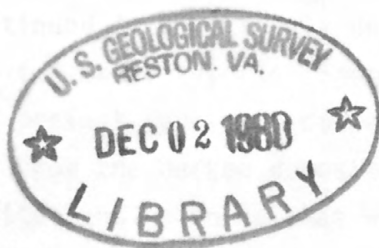UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

CHEMISTRY OF ZEOLITES AND ZEOLITIC TUFFS FROM A PLIOCENE

LACUSTRINE DEPOSIT NEAR DURKEE, BAKER COUNTY, OREGON

By

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INTRODUCTION

Zeolites in an unnamed Pliocene lacustrine and fluviatile deposit near Durkee were first mentioned by Eakle (1898). He described a new zeolite, erionite, from a small opal quarry in a "rhyolite" (welded ash-flow tuff) about 6 km southeast of Durkee. Eakle, unfortunately, provided only a vague description of the type locality of erionite; and more than half a century passed before the type locality was rediscovered by L. W. Staples, and additional specimens were compared with Eakle's original material (Staples and Gard, 1959). Prior to the late 1950's, the Durkee locality was the only confirmed occurrence of erionite in the world.

Our investigation of the zeolites and the diagenesis of tuffaceous rocks near Durkee began late in 1970 after a brief reconnaissance early in that year showed an abundance and variety of authigenic zeolites in silicic tuffs of the lacustrine deposit. Field studies continued intermittently until 1972, and laboratory studies continued intermittently until 1976. Preliminary findings have been published in two brief reports (Sheppard and Gude, 1975; Gude and Sheppard, 1978). This present report is concerned only with the chemistry of certain zeolitic tuffs from the Durkee deposit and with the chemistry of chabazite, clinoptilolite, and erionite that were separated from six of the tuffs.

GEOLOGIC SETTING

The deposit that contains the zeolitic tuffs was mapped as an unnamed unit of "tuffaceous lake and stream sediments" by Prostka (1967). This Pliocene deposit of lacustrine and fluviatile rocks and a welded ash-flow tuff occupies an irregularly shaped, northwesterly elongated basin. The deposit covers an area of about 118 km^2, but the zeolitic part of the deposit seems restricted to an area of about 27 km^2 in the southeastern part of the basin (Gude and Sheppard, 1978). The total exposed thickness of the deposit is about 350 m. Tuffs are interbedded with mudstone, siltstone, sandstone, and

diatomite. Zeolitic tuffs are chiefly in the lower 135 m of the deposit where diatomite is absent. Those tuffs interbedded with diatomite consist chiefly of fresh glass and occur stratigraphically higher in the section.

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF ZEOLITE-RICH TUFFS

Semiquantitative spectrographic analyses of 11 zeolitic tuffs (localities, fig. 1) rich in chabazite, clinoptilolite, and erionite are given in table 1. These analyses were performed on bulk samples that contained at least 90 percent of the stated zeolite. The chief impurities were trace amounts of other zeolites and smectite. Erionite-rich tuffs from the Durkee deposit have a consistently high potassium content and a highly variable calcium content relative to the other zeolitic tuffs. Clinoptilolite-rich tuffs seem to have relatively high contents of barium and strontium, although one sample (no. 8) of an erionite-rich tuff contains anomalously high contents of both elements. Chabazite-rich tuffs seem to be especially low in strontium relative to the clinoptilolite-rich and erionite-rich tuffs.

CHEMICAL ANALYSIS AND UNIT-CELL COMPOSITION OF CHABAZITE, CLINOPTILOLITE, AND ERIONITE

Relatively pure zeolite separates were prepared for chemical analysis from nearly monomineralic tuffs. The zeolites were separated by crushing the tuff and then disaggregating it in an ultrasonic bath. The zeolites were then concentrated by repeated centrifuging in a heavy-liquid mixture of bromoform and acetone, utilizing the technique described by Schoen and Lee (1964).

Conventional rock analyses were performed on zeolite separates of chabazite, clinoptilolite, and erionite, and the analyses are given in table 2. The analyses of those separates that contained minor calcite impurities were corrected by subtracting the analyzed CO_2 content plus the equivalent CaO content to make calcite and then recalculating the analyses so that they total 100 percent. These corrected analyses are also given in table 2.

The analyses were calculated into atoms per unit cell on the basis of 72 oxygen atoms, and the composition of the unit cell is given in table 2 and plotted on figures 2 and 3. Figure 2 shows that the plots for chabazite and erionite overlap. The Durkee clinoptilolites are more siliceous than the chabazites or the erionites. The Si: $Al+Fe^{+3}$ ratio of one clinoptilolite (no. 3) is anomalously low, inasmuch as most clinoptilolites have a Si: $Al+Fe^{+3}$
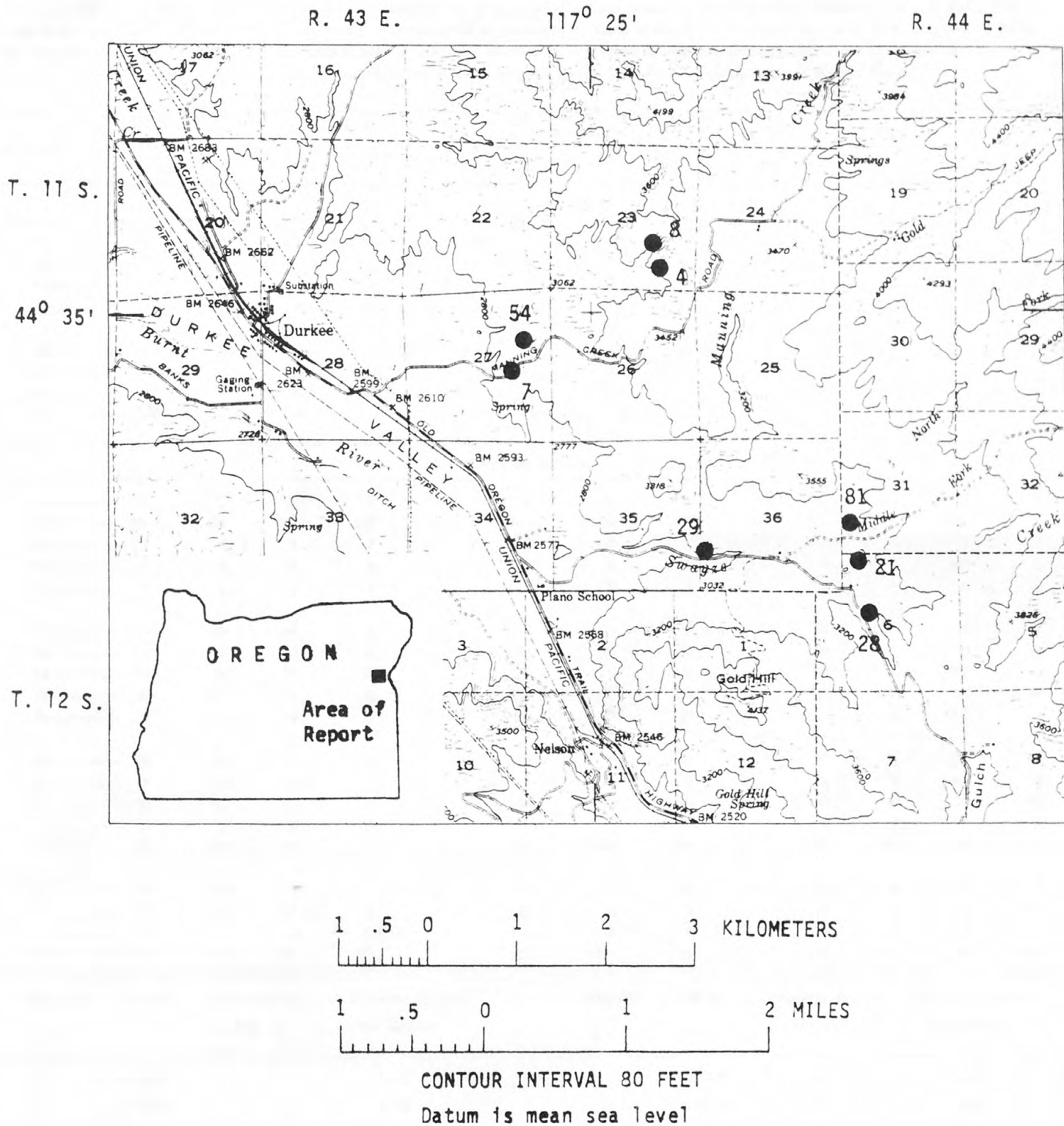
Figure 1.--Part of the U.S. Geological Survey Durkee, Oregon 15-minute
quadrangle topographic map showing sample localities indicated by dots.
Analyses of the samples are given in tables 1 and 2.

	Chabazite-rich tuff				Clinoptilolite-rich tuff			Erionite-rich tuff			
	1	2	3	4	5	6	7	8	9	10	11
Weight percent											
Si	G	G	G	G	G	G	G	G	G	G	G
Al	7	7	5	5	7	7	10	7	7	7	5
Fe	.5	.7	.7	.7	2	3	3	2	3	3	.5
Mg	.2	.1	.7	.7	.5	.7	.5	.3	.5	.7	1.5
Ca	2	5	1.5	2	3	1.5	2	5	2	2	.02
Na	1.5	1	.5	.7	.7	2	3	.7	.3	1	1.5
K	.7	2	2	2	2	3	3	5	3	3	5
Ti	.07	.05	.1	.1	.07	.15	.2	.05	.03	.2	.02
Parts per million											
B	N	L	L	L	N	L	L	L	L	N	N
Ba	200	300	200	200	1,500	1,000	1,000	2,000	150	150	70
Be	2	2	N	N	2	N	N	5	2	3	2
Ce	N	N	N	N	N	N	N	N	N	150	L
Cr	L	1	L	L	1	2	1	1	L	L	L
Cu	L	10	10	7	3	30	15	15	30	20	3
Ga	20	15	10	15	20	10	15	30	30	30	30
La	50	30	30	30	30	N	N	50	N	100	50
Mn	30	100	50	30	500	70	100	70	30	150	50
Mo	N	N	N	N	N	50	30	7	15	3	N
Nb	10	30	L	L	10	N	L	10	10	50	15
Nd	N	N	N	N	N	N	N	N	N	100	N
Pb	10	20	15	10	20	20	10	20	20	30	20
Sc	L	N	L	N	L	5	7	N	N	L	N
Sr	30	100	70	70	200	1,000	1,000	700	150	150	70
V	N	15	5	7	20	15	10	20	30	70	N
Y	30	30	15	15	70	N	N	10	10	70	10
Yb	5	3	1.5	1.5	7	N	N	L	1	7	L
Zr	200	100	150	100	200	200	100	150	200	300	150

Analysis	Lab. No.	Locality No. (fig. 1)	Thickness of tuff (in meters)	Analysis	Lab No.	Locality No. (fig. 1)	Thickness of tuff (in meters)
1	D152183	4	0.91	7	D152188	8	0.05
2	D152184	4	0.55	8	D152179	21	0.04
3	D152185	4	1.68	9	D152180	28	0.10
4	D152186	4	1.52	10	D152182	29	0.46
5	D152181	29	1.22	11	D152191	8	0.20
6	D152187	8	0.10				

Table 2.--Chemical analyses and composition of unit cell of chabazite, clinoptilolite, and erionite

[a, uncorrected analysis; b, analysis corrected for CO_2 plus equivalent CaO to make calcite]

	Chabazite		Clinoptilolite			Erionite			
	1	2	3		4	5		6	
	a	a	a	b	a	a	b	a	b

Chemical analyses, in weight percent

[Analysts: Edythe E. Engleman and Vertie C. Smith, U.S. Geological Survey]

	1 a	2 a	3 a	3 b	4 a	5 a	5 b	6 a	6 b
SiO_2	57.91	58.65	61.59	62.87	64.72	59.40	59.81	59.53	60.67
Al_2O_3	14.25	13.51	12.57	12.83	12.10	13.51	13.61	13.59	13.85
Fe_2O_3	.42	.61	2.28	2.33	1.13	1.49	1.50	.22	.22
FeO	.02	.00	.03	.03	.06	.05	.05	.07	.07
MgO	.40	1.27	1.13	1.15	.74	1.09	1.10	1.67	1.70
CaO	3.85	3.78	2.84	1.92	1.52	3.73	3.43	2.04	1.09
BaO	.01	.00	--	--	.11	--	--	.00	.00
Na_2O	2.46	.77	2.79	2.85	3.09	.38	.38	2.30	2.34
K_2O	1.33	1.76	1.84	1.88	2.41	3.53	3.55	3.35	3.41
H_2O^+	10.58	11.77	8.93	9.12	6.81	10.63	10.70	8.33	8.49
H_2O^-	7.80	7.19	4.72	4.82	6.51	5.74	5.78	7.95	8.11
TiO_2	.15	.02	.13	.13	.06	.07	.07	.03	.03
P_2O_5	.03	.01	.02	.02	.01	.01	.01	.02	.02
MnO	.01	.00	.06	.06	.00	.01	.01	.00	.00
CO_2	.04	.02	.75	--	.04	.25	--	.76	--
Total	99.26	99.36	99.68	100.00	99.31	99.89	100.00	99.86	100.00

Composition of unit cell, in atoms per unit cell

[Fe^{+2}, Ti, P, and Mn were omitted in the calculation of the unit cell]

	1 a	2 a	3 a	3 b	4 a	5 a	5 b	6 a	6 b
Si	27.90	28.21	--	28.51	29.23	--	28.08	--	28.32
Al	8.09	7.66	--	6.85	6.44	--	7.53	--	7.62
Fe^{+3}	.15	.22	--	.80	.38	--	.53	--	.08
Mg	.28	.91	--	.78	.50	--	.77	--	1.18
Ca	1.98	1.95	--	.93	.74	--	1.73	--	.54
Ba	--	--	--	--	.02	--	--	--	--
Na	2.30	.72	--	2.51	2.70	--	.34	--	2.12
K	.82	1.08	--	1.09	1.39	--	2.13	--	2.03
H_2O^+	17.00	18.88	--	13.79	10.26	--	16.76	--	13.22
H_2O^-	12.54	11.54	--	7.29	9.81	--	9.05	--	12.63
O	72.00	72.00	--	72.00	72.00	--	72.00	--	72.00
Si: $Al+Fe^{+3}$	3.38	3.58	--	3.73	4.28	--	3.48	--	3.68

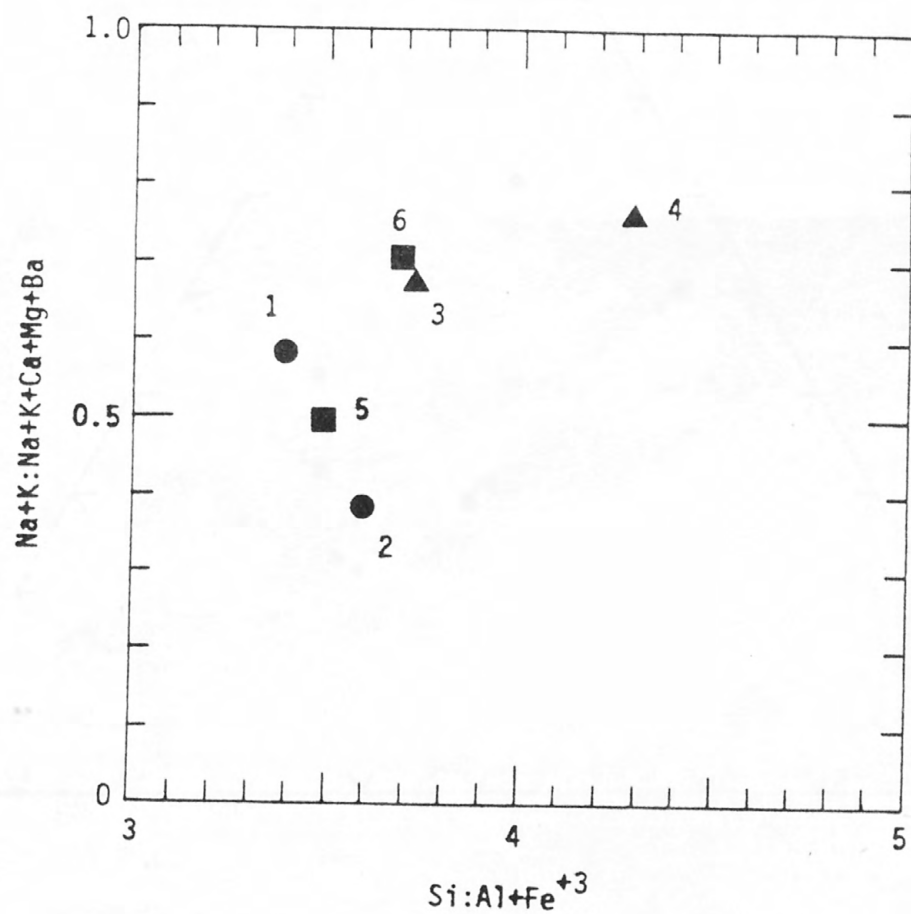| Analysis	Lab No.	Locality No. (fig. 1)	Analysis	Lab No.	Locality No. (fig. 1)
1	D103736	4	4	D103738	54
2	D103737	4	5	D103020	28
3	D103021	7	6	D103739	81

Figure 2.--Plot showing the compositional variation of chabazite (dots), clinoptilolite (triangles), and erionite (squares). Numbers refer to analyses given in table 2.
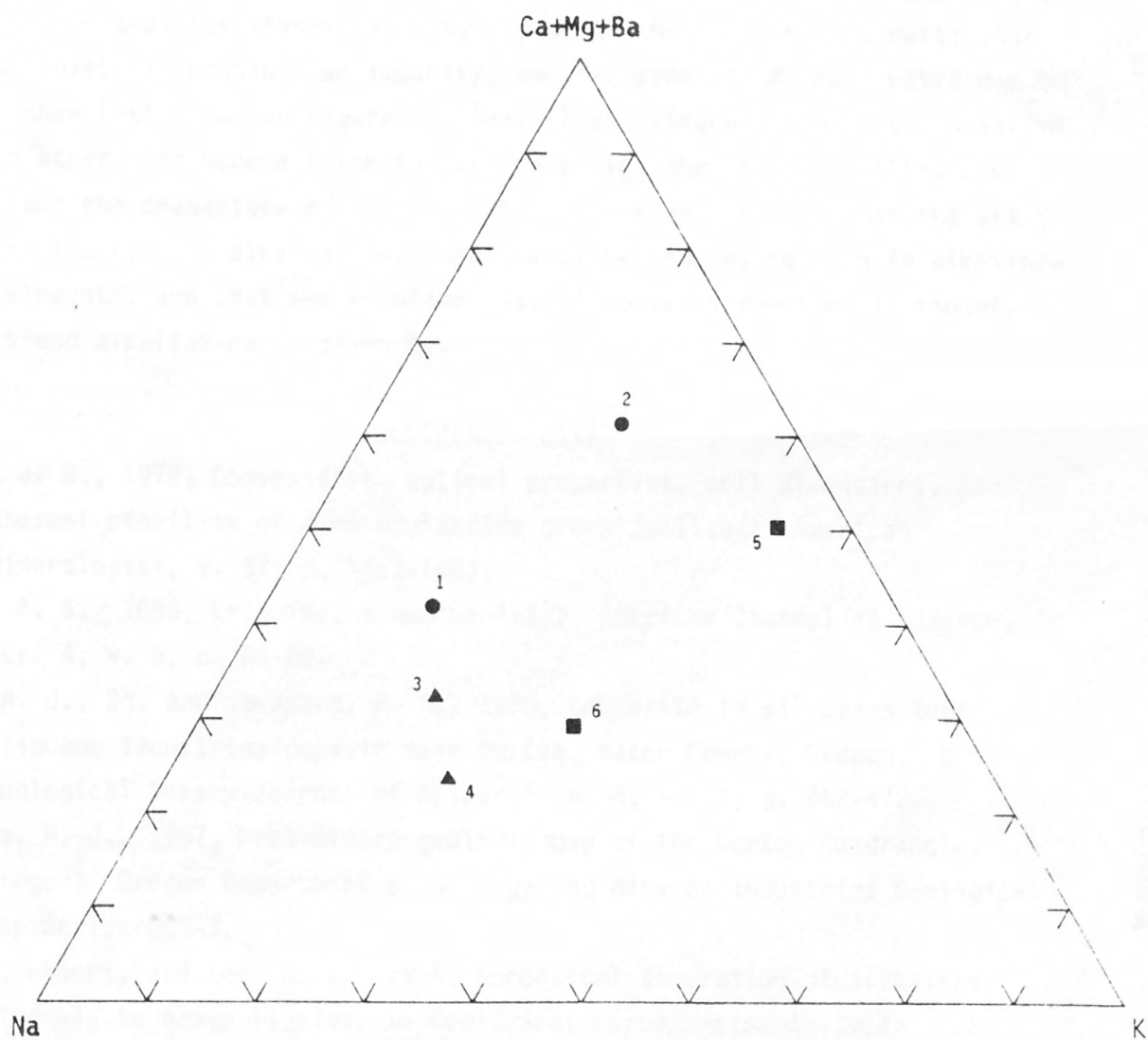
Figure 3.--Atomic percentages of Na, K, and Ca+Mg+Ba for chabazite (dots), clinoptilolite (triangles), and erionite (squares). Numbers refer to analyses given in table 2.

ratio greater than 4 (Boles, 1972). The $Al+Fe^{+3}$:Na+K+2(Ca+Mg) ratio for zeolites should be unity, but this ratio is about 1.1 for analysis no. 3. The Fe_2O_3 content of this clinoptilolite is much higher than that for any of the other Durkee zeolites (table 2). Thus, some of the iron in this particular clinoptilolite is probably an impurity, and the true Si: $Al+Fe^{+3}$ ratio may be higher than that shown on figure 2. Table 2 and figure 3 show that, relative to each other, the Durkee erionites are potassic, the clinoptilolites are sodic, and the chabazites are calcic. Figure 3 shows that four of the six zeolites are rich in alkalis, that one chabazite (no. 2) is rich in alkaline-earth elements, and that one erionite (no. 5) contains about equal amounts of alkalis and alkaline-earth elements.

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