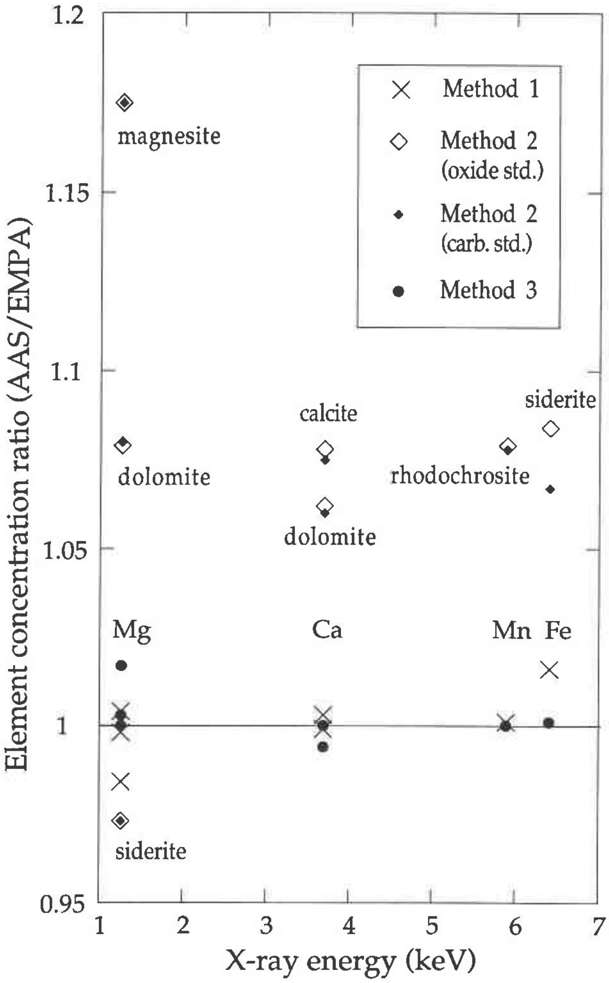

Fig. 1. Plot of analytical element concentration ratio (AAS/EMPA) vs. X-ray energy from the data given in Table 1. Correct analytical data plot at a concentration ratio of unity. It can be seen quite clearly that significant errors occurred when carbonates were analyzed using a standard silicate mineral technique (method 2). Labels refer to data from method 2. Data from methods 1 and 3 plot within error of the unity ratio line.

Table 2 documents the simulated data. Figure 2 shows a plot of the ratio of stoichiometric to processed element concentration vs. analyzed X-ray energy from the data from Table 2.

Discussion and conclusions

Carbonates analyzed using either oxide or carbonate standards (Fig. 1) agreed within 2 sd of the X-ray generation statistics. This provided confidence in the composition of the oxide standards, the AAS data for the carbonate compositions, and the integrity of the matrix correction routine. The reasonable agreement between errors calculated from 25 analyses and the X-ray generation statistics demonstrated that the analyzed carbonates were

Table 2. Simulated carbonate analyses by methods 2 and 3

Method	A wt%	ZAF	ELMT	Total	A wt%	ZAF	ELMT	Total	A wt%	ZAF	ELMT	Total
Metal	Mg		28.83*		Sr		59.35*		Ca		40.04*	
2	28.83	1.186	24.32	40.32	59.35	1.074	55.26	65.35	40.04	1.075	37.25	52.12
3	27.53	1.000	27.53	100.00	57.79	1.000	57.79	100.00	38.51	1.000	38.51	100.00
3 recalc			28.83	100.00			59.35	100.00			40.04	100.00
O			56.93*				32.51*				47.96*	
2		0.000	16.01			0.000	10.09			0.000	14.87	
3		0.000	72.47			0.000	42.21			0.000	61.49	
3 recalc			56.93				32.51				47.96	
C			14.24*				8.14*				12.00*	
3 recalc			14.24				8.14				12.00	
Metal	Ba		69.59*		Mn		47.79*		Fe		48.20*	
2	69.59	1.069	65.11	72.69	47.79	1.079	44.30	57.20	48.20	1.077	44.77	57.60
3	68.21	1.000	68.21	100.00	46.19	1.000	46.19	100.00	46.60	1.000	46.60	100.00
3 recalc			69.59	100.00			47.79	100.00			48.20	100.00
O			24.32*				41.76*				41.43*	
2		0.000	7.59			0.000	12.90			0.000	12.83	
3		0.000	31.79			0.000	53.81			0.000	53.40	
3 recalc			24.32				41.76				41.43	
C			6.09*				10.45*				10.37*	
3 recalc			6.09				10.45				10.37	

* Calculated stoichiometric composition.

effectively homogeneous (Table 1). There were no errors (except rounding errors) associated with the idealized simulation data (Table 2).

Method 1

This method yielded compositions close to those given by AAS (Fig. 1) and allowed accurate analysis of carbonates from both oxide and carbonate standards. Direct EMPA of O in geological materials has been documented by McGuire et al. (1992) and Nash (1992) but is not yet practiced routinely.

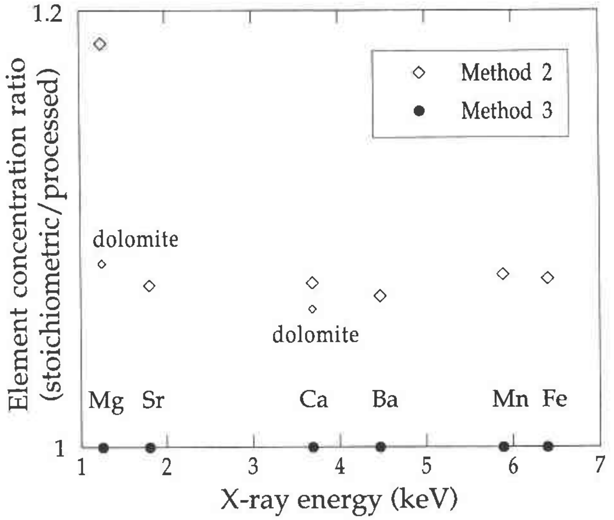

Fig. 2. Plot of simulated element concentration ratio (stoichiometric to processed) vs. X-ray energy. Using method 2, maximum errors occurred for single-metal carbonates, but these are correctable. Errors for more complex carbonates were smaller but not correctable. Data from method 3 plot at a concentration ratio of unity.

Method 2

For single-metal carbonates (magnesite, calcite, etc.), the real to analyzed concentration ratio was approximately 1.07 (7% error) at X-ray energies of >2 keV (e.g., $CaCO_3$). The ratio rapidly increased with decreasing X-ray energy to approximately 1.19 (20% error) for Mg ($MgCO_3$). These errors were generated because all the C and most of the O within the carbonate were not accounted for by the stoichiometry routine, thus leading to the calculation of incorrect ZAF factors for each analyzed element. Analyses of single-metal carbonates can be corrected by adding the stoichiometric amount of CO_2 and normalizing to 100%. Analyses of multimetal carbonates (dolomite, siderite, etc.) were also incorrect. The ratio for Ca in dolomite was similar to that for calcite (1.07), but for Mg the ratio was reduced to approximately 1.08, as opposed to 1.19 in magnesite. Siderite data had errors of 3% for Mg and 8% for Fe. Thus the errors generated are dependent on composition for multication carbonates. This was demonstrated by the spread of data points for each element in Figure 1. A correction to siderite was obtained by adding CO_2 and normalizing, which gave weight-percent compositions of Fe 21.49 (22.80) and Mg 15.66 (14.92) (AAS in parentheses). This represented an error of 6% on Fe and 5% on Mg, together with the assumption of 100% total. Data obtained by this method are fundamentally incorrect because the ZAF factors were calculated using inappropriate compositional information.

Method 3

Samples analyzed gave accurate results (Figs. 1 and 2). In this method, the matrix correction program, at both the standardization and sample stages of analysis, incorrectly employed all the elements present in the sample. This was demonstrated by the analyses yielding correct totals before recalculation from MO_4 back to MCO_3.

Indicators of analytical quality

The failure of method 2 to yield correct compositional data resulted from not providing information concerning every element of significant concentration to the iterative ZAF factor program. This was demonstrated by ZAF factors that were not equal to unity for the simulated data using method 2, whereas those for method 3 were correct (Table 2). The use of the ZAF factor as an indicator of analysis quality was negated when standards and samples had different compositions. The possibility of standard and sample compositions matching were remote, since most natural and experimental geological carbonates exist as extensive $(Mg,Ca,Mn,Fe)CO_3$ solid solutions. The most useful indicator of quality here is the analytical total, which should, canceling errors excepted, always be 100% $\pm \sqrt{N}$, where $\sqrt{N}$ are errors due to X-ray generation statistics, if apparent concentrations for all significant elements have been presented to the matrix correction routine. The analyses presented in Tables 1 and 2 that have totals in this range provided correct compositional data; those with low or high totals gave erroneous data. This is why analysis by means of difference or normalization, which assume totals of 100% ± 0, was undesirable.

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