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IDENTIFICATION OF NORMAL AND ANOMALOUS COMPOSITIONS OF MINERALS BY ELECTRON-MICROPROBE ANALYSIS: K-RICH FELDSPAR AS A CASE STUDY

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ABSTRACT

The precision of electron-microprobe (EMP) measurements at a 4σ level of confidence is about 1%. By using internally consistent standards with compositions compatible with stoichiometries of the structural formulae, minerals with a generally similar matrix may be analyzed with ≤2% accuracy. Systematic analytical error of a standard may be greatly reduced by examination of the results of analysis of closely related unknown minerals. If a standard is compositionally and structurally well characterized, the accuracy of analysis of samples of near-identical composition may then approach 1% absolute. The bulk of the results, which give the expected stoichiometry of the structure, may be classified as normal. Anomalous measurements, which do not conform to ideal stoichiometry of feldspar, were used to identify analytical overlap with hematite micro-inclusions, light-element substitution, and a compositional trend toward $\square Si_4O_8$ in adularia from granitic pegmatites.

Keywords: electron-microprobe analysis, framework silicates, alkali feldspar, Eifel sanidine, adularia, granitic pegmatite.

SOMMAIRE

La précision de mesures effectuées à la microsonde électronique, à un niveau de confiance de 4σ, est d'environ 1%. En utilisant des étalons bien caractérisés, ayant une composition compatible avec la stoechiometrie indiquée par la formule structurale, il est possible d'atteindre une justesse inférieure ou égale à 2% dans l'analyse de minéraux dont les effets de matrice sont minimes. On peut minimiser les effets d'une erreur systématique dans l'analyse d'un étalon en examinant les résultats d'analyse de minéraux inconnus dont la composition est voisine. Si un étalon est jugé bien caractérisé selon sa composition et sa structure, la justesse d'une analyse d'échantillons de composition voisine peut atteindre 1% en termes absolus. L'ensemble des résultats qui donne la réponse attendue quant à la stoechiométrie de la structure pourrait être considéré une composition normale. Les compositions anormales, qui ne se conforment pas à la stoechiométrie attendue d'un feldspath du type adulaire prélevé de pegmatites granitiques, par exemple, pourrait résulter de l'analyse de microgermes d'hématite, l'incorporation d'éléments légers, ou un écart de la composition vers le pôle $\square Si_4O_8$.

(Traduit par la Rédaction)

Mots-clés: données à la microsonde électronique, tectosilicate, feldspath alcalin, sanidine d'Eifel, adulaire, pegmatite granitique.

INTRODUCTION

In the routine analysis of minerals, analytical error is tacitly assumed or explicitly stated, and the compositions are considered adequate for purposes of identification, compositional characterization, and petrochemical applications, based on such specific features as alkali ratios or Mg numbers. However, the origin and nature of systematic deviations from compositional ideality become critical when examining fine points of crystal chemistry or correlating chemical composition with structural parameters. In such cases, it is necessary to distinguish between apparent deviations generated by problems pertaining to standardization, analytical procedure, data processing or micro-inclusions, and real deviations inherent in the sample itself. The problem is further compounded in cases of incomplete analysis resulting from limited quantity of sample or technical limitations of the available instrumentation. A typical example is the chemical analysis by electron microprobe (EMP), which cannot deal with some of the light ($Z < 9$) elements.

A key feature of accurate analysis of a mineral is the use of proper standards; these must have been analyzed accurately and precisely. An excellent check on accuracy is the formula of the standard: it must agree with the stoichiometry indicated by the crystal structure. In turn, this requires that the crystal chemistry of that

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structure type must be properly understood. If this is the case, we may require that the standard composition give the exact stoichiometry of the structure on calculation of the mineral formula. Analysis of well-characterized minerals of similar composition provides a further check on the composition of this standard, as this should provide average formulae of correct stoichiometry, varying only in a random fashion within the precision of the analysis. If this is the case for a specific standard, then subsequent analysis of similar minerals that show significant deviation(s) from ideal stoichiometry indicates the presence of a crystal-chemical feature of the structure that is not currently incorporated in the structural model of that mineral. Examination of the deviation(s) of the mineral from ideal stoichiometry must allow identification of the relevant mechanism of substitution, as the data that define the mechanism are also the data that show the mineral's stoichiometry as being anomalous. Here, we use this procedure to evaluate the presence of vacancies (□) in the structure of alkali feldspar.

TABLE 1. ANALYTICAL CONDITIONS FOR FELDSPAR

Standard	Element	Line	Time (s)	Detection limit (wt.%)	
Eifel sanidine	K	*K*α	20	K_2O	0.036
	Al	*K*α	20	Al_2O_3	0.045
	Si	*K*α	20	SiO_2	0.060
anorthite	Ca	*K*α	20	CaO	0.025
Amelia albite	Na	*K*α	20	Na_2O	0.049
$Rb_2ZnSi_5O_{12}$	Rb	*L*α	20	Rb_2O	0.014
almandine	Fe	*K*α	60	Fe_2O_3	0.086
	Mg	*K*α	60	MgO	0.010
pollucite	Cs	*L*α	60	Cs_2O	0.032
$SrTiO_3$	Sr	*L*α	60	SrO	0.059
	Ti	*K*α	80	TiO_2	0.057
riebeckite	F	*K*α	120	F	0.069
VP_2O_7	P	*K*α	60	P_2O_5	0.073
barite	Ba	*L*β	60	BaO	0.087
spessartine	Mn	*K*α	120	MnO	0.025
$GdGaO_3$	Ga	*K*α	60	Ga_2O_3	0.031
PbTe	Pb	*M*α	60	PbO	0.041

Notes: Limits of detection were calculated using L.D. = $[3(\text{wt.\% oxide})(R_b/t_b)^{1/2}] / (R_p-R_b)$ where R_b = background count rate (count/s), t_b = background count time (s), R_p = peak count rate

EXPERIMENTAL

Compositions were established using wavelength-dispersion (WDS) analysis on a CAMECA SX–50 electron microprobe operating at 15 kV and 20 nA, with a beam diameter of 5 μm. Using these conditions, alkali loss from the analyzed volume was insignificant for all minerals except scapolite; in this case, a 20-μm beam diameter was used (details are given in Teertstra & Sherriff 1997). For analysis of feldspars, the standards, X-ray line used, count times and calculated limits of detection are given in Table 1. Data were reduced using the *PAP* procedure of Pouchou & Pichoir (1985). Limitations of the data-reduction routines are shown by increased relative error if, for example, a mineral with low mean atomic number is used to analyze a mineral containing constituents of much higher atomic number: the resulting stoichiometry of the mineral with high-*Z* atoms tends to deviate from the expected values determined either by stoichiometry arguments or by other analytical methods. Although potential analytical error of this form can be minimized by using standards similar to the analyzed mineral, in many cases, one cannot distinguish between error in the analytical method and inaccuracy in composition of the standard. In this study, we restricted the choice of standards and "unknowns" to the following aluminosilicate minerals, all containing major elements with atomic number *Z* less than 22: leucite, jadeite, diopside, tugtupite and members of the scapolite and feldspar groups.

If the composition of a chosen standard is inaccurate, systematic error will appear in cross analysis with the other standards. The composition of the standard may be adjusted to achieve ideal stoichiometry. Successive minimization of error generates an internally consistent set of alkali-bearing aluminosilicate standards. If the adjustments are correct, analysis of "unknowns" should also give agreement with the ideal formula of the mineral. Here, any particular analytical result is judged anomalous if it does not conform to the ideal formula within error of measurement. If a statistically anomalous result is not caused by experimental difficulties, it then represents a real variation in chemical composition (Dollase & Newman 1984).

CHARACTERIZATION OF STANDARDS

Tugtupite

Analysis of tugtupite indicates compositional homogeneity and a calculated formula close to the ideal formula $Na_8Al_2Be_2Si_8O_{24}Cl_2$; wavelength-dispersion scans showed no additional minor elements. Our sample is from the type locality (ROM #M32790), and our measurements agree well with those of Danø (1966). Compared to the ideal formula, average measurements of SiO_2 and Al_2O_3 were high by 2.6 and 2.5 wt.%, respectively, and Na_2O was low by 2.3 wt.%. Crystal-structure refinement (Hassan & Grundy 1991) and NMR spectroscopy (Xu & Sherriff 1994) show that this sample is highly ordered. Because of these crystallographic constraints on the compositional range, tugtupite may be our most accurately known standard. The differences between the measured and ideal compositions were assumed to be due to EMP-

TABLE 2. RESULTS OF ANALYSIS AND FORMULA CALCULATION USING TUGTUPITE AS A STANDARD FOR Na, Al AND Si

Amelia albite						
oxide	ideal	meas. (N=3)	formula (*apfu*)			
SiO_2	68.16	67.97 (31)	Si	2.976	ΣM	1.003
Al_2O_3	19.76	19.85 (1)	Al	1.024	M^+	1.021
Na_2O	11.46	11.51 (11)	Na	0.972	TO_2^-	1.024
K_2O	0.22	0.15 (3)	K	0.013	ΣT	4.000
CaO	0.40	0.38 (9)	Ca	0.018	Si/Al	2.91
sum	100.00	99.86	O	8		
orthoclase						
oxide	ideal	meas. (N=3)	formula (*apfu*)			
SiO_2	64.80	64.95 (31)	Si	3.032	ΣM	0.992
Al_2O_3	16.72	16.31 (6)	Al	0.897	M^+	0.992
Fe_2O	2.08	1.86 (7)	Fe	0.063	TO_2^-	0.960
Na_2O	0.91	0.93 (2)	Na	0.084	ΣT	3.992
K_2O	15.48	15.24 (7)	K	0.908	Si/Al	3.16
sum	100.00	99.29	O	8		
Sitkin anorthite						
oxide	ideal	meas. (N=3)	formula (*apfu*)			
SiO_2	43.84	43.64 (42)	Si	2.051	ΣM	1.000
Al_2O_3	35.90	34.88 (9)	Al	1.932	M^+	1.952
Fe_2O	0.72	0.49 (2)	Fe	0.017	TO_2^-	1.949
Na_2O	0.53	0.53 (1)	Na	0.048	ΣT	4.000
CaO	19.02	18.91 (3)	Ca	0.952	Si/Al	1.05
sum	100.00	98.45	O	8		
Vesuvius leucite						
oxide	ideal	meas. (N=12)	formula (*apfu*)			
SiO_2	55.37	55.52 (32)	Si	2.016	ΣM	0.996
Al_2O_3	23.37	22.67 (6)	Al	0.970	M^+	0.996
Fe_2O_3	0.19	0.26 (14)	Fe	0.007	TO_2^-	0.997
K_2O	19.85	19.69 (16)	K	0.912	ΣT	2.993
Na_2O	1.22	1.19 (16)	Na	0.084	Si/Al	2.06
sum	100.00	99.33	O	6		
jadeite						
oxide	ideal	meas. (N=10)	formula (*apfu*)			
SiO_2	59.39	60.40 (23)	Si	2.002	ΣM	0.998
Al_2O_3	25.02	25.33 (25)	Al	0.990	TO_2^-	0.997
Fe_2O_3	0.28	0.29 (17)	Fe	0.007	ΣT	2.999
Na_2O	15.31	15.53 (13)	Na	0.998	Si/Al	2.01
sum	100.00	101.55	O			

Eifel sanidine					
oxide	meas. (N=12)	formula (*apfu*)			
SiO_2	64.48 (17)	Si	2.976 (5)	ΣM	1.008 (4)
Al_2O_3	18.67 (3)	Al	1.015 (6)	M^+	1.032 (6)
Fe_2O_3	0.17 (2)	Fe	0.006 (1)	TO_2^-	1.021 (6)
Na_2O	2.88 (7)	Na	0.258 (5)	ΣT	3.997 (2)
K_2O	12.33 (7)	K	0.726 (4)	An	2.6 (3)
BaO	1.15 (13)	Ba	0.020 (2)	Si/Al	2.92 (23)
SrO	0.15 (4)	Sr	0.004 (1)		
sum	99.84	O	8		

Average and (1σ) standard deviation based on N analyses.

related analytical error. The formula was considered to obey ideal stoichiometry, and tugtupite was used as a standard for Na, Al, Si and Cl. The validity of the adjustment of composition to conform to the ideal formula was then tested by analysis of standards and Eifel sanidine, the results of which are given below.

Scapolite, albite, orthoclase, leucite, jadeite and sanidine

Electron-microprobe analysis of 20 samples of scapolite, the compositions of which were previously determined by bulk-chemical analysis, indicate an accuracy (including 90% of the data) of ±0.7 wt.% Na_2O, ±1.2 wt.% CaO, ±0.7 wt.% Al_2O_3, ±1.4 wt.% SiO_2 and ±0.5 wt.% Cl (Teertstra & Sherriff 1997). Analytical results for Amelia albite, orthoclase, anorthite, leucite, jadeite and Eifel sanidine (Table 2) conform closely to previously determined compositions and to the ideal formulae, indicating an accuracy for the major oxides of about 2% relative, and confirming the accuracy of the composition of the tugtupite standard. An example of the minor adjustments required to refine mineral compositions to agreement with analysis and with crystal-structural models is given below.

Eifel sanidine

The general formula of a feldspar is MT_4O_8, where M = Na, K, Rb, NH_4, Ca, Sr or Ba, and T = Si, Al, Fe^{3+} or B. The proportion of oxygen is calculated by charge balance, and the cation contents are normalized to 8 atoms of oxygen per formula unit (*apfu*). The formula may also be normalized to 4 T cations. The formula is calculated by assigning monovalent and divalent cations to the M sites and higher-valence cations to the T sites. This calculation conforms to models of the crystal structure in which T cations are in tetrahedral coordination, and each oxygen atom is linked to two T sites to form a framework with M cations in the interstices.

The composition of Eifel sanidine determined by EMP analysis (Table 2) required minor adjustments to attain the ideal formula; constraints applied were full occupancy of each site, electroneutrality, and conformity to the plagioclase substitution $CaAl(NaSi)_{-1}$. Analysis of the feldspar for the minor elements Ba, Sr and Fe was assumed to give accurate results (Table 2). Fe was included with Al and Si, and was assumed to be trivalent (Petrov & Hafner 1988, Kuehner & Joswiak 1996). Analysis and wavelength-dispersion scans showed no additional minor elements. Potassium was calculated as K = 1 – (Na + Ba + Sr) *apfu*, giving an M cation charge of M^+ = K + Na + 2(Ba + Sr). Aluminum was calculated as Al = M^+ – Fe^{3+} *apfu*, and silicon was calculated as Si = 4 – (Al + Fe^{3+}) *apfu* [equivalent to (4 – M^+)]. Eifel sanidine was then used as a standard for K, Al and Si (Table 1); cross-analysis of the other standards was used to check for systematic error. To ensure that no error arose from the *PAP* corrections (related to measurements from minerals with a different matrix), we analyzed samples of microcline perthite (ROM #M36144, M36145, M36146, M36148 and M36150), which showed minimal incorporation of divalent cations or Fe. Initial analysis of the ROM samples gave

TABLE 3. MEASURED COMPOSITION (wt.%) AND FORMULA (*apfu*) USING OPTIMIZED EIFEL SANIDINE COMPOSITION

	M36144	M36145	M36146	M36148	M36150	EIFEL
SiO_2	64.56	64.16	64.39	63.99	64.76	64.63(29)
Al_2O_3	18.31	18.46	18.30	18.43	18.33	18.78(7)
Fe_2O_3	0.05	0.00	0.00	0.05	0.04	0.18(2)
Na_2O	0.63	0.58	0.64	0.80	0.88	2.84(4)
K_2O	15.89	15.83	15.85	15.52	15.58	12.30(7)
SrO	0.03	0.04	0.04	0.09	0.03	0.15(4)
BaO	0.00	0.10	0.11	0.29	0.06	1.11(14)
sum	99.47	99.17	99.13	99.17	99.68	99.99(75)
Si	2.997	2.990	2.996	2.986	2.998	2.975(4)
Al	1.002	1.014	1.004	1.013	1.000	1.019(4)
Fe	0.002	0.000	0.000	0.002	0.001	0.006(1)
Na	0.057	0.053	0.058	0.073	0.079	0.254(4)
K	0.941	0.941	0.941	0.924	0.920	0.722(4)
Sr	0.001	0.001	0.001	0.002	0.001	0.004(1)
Ba	0.000	0.002	0.002	0.005	0.001	0.020(3)
ΣM	0.999	0.997	1.002	1.004	1.001	1.000(5)
M^+	1.000	1.000	1.005	1.012	1.003	1.024(6)
TO_2^-	1.003	1.014	1.004	1.015	1.001	1.025(5)
ΣT	4.001	4.004	4.000	4.001	3.999	4.000(2)
Si/Al	2.99	2.95	2.98	2.94	3.00	2.92(2)

systematically high K values (K > 1 *apfu*). Systematic error was removed by iterative change of the Na and K values of the Eifel sanidine through three cycles of measurement and compositional adjustment using the relations K = 1 – (Na + Ba + Sr) and Na = 1 – (K + Ba + Sr) *apfu*. Subsequent analysis of both the ROM and Eifel samples was in good agreement with the ideal formula of a feldspar (Table 3). The refined composition of Eifel sanidine (Table 3) is in close agreement with the results of other determinations of megacrystic gem-quality sanidine from the Volkesfeld area, Eifel, Germany (Behrens & Müller 1995, Hovis 1988, Bernotat-Wulf *et al.* 1988, Beran 1986, and references therein).

In an ideal feldspar, the negative charge of the [TO_2^-] framework is balanced by the charge of the *M* cations (M^+), and this is observed (Fig. 1A). In a compositionally homogeneous sample, there should be no correlation among elements determined from multiple analysis; the data should show random scatter about mean values. Such scatter is observed for Si *versus* (Na + K) for Eifel sanidine (Fig. 1B). At the 4σ level of confidence, variation in measurement of the major oxides of Eifel sanidine is around ±1 wt.%. Measurement of SiO_2 (wt.%) is the main contributor to variation in the oxide total (Table 3). On a unit-formula basis, the analytical error in the major components is about ±1 at.% (4σ) (±0.01 *apfu*; Fig. 1); however, combined variations in Al and Si, represented by ΣT = (Si + Al + Fe^{3+}) are remarkably low: ±0.008 *apfu* (4σ).

ANALYSIS OF ADULARIA

Černý & Chapman (1984, 1986) used Amelia albite as a standard for Na, Al and Si, and orthoclase as a standard for K, to analyze adularia from pegmatites and hydrothermal veins; the results indicate compositions close to Or_{100}. In the present study, 20 of the same samples were analyzed, most of which gave Al values that were within ± 0.02 *apfu* of the sum of the *M*-cation charges (which is 1.00 *apfu* for most of the samples, Fig. 2A). Accordingly, most of the data cluster about Si = 3.00 *apfu* and ΣM = 1.00 *apfu* (Fig. 2B). These values indicate accurate analysis and close agreement to the ideal formula $KAlSi_3O_8$.

A few of the determinations depart from ideality along directions labeled (1), (2) and (3) in Figure 2A, B. These directions are vectors in compositional space, and the dispersion of the data may represent real

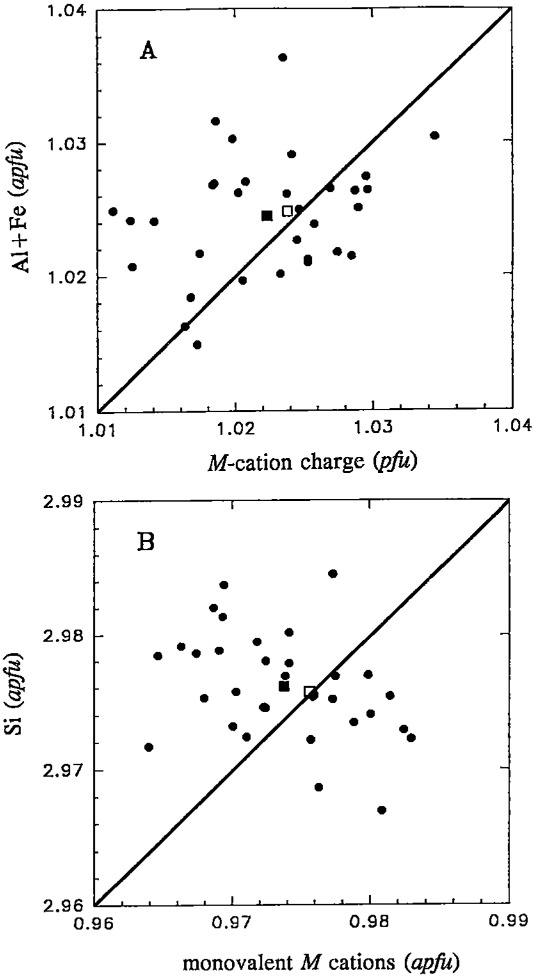

FIG. 1. Composition of Eifel sanidine. (A) (Al + Fe) *versus* *M*-cation charge; the diagonal line shows a 1:1 trend. (B) Si *versus* monovalent *M*-cations; the diagonal line represents a plagioclase-like substitution. Symbols: (●) measurements, (■) mean value, (□) the iterated composition.

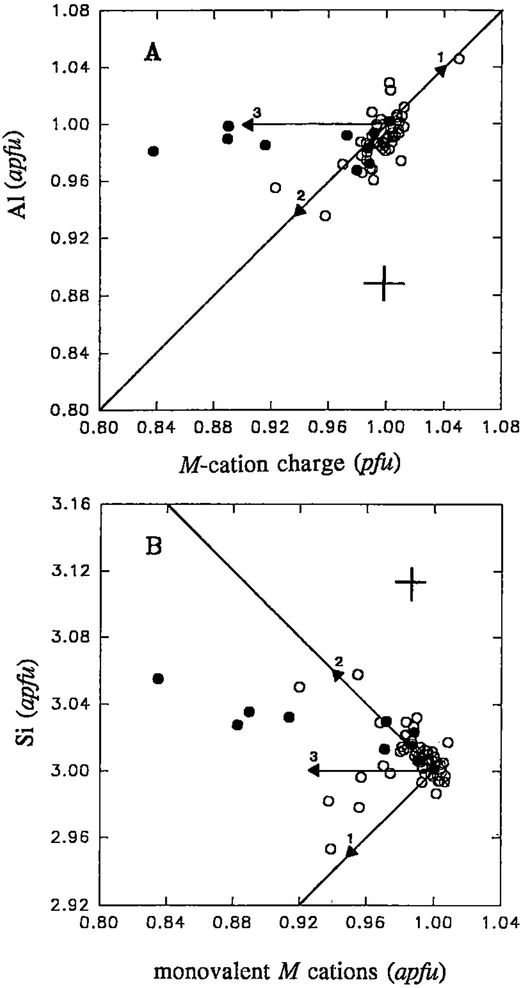

FIG. 2. Composition of adularia. (A) Al *versus* M-cation charge. (B) Si *versus* monovalent M-cations. The analytical precision (4σ) is indicated by the crosses. The arrows mark the trends for (1) the plagioclase-like substitutions, (2) the incorporation of $\square Si_4O_8$, and (3) decreasing M-cation charge at constant Al (or Si). Data for the Tanco adularia are indicated by solid circles.

chemical variations. Vector (1) shows the direction of plagioclase-type substitution (Al > 1, balanced by divalent cations). The principal divalent cation in adularia is Ba, but Ba was not detected in the majority of samples examined, and plagioclase-like substitutions play a negligible role. In feldspar, the negative charge of the framework must balance the positive charge of the M cations; hence compositions should show equal values of Al and the sum of the M-cation charge, and this is observed (measured Fe is less than 0.002 *apfu*).

TABLE 4. RESULTS OF ANALYSIS (wt.%) AND FORMULA CALCULATIONS (*apfu*) OF ADULARIA FROM THE TANCO PEGMATITE, SE MANITOBA

oxide	1	2	3	4	5	6
SiO_2	64.85	65.66	65.96	66.23	65.95	66.95
Al_2O_3	17.85	18.01	17.99	18.32	17.97	17.09
Na_2O	0.07	0.01	0.03	0.01	0.01	0.01
K_2O	16.50	16.71	16.84	15.20	14.09	15.80
SrO	0.00	0.00	0.00	0.00	0.05	0.06
sum	99.27	100.39	100.82	99.76	98.07	99.91
Si	3.018	3.021	3.023	3.017	3.027	3.043
Al	0.979	0.977	0.972	0.984	0.973	0.954
Na	0.006	0.001	0.003	0.001	0.001	0.001
K	0.980	0.981	0.985	0.888	0.825	0.916
Sr	0.000	0.000	0.000	0.000	0.001	0.002
M^*	0.007	0.006	0.016	-0.101	-0.134	-0.033
ΣM	0.986	0.982	0.988	0.990	0.961	0.922
M^+	0.986	0.982	0.988	0.889	0.828	0.921
TO_2^-	0.979	0.977	0.972	0.984	0.972	0.954
ΣT	3.998	3.999	3.996	4	4	4
Si/Al	3.08	3.09	3.11	3.07	3.12	3.19

1–3: Core; formulae normalized to 8 O *apfu*.
4–6: Rim; formulae normalized to (Al + Si) = 4 *apfu*.
M^* calculated as ($M^+ - TO_2^-$) *pfu*.

Vector (2) represents the $\square Si_4O_8$ substitution [in exchange notation, $\square Si(KAl)_{-1}$], which results in Si > 3.00 *apfu*, coupled with Al < 1.00 *apfu*, maintaining ΣT at 4.00 *apfu* with an equivalent decrease in ΣM < 1.00 *apfu*. A vacancy is also generated if one divalent cation replaces two monovalent cations at a constant Si/Al ratio. Vector (3) indicates an apparent deficiency in cations at constant Al, which may be caused by the presence of light M cations (H, Li, NH_4).

Deviation from stoichiometric $KAlSi_3O_8$ occurs in samples of euhedral late-hydrothermal adularia from vugs or leached cavities in the Tanco pegmatite, southeastern Manitoba (Černý 1972). Crystals from one of the vugs are zoned; the core shows near-ideal stoichiometry, but the rims have an apparent deficiency of M-cations. The T-sums range from 3.998 to 4.002 *apfu*, but values for the M-cation deficiency (M^+ – Al) range up to –0.13 *apfu* (Table 4). Back-scattered electron (BSE) imaging shows that the rim of these crystals has a lower grey-level than the core, indicative of decreased mean-atomic-number (Fig. 3B). These features suggest that those data points with compositional anomalies well beyond the 99% confidence level of analysis may have light-element M cations (*i.e.*, H, Li, NH_4). Low oxide totals correlate with the "missing" M-cations (No. 5 in Table 4). Samples that do not show significant light-element incorporation, but that have compositions along the $\square Si_4O_8$ trend, also were examined. Increase in Si above 3.00 *apfu* correlates with decrease in Al below 1.00 *apfu* (No. 5 and 6 in Table 4). The distribution of $\square Si_4O_8$ is patchy, and occurs in domains less than 20 μm in size. The samples that plot along the vector (3) (Fig. 2) are therefore prime candidates for further study because it is possible that the apparent vacancy in the M site may contain H_2O, which cannot be detected by EMP analysis.

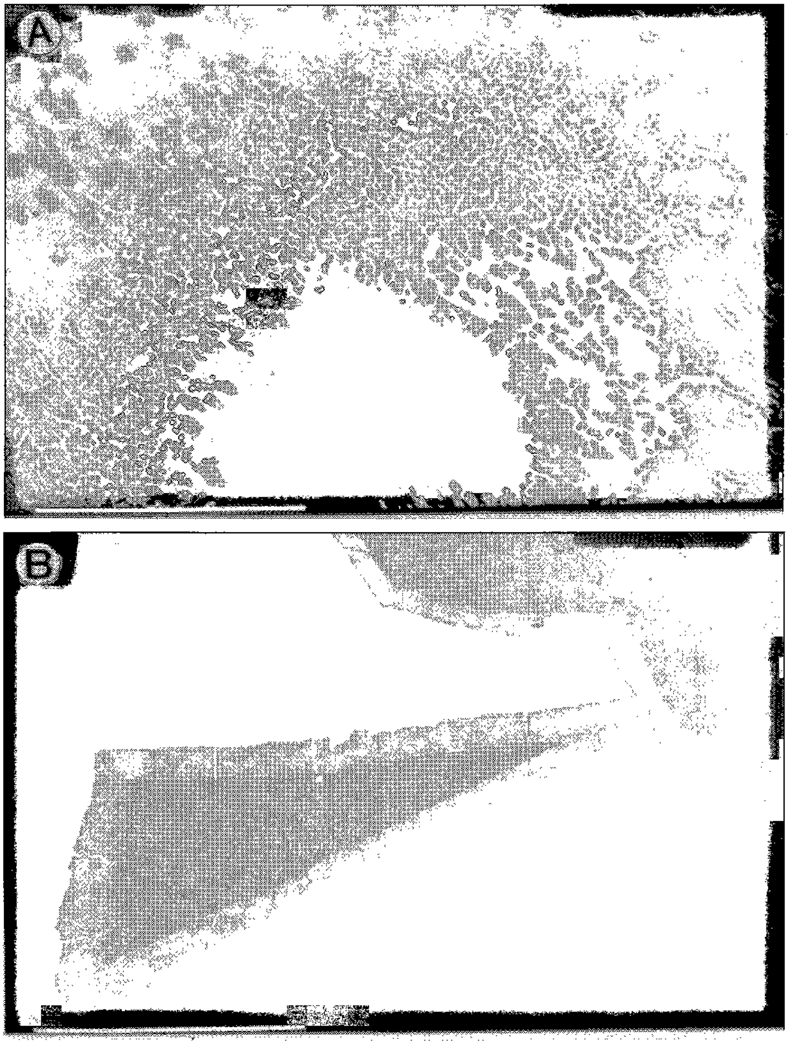

FIG. 3. Back-scattered electron (BSE) images of adularia from Tanco, southeastern Manitoba. (A) Section across the base of a crystal of adularia (grey) overgrowing a fine-grained aggregate of mica + a clay phase (black center). Light blebs and spots mark the Fe-rich material. (B) A zoned crystal with a core of ideal-formula K-feldspar and a dark rim, corresponding to material with a lower mean atomic number. Scale bar corresponds to 100 μm in A and to 200 μm in B.

If data do not conform to the ideal formula, a faulty analysis may be suspected. Finely dispersed inclusions (near the limit of resolution of BSE imaging) occur in some samples of adularia, but were recognized by non-stoichiometric deviations from the ideal formula. Analysis of red adularia from the Tanco pegmatite, southeastern Manitoba, gave locally anomalous results attributed to the presence of micro-inclusions of an Fe-rich phase (Fig. 3A). Whereas the analytical total is near 100.0 wt.%, Si contents do not agree well with the expected sum of monovalent cations, and ΣT values attain 4.1 *apfu*.

In order to assess the accuracy of estimation of "missing" elements in a chemical analysis of feldspar, EMP analysis of Na-, H-, and Li-exchanged Eifel sanidine was done. The samples have been previously characterized by EMP and bulk-sample analysis, infrared spectroscopy and crystal-structure refinement (Behrens & Müller 1995, Deubener *et al.* 1991, Paulus & Müller 1988, Müller 1988). We did not find the wide range of composition noted by Behrens & Müller (1995). Crystals were found to be homogeneous and show no zoning in BSE imaging. As the formulae calculated from analysis of the Na-exchanged sanidine

TABLE 5. COMPOSITION OF CATION-EXCHANGED EIFEL SANIDINE (wt.%) AND CALCULATED FORMULAE (*apfu*)

oxide	1	2	3
SiO_2	66.97	72.79	72.65
Al_2O_3	19.68	21.12	20.96
Fe_2O_3	0.19	0.21	0.21
Na_2O	11.11	0.33	0.04
K_2O	0.35	0.18	0.14
SrO	0.21	0.20	0.22
BaO	0.86	0.91	0.91
sum	99.37	95.73	95.13
Si	2.970	2.976	2.982
Al	1.028	1.018	1.012
Fe	0.006	0.007	0.006
Na	0.955	0.026	0.003
K	0.020	0.009	0.007
Sr	0.005	0.005	0.005
Ba	0.015	0.015	0.015
M^*	–0.018	–0.950	–0.968
ΣM	0.996	1.005	1.000
M^+	1.016	0.075	0.053
TO_2^-	1.034	1.025	1.018
ΣT	4.004	4	4

1: Na-exchanged.
2: Li-exchanged.
3: H-exchanged.
M^* calculated as ($M^+ - TO_2^-$).
Average of 6 analyses per sample.

gave T sums very near 4.00 *apfu*, the formulae of the H- and Li-exchanged sanidine were calculated by normalization of (Al + Fe + Si) to 4 *apfu* (Table 5). Light-element contents were calculated from the electroneutrality requirement using $M^* = [(Na + K) + 2(Sr + Ba) - (Al + Fe)]$. Results indicate a fully occupied M site, and this suggests good analytical accuracy. We conclude that more than 1 at.% of light-element incorporation in feldspar can be recognized by EMP analysis, and we estimate that calculated values are accurate to within 5 at.%. The absolute accuracy remains to be verified by direct analysis of the material for the light elements.

DISCUSSION

If the composition of a mineral is well constrained by chemical analysis, then minor deviations from the ideal formula due to analytical error may be eliminated. If the mineral has suitable characteristics of homogeneity, adequate grain-size and freedom from inclusions, it may be used as a standard. The accuracy of this ideal-composition standard may be checked by analysis of other well-characterized matrix-matched minerals. The majority of the analytical results should be constrained by the requirement of electroneutrality, maximum site-occupancy and mechanisms of substitution extending toward end-member compositions.

Some analysts may be uncomfortable with changing measured compositions to agree with an ideal stoichiometry. We emphasize that the magnitude of change is within the accuracy of the analytical method, and note that this approach formally recognizes three long-standing methods of assessing the quality of analytical results: (1) oxide totals of 100 (within error), (2) constraints of electroneutrality, and (3) stoichiometric formulae. These methods rely upon complete chemical analysis and an understanding of the crystal chemistry of the structure type. To ensure accuracy, results of a number of chemical-analytical methods may be compared [*e.g.*, EMP, bulk-chemical analysis, secondary-ion mass spectrometry (SIMS), single-crystal structure refinement (SREF)], and structural information from a variety of sources may be taken into account [*e.g.*, SREF, infrared spectroscopy (IR), nuclear magnetic resonance (NMR), Mössbauer spectroscopy]. In contrast, most currently available standards rely upon the skill of an individual analyst using a (usually unstated) single method of analysis applied to a single sample. For the sample to be widely used in the community, the sample must be large, homogeneous and inclusion-free. Such conditions are rarely met: even the commonly used Amelia albite standard contains variable amounts of Ca on a millimetric scale. The approach developed here requires only a small homogeneous sample (*e.g.*, *any* sample of albite), the composition of which can be constrained by measurement against other well-characterized minerals, followed by analysis of a solid-solution series of minerals of the same structure-type.

The unit-cell parameters of feldspars correlate very precisely with feldspar composition and state of Al–Si order. However, the cell parameters of some feldspar samples do show significant deviation from the values expected from composition and state of order (Blasi & de Pol Blasi 1994). The most serious departures found with cell parameters outside the standard *b–c* plot (Smith & Brown 1988, Fig. 7.9, Table 7.1) are disordered synthetic members of the solid-solution series from high albite to high sanidine (*e.g.*, Luth & Querol-Suñé 1970) and natural members of the order–disorder series from low microcline to high sanidine (Martin 1982, Černý & Chapman 1984, 1986, Martin & Falster 1986, Ferguson *et al.* 1991, Dong & Morrison 1995). The latter order–disorder series contains low-temperature generations of adularia. Our examination of the samples of adularia of Černý & Chapman (1984, 1986) indicates that most have a normal chemical composition; however, those with anomalous cell parameters have an anomalous composition. Incorporation of light elements is not widespread, but may be significant in some feldspars and responsible for a shift of cell parameters outside the *b–c* plot. The principal deviation from stoichiometric $KAlSi_3O_8$ is the $\square Si_4O_8$ substitution. Such feldspars are prime candidates for partial occupancy of the M site by H_2O. The relationship between anomalous unit-cell parameters and composition remains to be investigated in more detail, particularly with regard to the $\square Si_4O_8$ substitution. In contrast to the above, examination of adularia from Buck Claim, some samples of which have anomalous parameters, did not reveal significant deviations from ideal $KAlSi_3O_8$. We consider it likely that the composition of the single crystal of high sanidine, the structure of which was refined by Ferguson *et al.* (1991), is close to the end member. The cell parameters, *a* 8.603(2), *b* 13.036(4), *c* 7.174(1) Å and β 116.03(2)°, are close to those expected for a disordered feldspar with the following fractional occupancy of Al: $t_1 = 0.25(1)$ and $t_2 = 0.25(1)$, with interatomic distances of $\langle T_1\text{–O}\rangle = 1.640(1)$ and $\langle T_2\text{–O}\rangle = 1.642(1)$ Å. These values may be taken as the most reasonable values for Or_{100} end-member high sanidine currently available (*cf.* Kroll & Ribbe 1987).

Substitution of up to 8 mol.% $\square Si_4O_8$ has been recorded in natural and synthetic plagioclase (Muramaki *et al.* 1992, Beaty & Albee 1980). Grew *et al.* (1993) reported Si-excess compositions for reedmergnerite: decrease in Na + B was found to couple with increase in Si, giving a range of Si from 2.91 to 3.06 *apfu*. They suggested that this may be due to a systematic error or a real, undefined compositional trend; however, it could be due to solid solution toward $\square Si_4O_8$. Linthout & Lustenhouwer (1993) analyzed Ti- and Mg-rich ferrian high sanidine; they found Si contents in excess of 3 *apfu*, suggesting up to 4 mol.% $\square Si_4O_8$ substitution. On the other hand, Kuehner & Joswiak (1996) proposed substitution of up to 5 mol.% $\square MgSi_3O_8$ in ferrian high sanidine. It is evident that in feldspar with considerable Ti and Mg, there may be mechanisms of substitution other than $\square Si_4O_8$ that can account for excess Si and a deficiency in *M* cations. However, the compositions examined in this study (near end-member K-feldspar and without divalent cations and Fe) more convincingly demonstrate the presence of a $\square Si_4O_8$ component.

CONCLUDING NOTE

The analytical procedure described here is applied to members of the feldspar group, one of our main areas of current research. However, the basic principles underlying this approach are applicable to the analysis of many other mineral groups. The key aspect of this approach is that the crystal chemistry of the standards and the samples must be well understood, and there must be sufficient stoichiometric relations of the structure type to constrain the behavior of the elements present in the standards and in the samples. If this is the case, the composition of each standard must correspond with the *exact* stoichiometry of the relevant structure-type on calculation of the unit formula. It is advisable to have considerable redundancy in one's set of self-consistent standards, such that several different standards should give the same results (within known precision) for a specific element in a group of samples of similar matrix composition. In this way, subtle deviations in stoichiometry from that expected for a specific sample of a structure-type can be identified with reasonable confidence. This approach led to the clear recognition of Li as a major constituent of *C*-group cations in some alkali amphiboles (Hawthorne *et al.* 1992, 1993), and of B as a constituent in some crystals of vesuvianite (Groat *et al.* 1995, 1996). A more subtle example is provided by the feldspars examined in the current study. In this regard, adequate standards for electron-microprobe analysis should be characterized for components that cannot be detected by electron-microprobe analysis. The light lithophile elements (H, Li, Be, B) and Fe^{3+}/Fe^{2+} ratios (where appropriate) are of major importance in this regard; we emphasize the need to characterize standards by methods sensitive to these constituents (*e.g.*, SIMS, H-line extraction, Mössbauer spectroscopy). Such standard characterization should broaden the range of minerals for which the calibration could be optimized by the method described here.

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