The EPMA Matrix Correction: All Elements Must Be Present for Accuracy: Four Examples with B, C, O and F

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Historically, many EPMA labs have neglected to measure all of the elements present in some samples, either because it was impossible or difficult to acquire low energy/long wavelength X-ray lines, or because they could be assumed to be present and correctly accounted for by stoichiometric apportionment and post-processing outside the matrix correction. With the availability of layered synthetic diffractors since the late 1980s, it became possible, with attention to detail, to quantify B, C, N, O and F [1]. It has been 24 years since Tingle et al [2] pointed out the importance of including "missing" oxygen in EPMA measurements, and there is the need to remind our community of this not insignificant aspect of EPMA, especially as new generations of microanalysts learn the technique. We present four examples where the inclusion of ALL elements is essential for accurate and complete correctionof matrix effects: carbonate minerals, hydrous minerals, hydrous carbonates, and borate minerals.

Common carbonate minerals are calcite, dolomite, and ankerite. Typically, one would measure Ca, Mg, Fe, Mn and possibly Sr and Ba. These elements in carbonate minerals have well-defined oxygen stoichiometry, and when the matrix correction includes that, the results total around 49 wt%. In the past, it has been common to put these values into a spreadsheet, generate atomic values and generate a value for CO2. There are two problems with this: the low analytical total does not directly inform the analyst whether there is an analytical problem, and the cation numbers are in error. One example: Mg is low by 6%, Ca by 4% and Fe by 3%.

Use of Probe for EPMA analytical software enables direct inclusion of the CO_2 into the matrix correction based upon the stoichiometric relationship of (total cations) : carbon : oxygen of 1:1:3. We show that microanalysts are able to implement this correction by post-processing experimental data in the free CALCZAF software program. This approach offers an excellent QC test: does the recast analytical total approach 100 wt% and does the mineral formula on 3 oxygens approach 5.000?

Another situation where it has been common to ignore "difficult/impossible" elements is the of borosilicatetourmaline minerals (e.g., schorl, dravite, elbaite). Published EPMA compositions typically show analytical totals of ~82-85 wt%. Residual components include a significant amount of B_2O_3 (~10-11 wt%), water (OH), and F (and Li). Our analytical routine involves: two beam conditions (7 kV for B, O and F, and 15 kV for the remaining elements), mounting the standards together with the unknowns, carbon coating standards and unknowns simultaneously, and using the correct MACs (Bastin or Pouchou) for the "light elements" (Z< 11). The EPMA measurements for B using this routine agree closely with results of other techniques [3[. Measurement of O is very useful, particularly where there is the potential presence of hydrogen (as OH), as this measurement provides a means to estimate this "missing element" and include it into the matrix correction. (Where Li is measured by another technique, its value may be also included into the matrix correction.)

When B, O, and F are not included in the matrix correction, there are errors, albeit generally small: Si (used for normalizing mineral formulas) is 1% high, Al is 1% low (except in elbaite, 3% low), both Fe

and Mg are 1% low, and Na 2-3% low. When B, O and F are measured, the analytical totals are in the 98.5-99 wt% range (Table 1).

A third example is apophyllite, $KCa_4Si_8O_{20}(F,OH) \cdot 8H_2O$, where measurement of the cations and stoichiometric apportionment of O yields an analytical total of 82 wt%. Explicit measurement of O and incorporation of it as H_2O yields a 99.6 wt% total (Table 2).

As an example of hydrocarbonates, we tested this approach with analysis of hydromagnesite, $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$. Here, both C and O must be directly measured. Application of Ir coating to the standards and sample aids in the determination of Mg, C and O; after O was apportioned stoichiometrically to Mg and C, there was 17 wt% residual and a low total of 95.9 wt%. If the "excess" O was defined as H2O (19.8 wt%), the resulting total was 99.74 wt%.

Results of this work show that incorporation of all elements present in a material results in a more accurate determination of chemical composition with EPMA, and the use of software programs for post-processing of matrix corrections enables complete characterization of challenging materials [4].

DRAVITE 108796.1		SiO2	TiO2	B2O3	Al2O3	FeO	MnO	ZnO	MgO	CaO	Na2O	K2O	*Li2O	F	OH	Total
No O, F	AVERAGE	34.30	1.65		22.72	14.77	0.01	BDL	8.44	2.46	1.60	0.06				85.99
		0.35	0.10		0.62	0.98	0.02		0.29	0.14	0.08	0.01				0.38
Measure O,F	AVERAGE	34.03	1.66	9.94	22.81	14.95	0.01	BDL	8.53	2.47	1.63	0.06		0.43	2.29	98.80
	stdev	0.33	0.10	0.47	0.63	1.00	0.02		0.30	0.14	0.09	0.01		0.06	0.40	0.41
	difference	1%			<1%	1%			1%		2%					
SCHORL 112566.1																
No O, F	AVERAGE	33.57	0.54		33.94	14.73	1.18	0.26	0.21	0.14	2.00	0.04				86.73
	stdev	0.24	0.03		0.59	0.67	0.10	0.08	0.08	0.02	0.08	0.01				0.48
Measure O,F	AVERAGE	33.27	0.55	9.64	34.23	14.89	1.19	0.26	0.21	0.14	2.02	0.04	*0.12	0.43	1.62	98.61
with Li	stdev	0.25	0.03	0.65	0.60	0.67	0.10	0.08	0.08	0.03	0.08	0.01	0.00	0.05	0.49	0.33
	difference	1%			1%	1%					1%					
ELBAITE 98144.1																
No O, F	AVERAGE	36.46	0.32		36.52	6.60	0.37	BDL	1.54	0.11	2.61	0.02				84.60
	Stdev	0.26	0.21		1.09	0.44	0.20		1.28	0.04	0.06	0.01				0.65
Measure O,F	AVERAGE	35.99	0.32	10.05	36.96	6.66	0.37	BDL	1.56	0.11	2.68	0.02	1.97	1.36	0.72	98.83
with Li	stdev	0.25	0.21	0.67	1.16	0.45	0.20		1.30	0.04	0.06	0.01	0.00	0.14	0.50	0.47
	difference	1%			3%	1%					3%					

Figure 1. Table 1

	Si	Al	Ca	K	F	O	"H"	Total
O by stoich	24.05	0.13	17.01	3.81	2.44	34.11		81.67
O measured	24.76	0.14	17.37	3.90	2.51	49.00	1.76	99.57
difference	3%	3%	2%	2%	3%			

Figure 2. Table 2

References
[1] Nash, 1992, American Mineralogist, 77, 453.
[2] Tingle, Neuhoff, Jones and Donovan, 1996, GSA Abstract, 28 (6), 212.
[3] Dyar et al., 2001, Geostandards Newsletter, 25 (2), 1.
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