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 Kα 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 $3 \times 4 \ \mu m^2$.   In zeolite group minerals, HgBr and some sulfide minerals, live time and area are 60 seconds and $12 \times 17 \ \mu m^2$, repsectively.   Spectrum is corrected for drift in the zero position.   Cobalt Kα is used for monitoring the drift in the high-energy side.   After apparent compositions were obtained by digital filter methods, chemical compositions

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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_2SiO_4	orthopyroxene, clinopyroxene, garnet
Al	Al_2O_3	sillimanite	plagioclase, garnet, jadeite
Si	$CaSiO_3$	wollastonite	quartz, plagioclase, sillimantie
P	GaP	GaP	apatite, monazite, variscite, xenotime
S	FeS_2	pyrite	chalcopyrite, alabandite, hawleyite
Cl	NaCl	NaCl-albite	vanadinite, bromargyrite
K	aduralia	aduralia	chabazite, laumontite, eri nite
Ca	$CaSiO_3$	wollastonite	hedenbergite, grossular, plagioclase
Sc	ScP_3O_9	ScP_3O_9	thortveitite
Ti	Ti	TiO_2	ilmenite, kimzeyite
V	V	V	vanadinite
Cr	Cr	Cr_2O_3	crocoite, spinel
Mn	Mn	Mn, tephroite	rhodonite, tantalite, wolframite
Fe	Fe	Fe_2SiO_4	ilmenite, pyrite, garnet, kamiokaite
Co	Co	Co	Co-olivine, siegenite
Ni	Ni	Ni	nitckeline, breithauptite, siegenite
Cu	Cu	Cu	roquesite, sakuraiite, chalcopyrite
Zn	Zn	Zn	sakuraiite, sphalerite
Ga	GaP	GaP	
Ge	Ge	Ge	germanite
As	InAs	InAs	orpiment, eulytite, nickline
Se	Se	TeSe	paraguanajuatite, kawazulite, naumannite
Br	(bromargyrite)		
Sr	SrF_2	SrF_2	slawsonite, thomsonite
Y	Y	YP_5O_{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, tetradymite, tellurobismuthite
Cs	(pollucite)		
Ba	BaF_2	BaF_2	barite, celsian, harmotome
La	LaF_3	LaP_5O_{14}	monazite, lanthanite, florencite
Ce	CeF_3	CeP_5O_{14}	monazite, florencite
Pr	PrF_3	PrP_5O_{14}	monazite
Nd	NdF_3	NdP_5O_{14}	monazite, lanthanite

Table 1.   Continued

element	standards		analysed samples
	profile	ratio factor	
Pm	Sm	SmP_5O_{14}	monazite
Eu	EuF_3	EuF_3	
Gd	Gd	GdP_5O_{14}	monazite, gadolinite
Dy	Dy	DyO_5P_{14}	xenotime, yttrialite, fergusonite
Ho	Ho	Ho	
Er	Er	ErP_5O_{14}	xenotime, yttrialite, fergusonite
Tm	Tm	Tm	
Yb	Yb	YbP_5O_{14}	xenotime, thortveitite, yttrialite
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, paraguanajuatite
Th	ThO_2	ThO_2	thorianite, monazite, yttrialite
U	U	U	thorianite, yttrialite, 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 sto-ichiometry.   Namely after analyses of $CaSiO_3$, ratio factor of Mg was determined by analyses of Mg_2SiO_4; Al from Al_2SiO_5, Fe from Fe_2SiO_4, Na from $NaAlSi_3O_8$ and Mn from $(Mn, Fe)_2SiO_4$.   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
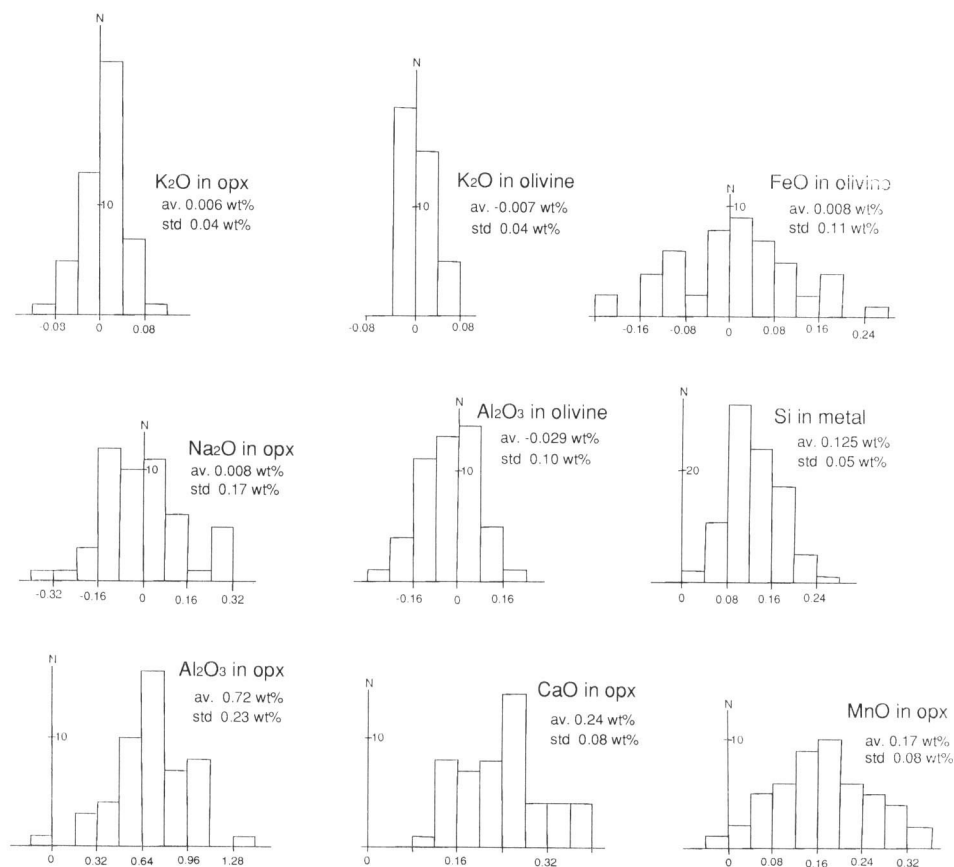
Fig. 1. Histograms of element and oxide values with savarage of 50 analyses and standard
         deviation (1 sigma).   Vertical axis is number of analysis.   Details are in text.

rather than fluorides.

Proper standards for Br and Cs elements have not been obtained, though their
ratio factors are tentatively calculated from bromargyrite, Ag(Br, Cl), and pollucite
$(Cs, Na)_2Si_4O_{12} \cdot H_2O$, respectively.

Analyses of Minor Elements

In the EDS analysis, three points should be checked before the quantitative analy-
sis.   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
$(SrAl_2Si_2O_8)$ 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 analystical 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 SiO_2. 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). K_2O in orthopyroxene and Mg_2SiO_4 and FeO in Mg_2SiO_4 are 0.006 to 0.008 wt%, within a standard deviation 0.04–0.11 wt%. Analyses of Al_2O_3 in Mg_2SiO_4 are shown in Fig. 2. High peaks appear at both sides of the activation energy for Al Kα. The average was −0.03 wt%, negligible in the analyses of Al_2O_3 content. Average of Na_2O 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_2O_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_2O	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
SiO₂	11.27	39.48	CaO		0.91	Cr₂O₃	46.29	TiO₂	0.94	SiO₂	37.35
TiO₂	5.43		Y₂O₃		1.85	Al₂O₃	20.81	MnO	6.37	Al₂O₃	30.45
Al₂O₃	7.22	21.17	PbO	3.20	11.25	Fe₂O₃	4.72	FeO	12.97	SrO	30.47
Fe₂O₃	14.53	2.31	Ce₂O₃		1.99	FeO	13.72	Nb₂O₅	55.67	BaO	1.56
MgO	0.26		ThO₂	76.51	7.41	MgO	14.02	Ta₂O₅	24.82	total	99.83
CaO	28.68	37.22	UO₂	21.23	76.29	total	99.56	total	100.77		
ZrO	30.85		total	100.9	99.69						
Nb₂O₅	1.08									O	8
total	99.32	100.18	O	2	2	O	4	O	12	Si	2.035
			Ca		0.043	Cr	1.131	Ti	0.087	Al	1.956
O		12	Y		0.043	Al	0.758	Mn	0.664	Sr	0.963
Si	1.106	2.982	Pb	0.038	0.133	Fe³⁺	0.110	Fe	1.335	Ba	0.033
Ti	0.400		Ce		0.032	Fe²⁺	0.355	Nb	3.099	total	4.987
Al	0.836	1.885	Th	0.771	0.075	Mg	0.646	Ta	0.831		
Fe³⁺	1.073	0.131	U	0.209	0.750	total	3.000	total	6.017		8
Mg	0.038		total	1.019	1.077					CrO₃	30.98
Ca	3.013	3.012								PbO	69.05
Zr	1.477									total	100.03
Nb	0.048										
total	7.990	8.010								O	4
										Cr	1.000
										Pb	0.999
										total	1.999

	9		10		11		12		13		14
MnO	14.51	MnO	11.28	MnO	0.97	SiO₂	22.60	SiO₂	32.24		
Nb₂O₅	6.83	FeO	13.11	FeO	25.58	CaO	21.17	ZrO₂	66.06		14
Ta₂O₅	79.27	WO₂	76.72	MoO₂	72.85	SnO₂	56.73	HfO₂	0.87	CaO	19.48
total	100.61	total	101.11	total	99.20	total	100.49	total	99.17	WO₃	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 Al_2O_3. This may be partly due to the inhomogeniety 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		Chalcopyrite			Alabandite			Pyrite	
Sn	11.13	5.06		wt%	atm%		wt%	atm%		wt%	atm%
total	99.80		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 $Fe^{2+}Fe_2^{3+}O_4$. 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,

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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
					O=4
PbO	79.15	Pb=5			
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 MgO_4 and 0.887 as $MgCO_3$. On the other hand, analyses of heavy metal carbonates are not affected by the calculation methods. *e.g.* 0.886 as FeO_4 and 0.890 as $FeCO_3$, 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 heterogenieties 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_2O_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_2O	12.63	16.66		0.36	0.66	0.39	0.32	1.49	4.60
K_2O					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_2O*	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_2O_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_2O	1.71	0.37	1.20	0.96	1.09	4.57	4.27	3.83
K_2O	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_2O*	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, phillipsite, 16 & 17, Sr-proor and Sr-rich thomsonites.

H_2O 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 formura			
	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_2O_5		26.01		36.47	P		0.909		1.025
CaO					Ca				
Sc_2O_3			47.86		Sc			1.834	
MnO	1.67		0.51		Mn	0.097		0.019	
FeO	2.40				Fe^{2+}	0.137			
Fe_2O_3			1.78		Fe^{3+}			0.059	
Y_2O_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_2O_3		8.87			La		0.135		
Ce_2O_3	0.92	23.11			Ce	0.022	0.349		
Pr_2O_3		2.76			Pr		0.042		
Nd_2O_3	1.39	13.00			Nd	0.034	0.192		
Sm_2O_3	1.63	3.53			Sm	0.038	0.050		
Gd_2O_3	3.02	2.56		1.88	Gd	0.069	0.035		0.021
Dy_2O_3	4.19			5.11	Dy	0.093			0.054
Er_2O_3	3.96			4.84	Er	0.085			0.050
Yb_2O_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＝yttrialite, 2＝monazite, 3＝thortveitite, 4＝xenotime.

Ratio factor of sulfur was determined from pyrite (FeS_2). 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 (Sb_2FeS_4) and stibnite (Sb_2S_3). 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, Sb_2O_3, 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 H_2O, 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. H_2O content of laumontite is easily changed during the preparation in spite of careful treatment. H_2O content (100%-total elements) was changed from place to places. Lowest H_2O 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 H_2O content are more than 103%. They are easily damaged against the electron beams and a part of H_2O comes out during the preparation. The difference in H_2O content may be inevitable in such zeolites. Although there is still problem whether the low H_2O 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.

Acknowledgements

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