

Analyses of Natural Minerals by Energy-dispersive Spectrometer

By

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Abstract Sixty six standard profiles were prepared for analyses by energy-dispersive spectrometer and accuracies of fifty five elements were evaluated by analyses of natural minerals. Analysed minerals, mostly stoichiometric compounds, are unhydrous and hydrous silicates, oxides, sulfides and metals. Although small excess of silicon is present (0.13 wt%) in silicon-free samples, most of the analytical results are acceptable in a view of stoichiometry and total amount and are well comparable with those by wavelength-dispersive spectrometer.

Introduction

Analyses by energy-dispersive spectrometer (EDS) are now a very convenient, accurate and fast method of mineral analyses. The system is compared well with wavelength-dispersive spectrometer (WDS) for accuracy and precision as far as the elements are more than about 1.0 wt%. DUNHAM and WILKINSON (1980) presented accuracy, precision and detection limits of the analyses by Link Systems EDS. Number of materials analyses by them were limited and each apparatus in laboratory has specific accuracy and precision each other. Hence, in this paper, we analysed most of the elements present in natural minerals which include various elements from Na to U and obtained the specific character of the Link Systems EDS set in our laboratory.

Analytical Procedures

The electron microscope used for the analyses is JEOL 5400 with fully quantitative Link Systems model QX2000 energy-dispersive spectrometer. The electron microscope was operated at 15 Kv with Falady cup current of 1 nA. The current drift was kept always less than 1%. Resolution was 138 eV at 5.9 Kev on the Mn $K\alpha$ peak. Analyses were made using a live-time of 50–100 seconds, depending on the complexity of the minerals. Analytical areas are mostly less than $3 \times 4 \mu\text{m}^2$. In zeolite group minerals, HgBr and some sulfide minerals, live time and area are 60 seconds and $12 \times 17 \mu\text{m}^2$, respectively. Spectrum is corrected for drift in the zero position. Cobalt $K\alpha$ is used for monitoring the drift in the high-energy side. After apparent compositions were obtained by digital filter methods, chemical compositions

Table 1. List of standard materials and representative minerals analysed.

element	standards		analysed samples
	profile	ratio factor	
Na	NaCl	albite	jadeite, natrolite, stilbite
Mg	MgO	Mg ₂ SiO ₄	orthopyroxene, clinopyroxene, garnet
Al	Al ₂ O ₃	sillimanite	plagioclase, garnet, jadeite
Si	CaSiO ₃	wollastonite	quartz, plagioclase, sillimantite
P	GaP	GaP	apatite, monazite, variscite, xenotime
S	FeS ₂	pyrite	chalcocopyrite, alabandite, hawleyite
Cl	NaCl	NaCl-albite	vanadinite, bromargyrite
K	aduralia	aduralia	chabazite, laumontite, erinite
Ca	CaSiO ₃	wollastonite	hedenbergite, grossular, plagioclase
Sc	ScP ₃ O ₆	ScP ₃ O ₆	thortveitite
Ti	Ti	TiO ₂	ilmenite, kimzeyite
V	V	V	vanadinite
Cr	Cr	Cr ₂ O ₃	crocoite, spinel
Mn	Mn	Mn, tephroite	rhodonite, tantalite, wolframite
Fe	Fe	Fe ₂ SiO ₄	ilmenite, pyrite, garnet, kamiokaite
Co	Co	Co	Co-olivine, siegenite
Ni	Ni	Ni	nickeline, breithauptite, siegenite
Cu	Cu	Cu	roquesite, sakuraiite, chalcocopyrite
Zn	Zn	Zn	sakuraiite, sphalerite
Ga	GaP	GaP	
Ge	Ge	Ge	germanite
As	InAs	InAs	orpiment, eulytite, nickline
Se	Se	TeSe	paraguajuatite, kawazulite, naumannite
Br	(bromargyrite)		
Sr	SrF ₂	SrF ₂	slawsonite, thomsonite
Y	Y	YP ₅ O ₁₄	xenotime, thortveitite, yttrialite
Zr	Zr	Zr	zircon, kimzeyite, thortveitite
Nb	Nb	Nb	columbite, tantalite, fergusonite
Mo	Mo	Mo	kamiokaite, molydenite
Ru	Ru	Ru	
Rh	Rh	Rh	
Pd	Pd	Pd	
Ag	Ag	Ag	bromargyrite, gold, hessite
Cd	Cd	CdTe	hawleyite
In	InAs	InSb	roquesite, sakuraiite
Sn	Sn	SnSe	malayaite, cassiterite, sakuraiite
Sb	Sb	InSb	breithauptite, valentinite, berthierite
Te	Te	TeSe, TeS	calvaerite, tetradyomite, tellurobismuthite
Cs	(pollucite)		
Ba	BaF ₂	BaF ₂	barite, celsian, harmotome
La	LaF ₃	LaP ₅ O ₁₄	monazite, lanthanite, florencite
Ce	CeF ₃	CeP ₅ O ₁₄	monazite, florencite
Pr	PrF ₃	PrP ₅ O ₁₄	monazite
Nd	NdF ₃	NdP ₅ O ₁₄	monazite, lanthanite

Table 1. Continued

element	standards		analysed samples
	profile	ratio factor	
Pm	Sm	SmP ₃ O ₁₄	monazite
Eu	EuF ₃	EuF ₃	
Gd	Gd	GdP ₃ O ₁₄	monazite, gadolinite
Dy	Dy	DyO ₃ P ₁₄	xenotime, yttrilite, fergusonite
Ho	Ho	Ho	
Er	Er	ErP ₃ O ₁₄	xenotime, yttrilite, fergusonite
Tm	Tm	Tm	
Yb	Yb	YbP ₃ O ₁₄	xenotime, thortveitite, yttrilite
Lu	LuF ₃	LuF ₃	
Hf	Hf	Hf	
Ta	Ta	Ta	columbite, tantalite, microlite
W	W	W	wolframite, scheelite, aeschynite
Os	Os	Os	iridium
Ir	rr	Ir	iridium, isolferroplatinum
Pt	Pt	Pt	isoferroplatinum
Au	Au	Au	gold, calaverite
Hg	HgTe	HgTe	cinnabar
Pb	PbTe	PbTe	vanadinite, crocoite, galena, uraninite
Bi	Bi	Bi	eulytite, bismuthinite, paraguanaujatite
Th	ThO ₂	ThO ₂	thorianite, monazite, yttrilite
U	U	U	thorianite, yttrilite, uraninite

were calculated by ZAF correction of STATHAM (1979) which has been fully set in the Link Systems EDS. These analytical procedures are essentially the same as those described by DUNHAM and WILKINSON (1978, 1980).

Standard Materials

Standard materials used were either pure metals or well characterized silicates, oxides and sulfides. One or two standards for each element were used for profile and ratio factor (Table 1). The ratio factor was used to correct the intensity of a profile prepared from a standard. In many elements, ratio factors are determined from the standard materials which were different from the materials for the profiles. Profiles for 66 elements were prepared. Accuracy of 55 elements were checked by natural minerals. As silicate minerals have been frequently analysed in our laboratory, ratio factors of common elements in the silicates were corrected using silicates with stoichiometry. Namely after analyses of CaSiO₃, ratio factor of Mg was determined by analyses of Mg₃SiO₄; Al from Al₂SiO₅, Fe from Fe₂SiO₄, Na from NaAlSi₃O₈ and Mn from (Mn, Fe)₂SiO₄. Such method give better results for the natural silicates, rather than no correction of ratio factor using pure metal as a standard. Rare earth elements usually occur as oxides, hence ratio factors are obtained from phosphate

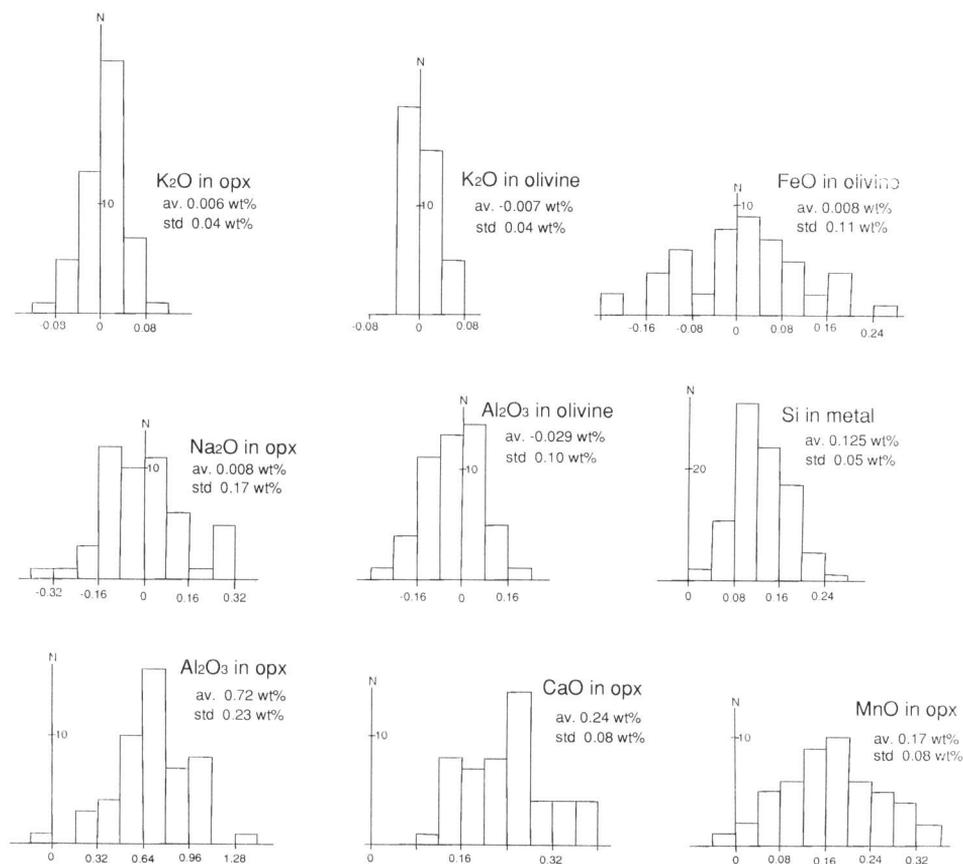


Fig. 1. Histograms of element and oxide values with saverage of 50 analyses and standard deviation (1 sigma). Vertical axis is number of analysis. Details are in text.

rather than fluorides.

Proper standards for Br and Cs elements have not been obtained, though their ratio factors are tentatively calculated from bromargyrite, $\text{Ag}(\text{Br}, \text{Cl})$, and pollucite $(\text{Cs}, \text{Na})_2\text{Si}_4\text{O}_{12} \cdot \text{H}_2\text{O}$, respectively.

Analyses of Minor Elements

In the EDS analysis, three points should be checked before the quantitative analysis. One is excess silicon in a silicon-free sample. Analysis of element which appears between two major peaks is also checked if it is a minor element. The other point is peak overlaps of profiles in natural minerals. Especially galena (PbS) and slawsonite ($\text{SrAl}_2\text{Si}_2\text{O}_8$) are usually problematic for the quantitative analyses by EDS.

Figure 1 shows the excess silicon in metal. Although there is no silicon in the metal, a small amount of excess silicon appears. Fortunately average amount of the silicon is 0.13 wt% as Si. The correction in silicates is not worth making, though corrections of minor silicon in analytical results in some oxides and metals are usually inevitable. A large number of analyses are required for such minerals to obtain silicon contents and the results should be subtracted 0.13 wt% as Si or 0.28 wt% as SiO₂. This is believed to be due to fluorescent excitation of silicon in the detector (DUNHAM & WILKINSON, 1980). The value is different by each system. It was 0.12 wt% in the apparatus used by DUNHAM and WILKINSON (1980) and was 0.30 wt% in the Link Systems 860-500 EDS in our laboratory.

If there is no peak around the profiles of elements which should be analysed, values of the elements which did not contain were usually less than 0.01 wt% as an average of 50 analyses (Fig. 1). K₂O in orthopyroxene and Mg₂SiO₄ and FeO in Mg₂SiO₄ are 0.006 to 0.008 wt%, within a standard deviation 0.04-0.11 wt%. Analyses of Al₂O₃ in Mg₂SiO₄ are shown in Fig. 2. High peaks appear at both sides of the activation energy for Al K α . The average was -0.03 wt%, negligible in the analyses of Al₂O₃ content. Average of Na₂O in orthopyroxene is 0.008 wt% with std. deviation of 0.17 wt%. Orthopyroxene has high peaks at the high energy side of sodium, but the result is acceptable as an EDS analyses. Hence, effects of the nearby major elements are not significant in the analyses. These data show that the discrimination between profiles from different elements are almost complete. Analyses of

Table 2. Analyses of silicate minerals and standard deviations of oxides.

	1	std	2	std	3	std	4	std	5	std	6	std
SiO ₂	44.49	0.25	58.03	0.49	48.55	0.28	40.50	0.25	46.20	0.20	59.67	0.34
Al ₂ O ₃	35.02	0.22	0.62	0.14	0.38	0.14	22.60	0.13			23.62	0.56
FeO	0.48	0.13	6.49	0.23	27.37	0.57	23.10	0.21			0.51	0.22
MnO					1.13	0.19			51.58	0.42		
MgO			34.85	0.47	0.19	0.08	13.89	0.27	0.84	0.14	0.98	0.33
CaO	19.55	0.15	0.24	0.07	22.75	0.29	2.54	0.11	1.08	0.18	1.55	0.35
Na ₂ O	0.55	0.04									14.10	0.23
total	100.09	0.46	100.23	1.04	100.37	0.92	99.63	0.57	99.70	0.44	100.42	0.82
O	8		6		6		12		6		6	
Si	2.060	0.008	1.992	0.007	1.991	0.011	3.015	0.012	2.002	0.006	2.008	0.008
Al	1.911	0.007	0.025	0.006	0.018	0.007	1.983	0.011			0.937	0.018
Fe ²⁺	0.019	0.005	0.186	0.006	0.939	0.015	1.252	0.013			0.014	0.006
Mn					0.039	0.006			1.893	0.016		
Mg			1.783	0.012	0.011	0.005	1.541	0.024	0.054	0.009	0.049	0.016
Ca	0.970	0.008	0.009	0.002	1.000	0.013	0.202	0.008	0.050	0.008	0.56	0.013
Na	0.049	0.004									0.920	0.015
total	5.009	0.005	3.995	0.006	3.999	0.012	7.993	0.010	3.998	0.006	3.984	0.012

1 = anorthite, 2 = orthopyroxene, 3 = hedenbergite, 4 = garnet, 5 = rhodonite, 6 = jadeite.

All the data are average and standard deviation (1 sigma) of ten analyses at 100 sec.

Table 3. Analyses of silicate and oxide minerals.

	1	2	3	4	5	6	7				
SiO ₂	11.27	39.48	CaO	0.91	Cr ₂ O ₃	46.29	TiO ₂	0.94	SiO ₂	37.35	
TiO ₂	5.43		Y ₂ O ₃	1.85	Al ₂ O ₃	20.81	MnO	6.37	Al ₂ O ₃	30.45	
Al ₂ O ₃	7.22	21.17	PbO	3.20	11.25	Fe ₂ O ₃	4.72	FeO	12.97	SrO	30.47
Fe ₂ O ₃	14.53	2.31	Ce ₂ O ₃	1.99	FeO	13.72	Nb ₂ O ₅	55.67	BaO	1.56	
MgO	0.26		ThO ₂	76.51	7.41	MgO	14.02	Ta ₂ O ₅	24.82	total	99.83
CaO	28.68	37.22	UO ₂	21.23	76.29	total	99.56	total	100.77		
ZrO	30.85		total	100.9	99.69					O	8
Nb ₂ O ₅	1.08							O	12	Si	2.035
total	99.32	100.18	O	2	2	O	4	Ti	0.087	Al	1.956
			Ca		0.043	Cr	1.131	Mn	0.664	Sr	0.963
O		12	Y		0.043	Al	0.758	Fe	1.335	Ba	0.033
Si	1.106	2.982	Pb	0.038	0.133	Fe ³⁺	0.110	Nb	3.099	total	4.987
Ti	0.400		Ce		0.032	Fe ²⁺	0.355	Ta	0.831		
Al	0.836	1.885	Th	0.771	0.075	Mg	0.646	total	6.017		8
Fe ³⁺	1.073	0.131	U	0.209	0.750	total	3.000			CrO ₃	30.98
Mg	0.038		total	1.019	1.077					PbO	69.05
Ca	3.013	3.012								total	100.03
Zr	1.477										
Nb	0.048									O	4
total	7.990	8.010								Cr	1.000
										Pb	0.999
										total	1.999
	9		10		11		12		13		
MnO	14.51	MnO	11.28	MnO	0.97	SiO ₂	22.60	SiO ₂	32.24		
Nb ₂ O ₅	6.83	FeO	13.11	FeO	25.58	CaO	21.17	ZrO ₂	66.06		14
Ta ₂ O ₅	79.27	WO ₂	76.72	MoO ₃	72.85	SnO ₂	56.73	HfO ₂	0.87	CaO	19.48
total	100.61	total	101.11	total	99.20	total	100.49	total	99.17	WO ₃	80.75
										total	100.23
O	12	O	4	O	0	O	5	O	12		
Mn	1.996	Mn	0.477	Mn	0.073	Si	0.999	Si	2.990	O	4
Nb	0.501	Fe	0.547	Fe	1.877	Ca	1.002	Zr	2.987	Ca	0.998
Ta	3.500	W	0.992	Mo	3.025	Sn	1.000	Hf	0.023	W	1.001
total	5.997	total	2.016	total	4.975	total	3.001	total	6.000	total	1.999

1=kimzeyite, 2=grossular, 3=thorianite, 4=uraninite, 5=spinel, 6=columbite, 7=slawsonite
8=crocoite, 9=tantalite, 10=wolframite, 11=kamiokaite, 12=malayaite, 13=zircon, 14=scheelite.

minor elements were done in orthopyroxene (Fig. 1). Both CaO and MnO have lower standard deviation than Al₂O₃. This may be partly due to the inhomogeneity in the minerals, but the deviations are still negligible as an analyses of minor element by EDS.

Trace elements which are too small in amount to be detected by EDS were less than 0.01 wt% on an average (Fig. 1). However, amount more than 2 sigma (2 std deviations) appears occasionally. Such a few data should be checked by repeated analyses or WDS.

Peak overlaps are inevitable in some minerals, *e.g.* galena, slawsonite, bismuthinite

Table 4. Analyses of sulfide minerals.

Sakuraiite			Roquesite			Sphalerite			Berthierite					
	wt%	atm%		wt%	atm%		wt%	atm%		wt%	atm%			
S	28.92	49.28	S	26.20	49.03	S	32.66	49.88	S	29.25	56.33			
Fe	7.15	6.97	Fe	1.28	1.38	Fe	0.72	0.58	Fe	12.65	13.98			
Cu	21.92	18.82	Cu	27.06	25.38	Zn	66.03	49.45	Sb	58.55	29.69			
Zn	14.39	12.04	In	46.01	24.04	Cd	0.40	0.18	total	100.45				
Cd	0.25	0.13	total	100.40		total	99.81							
In	16.12	7.72												
Sn	11.13	5.06												
total	99.80													
			Chalcopyrite			Alabandite			Pyrite					
				wt%	atm%		wt%	atm%		wt%	atm%			
			S	34.86	46.96	S	35.77	49.63	S	53.77	66.67			
			Fe	30.25	24.89	Mn	61.46	46.07	Fe	46.83	33.33			
			Cu	34.79	25.15	Fe	1.66	1.30	total	100.60				
			total	99.90		total	99.39							
			Hawleyite			Molybdenite			Stibnite			Cinnabar		
				wt%	atm%		wt%	atm%		wt%	atm%		wt%	atm%
			S	20.33	47.32	S	38.90	65.80	S	27.46	58.80	S	13.94	50.14
			Zn	2.00	2.30	Mo	60.51	34.20	Sb	73.05	41.20	Hg	86.70	49.85
			Cd	75.53	50.38	total	99.41		total	100.51		total	100.64	
			total	97.77										
			Orpiment			Galena			Bismuthinite					
				wt%	atm%		wt%	atm%		wt%	atm%			
			S	38.88	59.77	S	13.04	49.61	S	17.94	59.01			
			As	61.14	40.23	Pb	85.59	50.39	Bi	81.20	40.99			
			total	100.02		total	98.64		total	99.14				

and xenotime. Analytical results of these minerals were faintly depleted in total amount (Table 2–7), though structural formulas of the minerals were well acceptable, suggesting that the fitting operation of profile is working well even in minerals with highly overlapped peaks.

Unanalyzed Elements

Elements of lower atomic number than sodium can not be analysed in our equipment. Minerals analysed in our laboratory are mainly silicate and oxide minerals where elements are calculated as oxide. Different charges of element appear in some minerals, *e.g.* magnetite $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{O}_4$. In this case, correction factors of elements are calculated by assuming that (100-wt% element) is weight of oxygen.

Carbonates and hydrous silicates have two unanalyzable elements. In both categories, calculation based on the difference method produces mostly reasonable results. Even if H_2O content is more than 20 wt% as in some zeolite group minerals,

Table 5. Analyses of metal and other minerals.

Iridium			Isoferroplatinum			Nickeline			Breithauptite		
	wt%	atm%		wt%	atm%		wt%	atm%		wt%	atm%
Ir	75.17	74.37	Pt	85.41	69.38	Ni	44.29	50.76	Ni	32.76	49.95
Os	22.76	22.76	Fe	8.80	24.98	As	52.09	46.78	As	1.26	1.50
Ru	0.65	1.22	Ir	5.30	4.38	Sb	4.45	2.46	Sb	66.02	48.55
Rh	0.45	0.84	Rh	0.87	1.35	total	100.83		total	100.00	
Pt	0.83	0.82	total	100.38							
total	99.85										
Gold (2)			Gold (2)			Calaverite			Bromargyrite		
	wt%	atm%		wt%	atm%		wt%	atm%		wt%	atm%
Au	65.29	51.34	91.42	85.50	Te	58.48	68.60	Ag	69.38	50.26	
Ag	34.06	48.65	8.49	14.50	Au	41.31	41.40	Cl	14.99	33.04	
total	99.35		99.91		total	99.79		Br	17.07	16.69	
								total	101.44		
Vanadinite			Barite								
	wt%	atm		wt%	atm						
PbO	79.15	Pb=5			O=4						
V ₂ O ₅	19.24	2.983	SOt	34.80	1.002						
Cl	2.23	0.885	BaO	66.15	0.996						
total	100.61		total	100.95	1.998						
O=Cl	-0.50										
total	100.11										

analytical results were satisfactory. However, carbonates with elements of low atomic number such as magnesite and dolomite cannot be analysed properly in spite of calculation of the difference method, *i.e.* correction factor for Mg is 0.846 calculated as MgO₄ and 0.887 as MgCO₃. On the other hand, analyses of heavy metal carbonates are not affected by the calculation methods. *e.g.* 0.886 as FeO₄ and 0.890 as FeCO₃. It is important to check the results of light carbonates and use different standard materials close to the minerals in question.

Analytical Results and Discussions

More than several thousand analyses have been done by the present equipment. Representative minerals are listed in Table 2-7. As most of the minerals analysed are stoichiometric and anhydrous, analytical results are evaluated by the deviation from stoichiometry and/or total amount of all the elements.

Averages and standard deviations of ten analyses of silicate minerals are shown in Table 2. Even though there are more or less heterogeneities in the natural minerals, all the analyses obtained give reasonable results in total amount and structural formula. Relatively high standard deviations of major elements and total amounts are probably due to drift of current in addition to the heterogeneities.

Table 6. Analyses of zeolite group minerals.

	1	2	3	4	5	6	7	8	9
SiO ₂	58.78	47.27	45.50	54.86	54.76	60.70	48.86	55.58	59.92
Al ₂ O ₃	20.58	26.79	25.66	23.09	18.92	16.57	18.97	16.53	16.46
CaO			13.79	12.32	8.88	8.88	9.72	7.98	3.18
Na ₂ O	12.63	16.66		0.36	0.66	0.39	0.32	1.49	4.60
K ₂ O					1.27		0.24		2.88
total	91.99	90.72	84.96	90.64	84.49	86.54	78.11	81.58	87.04
H ₂ O*	8-9	9-10	14	8.5	13-15	12-13	22	18.5	14-18
O	6	10	10	12	12	16	12	72	72
Si	2.122	2.991	3.010	4.012	4.269	6.047	4.125	26.61	27.19
Al	0.876	1.998	2.001	1.990	1.739	1.946	1.888	9.33	8.81
Ca			0.978	0.965	0.742	0.948	0.880	4.10	1.55
Na	0.884	2.044		0.052	0.100	0.076	0.052	1.39	4.05
K					0.126		0.026		1.67
total	3.882	7.032	5.989	7.019	6.975	9.017	6.970	41.42	43.26
E%	-0.9	-2.2	2.3	0.4	1.8	-1.2	2.9	-2.5	-0.0
	10	11	12	13	14	15	16	17	
SiO ₂	48.04	70.66	59.28	47.31	59.26	49.62	37.19	34.79	
Al ₂ O ₃	23.30	13.03	17.61	17.84	16.50	21.15	28.83	29.03	
CaO	10.38	5.75	8.40		6.42	4.87	9.88	9.06	
BaO				21.85					
SrO					1.48	1.37	4.89	7.79	
Na ₂ O	1.71	0.37	1.20	0.96	1.09	4.57	4.27	3.83	
K ₂ O	1.04	1.72		0.89	1.49	2.53			
total	84.47	91.51	86.49	88.84	86.24	84.12	85.06	84.49	
H ₂ O*	20	9	15	15	15-16	17	15	15	
O	36	24	48	32	72	32	20	20	
Si	11.47	9.867	17.80	11.11	27.10	10.68	5.204	5.011	
Al	6.56	2.141	6.23	4.94	8.90	5.37	4.756	4.929	
Ca	2.66	0.861	2.70		3.15	1.12	1.481	1.398	
Ba				2.01					
Sr					0.39	0.17	0.397	0.651	
Na	0.79	0.100	0.70	0.44	0.96	1.91	1.159	1.068	
K	0.32	0.306		0.27	0.87	0.70			
total	21.80	13.270	27.43	18.77	41.37	19.94	13.00	13.06	
E%	2.2	0.7	2.1	4.6	-0.1	3.4	-3.2	-4.6	

1, analcime, 2, natrolite, 3, scolecite, 4, wairakite, 5, laumontite, 6, yugawaralite, 7, chabazite, 8, stilbite, 9, erionite, 10, levyne, 11, dachiardite, 12, epistilbite, 13, harmotome, 14, heulandite, 15, philipsite, 16 & 17, Sr-poor and Sr-rich thomsonites.

H₂O contents are from zeolite compositions summarized by Gottardi and Galli (1985).

Various oxide minerals were analysed (Table 3). These results also give well structural formulas and total amounts. Thorianite and uraninite are rich in radioactive elements. Radiogenic lead induces deviation from stoichiometry.

Table 7. Analyses of rare-earth-bearing minerals.

	oxide wt%				structural formula			
	1	2	3	4	1 (O=7)	2 (O=4)	3 (O=7)	4 (O=4)
SiO ₂	28.83	2.90	45.26		Si	1.975	0.120	1.991
P ₂ O ₅		26.01		36.47	P		0.909	1.025
CaO					Ca			
Sc ₂ O ₃			47.86		Sc			1.834
MnO	1.67		0.51		Mn	0.097		0.019
FeO	2.40				Fe ²⁺	0.137		
Fe ₂ O ₃			1.78		Fe ³⁺			0.059
Y ₂ O ₃	32.12		1.51	46.45	Y	1.179		0.036 0.816
ZrO ₂			1.59		Zr			0.034
PbO		0.37			Pb			
La ₂ O ₃		8.87			La		0.135	
Ce ₂ O ₃	0.92	23.11			Ce	0.022	0.349	
Pr ₂ O ₃		2.76			Pr		0.042	
Nd ₂ O ₃	1.39	13.00			Nd	0.034	0.192	
Sm ₂ O ₃	1.63	3.53			Sm	0.038	0.050	
Gd ₂ O ₃	3.02	2.56		1.88	Gd	0.069	0.035	0.021
Dy ₂ O ₃	4.19			5.11	Dy	0.093		0.054
Er ₂ O ₃	3.96			4.84	Er	0.085		0.050
Yb ₂ O ₃	3.82		1.92	2.84	Yb	0.080		0.026 0.029
ThO ₂	8.02	14.79			Th	0.125	0.251	
UO ₂	5.39				U	0.082		
total	97.36	97.90	100.40	97.61	total	4.016	1.974	3.998 1.988

1=ytttrialite, 2=monazite, 3=thortveitite, 4=xenotime.

Ratio factor of sulfur was determined from pyrite (FeS₂). On the other hand, factors of most of the cations in sulfide were from metals, oxides and silicates. Although many analyses of sulfide minerals are well acceptable in a view of total amount and structural formula, structural site for sulfur is insignificantly depleted in most of sulfide analyses (Table 4). Wide departure from ideal structural formula was found in berthierite (Sb₂FeS₄) and stibnite (Sb₂S₃). Atomic ratio of Sb in berthierite is 29.69, higher than the ideal formula 28.6 (Table 4). The ratio of stibnite is 41.2, higher than ideal ratio 40.0. Satisfactory results are obtained for Sb element in both metal and oxide. Aalentinite, Sb₂O₃, gives 99.77 wt% in total. Breithauptite, (Sb, As)Ni, was (Sb_{0.971}, As_{0.030})Ni_{0.999} as listed in Table 5. Hence, it may be rather better to use a different ratio factor for Sb in sulfide minerals. Depleted total of galena is probably caused by the peak overlaps of sulfur and lead. On the other hand, low value of total of hawleyite is due to that the mineral was too fine powder to obtain a flat polished surface. In the analyses of metal (Table 5), all the results are well acceptable as EDS analyses, because standard profiles of elements used in the analyses were obtained mostly from metals.

As zeolite group minerals contain abundant H₂O, it is important to take care of dehydration and hydration during preparation of a polished section. Two type of

resins were used for making thin section; one solidifies as temperature more than 100°C and the other at room temperature. Samples using the high temperature resin mostly obtained higher totals than the room temperature one. All the data in Table 6 were analysed in sections made by room temperature resin. They are well comparable with zeolite compositions summarized by GOTTARDI and GALLI (1985).

Accuracy of zeolite minerals have been checked by E% value which is calculated as follows;

$$E\% = 100 \times (Al + Fe - Na - K - 2Mg - 2Ca - 2Sr - 2Ba) / (Na + K + 2Mg + 2Ca + 2Sr + 2Ba)$$

E% is 0 in a "perfect" analysis. In any case, it should be low (< 10%) in acceptable ones. E% values in Table 6 are mostly less than 3.0 which is well acceptable as zeolite analyses. There are a few minerals with uncertainty in total. H₂O content of laumontite is easily changed during the preparation in spite of careful treatment. H₂O content (100%-total elements) was changed from place to places. Lowest H₂O content, listed in Table 6, fits well with the data reported. Analysed composition of levyne and harmotome are fairly different from the reported ones. Their total amounts including reported H₂O content are more than 103%. They are easily damaged against the electron beams and a part of H₂O comes out during the preparation. The difference in H₂O content may be inevitable in such zeolites. Although there is still problem whether the low H₂O contents are due to the dehydration during preparation or during analyses by electron beam, present results show that most of zeolite group minerals can be analysed well by EDS.

Totals of rare earth-bearing minerals were mostly less than 100 wt% (Table 7). The minerals contain usually more than several rare-earth elements, and serious overlaps occur among profiles of the elements. In addition, 2 sigma (2 standard deviations) of the elements is usually high, around 1.0 wt%. Hence many elements were not listed in Table 7. Especially odd number elements were rarely more than 2 sigma. In these minerals, analyses of minor elements by WDS or far longer live-time will improve the total amounts.

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