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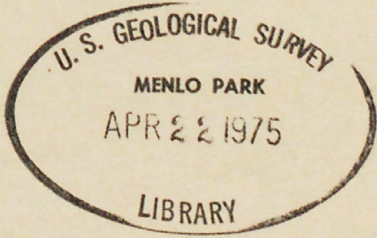
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INFLUENCE OF CAUSTIC AND WATER LEACHING ON ANALCIME-BEARING AND
ANALCIME-FREE PYROLYZED OIL SHALE FROM THE GREEN RIVER FORMATION,
PICEANCE CREEK BASIN, COLORADO

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George A. Desborough, Wayne Mountjoy, and Irving C. Frost

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This report is preliminary and has not been edited or reviewed for conformity with U.S. Geological Survey standards and nomenclature.

Contents

	Page
Abstract.....	1
Introduction.....	2
Sample preparation, X-ray diffraction, and Fischer assay results.....	6
Experimental procedure for leaching pyrolyzed oil shale and analysis of leachate solutions.....	10
Results of leaching pyrolyzed oil shale.....	11
H ₂ O solvent.....	11
0.1M KOH solvent.....	17
0.5M KOH solvent.....	17
Influence of analcime.....	19
Extractable Al ₂ O ₃ and SiO ₂	19
Discussion of results and conclusions.....	23
References cited.....	27

Illustrations

	Page
Figure 1. Map showing the location of drill core samples studied and the outline of the Green River Formation in the Piceance Creek basin.....	4
2. Diagram showing stratigraphic position, sample numbers, and major minerals in oil shale samples investigated.....	5
3. Ternary diagram showing proportions of Al_2O_3 , SiO_2 , and Na_2O extracted from spent shale with H_2O	16
4. Ternary diagram showing proportions of Al_2O_3 , SiO_2 , and Na_2O extracted from spent shale with 0.1M KOH.....	18
5. Ternary diagram showing proportions of Al_2O_3 , SiO_2 , and Na_2O extracted from spent shale with 0.5M KOH.....	20
6. Diagram showing contribution of analcime to the amount of $Na_2O+SiO_2+Al_2O_3$ extractable from non-dawsonitic spent shale from core C173.....	21
7. Diagram showing relations of Al_2O_3 and SiO_2 extracted from 30 spent shale samples from core C173 and C176 using 0.1M NaOH and 0.5M NaOH.....	22
8. Diagram showing relations of Al_2O_3 and SiO_2 extracted from 30 spent shale samples from C173 and C176 using 0.1M KOH and 0.5M KOH.....	24
9. Diagram showing relations of the analcime concentration of raw oil shale to the ratio of weight percent Al_2O_3 /weight percent SiO_2 extracted from spent shale.....	25

Tables

	Page
Table 1. Fischer assay data for oil-shale samples from cores C173, C176, and the composite sample of the Mahogany zone from the Colony mine.....	7
2. Concentration of elements extracted from Fischer assay spent oil shale.....	12

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ABSTRACT

The influence of oil-shale mineral constitution on the amounts of Na_2O , Al_2O_3 , and SiO_2 extractable from pyrolyzed oil shale using hot water and hot caustic solvents has been examined. Samples of oil shale from two drill cores and one composite sample from the Colony mine were split and studied by X-ray diffraction methods to determine their bulk mineralogy. Oil yield data were obtained for these samples by conventional Fischer assay analysis and samples of the spent oil shale were studied by X-ray diffraction to determine the changes which resulted from pyrolysis. The amounts of Na_2O , Al_2O_3 , and SiO_2 extractable from 31 spent oil-shale samples were determined using hot distilled water, hot 0.1M KOH, and hot 0.5M KOH as solvents. Extractable Al_2O_3 and SiO_2 were also determined for the 31 spent oil-shale samples using hot 0.1M NaOH and hot 0.5M NaOH.

Correlation of the relative abundance of analcime-- $\text{Na}[\text{Al}, \text{Si}_2\text{O}_6]\cdot\text{H}_2\text{O}$ -- in raw oil-shale samples with the amounts of Na_2O , Al_2O_3 , and SiO_2 extracted from pyrolyzed oil shale demonstrates that analcime contributes significantly to all of these elements after it has been subjected to pyrolysis. Because of the large contribution of SiO_2 extractable from pyrolyzed analcime-bearing oil shale using caustic solvents, there may be significant problems in obtaining leachates high in Al_2O_3 content and low in SiO_2 content where analcime is present with dawsonite-- $\text{NaAl}(\text{OH})_2\text{CO}_3$. This consideration is important to assessment of potential aluminum resources in oil shale. In addition, the concentrations of water soluble Na_2O , Al_2O_3 , and SiO_2 in analcime-bearing pyrolyzed oil shale are expected to be significantly greater than from oil shale which is free of analcime and dawsonite and this factor reflects the importance of oil-shale mineralogy to aspects of spent shale disposal.

INTRODUCTION

Assessment of potentially extractable aluminum which is not combined in a silicate mineral in oil shale of the Piceance Creek basin of Colorado has been done principally by three methods as follows:

- (1) Hydrochloric acid leaching of analcime-free oil shale (Smith and Young, 1969; Young and Smith, 1970)
- (2) Determination of the dawsonite content by semiquantitative X-ray diffraction studies (Hite and Dyni, 1967)
- (3) An indirect method using Fischer assay values of oil, water, and noncondensable gases (gas + loss) for analcime-free oil shale (Smith, Beard, and Wade, 1972)

The HCl acid leaching method is limited to analcime-free oil shale because of the solubility of analcime in this acid. Also this acid could not be used on a commercial basis even in analcime-free oil shale because the abundant Ca-Mg-Fe carbonates would consume too much of the acid.

The X-ray method for determination of dawsonite content is complicated by X-ray peak interferences with analcime (for the strongest dawsonite X-ray peak) and siderite (for the second most intense dawsonite X-ray peak). In addition the X-ray diffraction method does not detect the X-ray amorphous aluminum compound referred to by Smith and Young (1969) as excess alumina (alumina not combined in silicates or with sodium).

The indirect method using Fischer assay values does not apply to analcime-bearing oil shales because analcime yields water during pyrolysis (Beard, Tait, and Smith, 1974).

Previous studies of oil-shale leachates have reported values for sodium and aluminum from one drill core but have not reported silicon concentrations (Young and Smith, 1970). Hite and Dyni (1967) reported values of extractable Al_2O_3 for three fired oil-shale samples using hot distilled water, 2% NaOH, and 2% H_2SO_4 but did not report values of Na_2O and SiO_2 .

Because of these problems associated with evaluation of extractable aluminum in a nonsilicate mineral which occurs in analcime-bearing and analcime-free oil shale we have attempted to study the effect of both water and caustic leaching on oil shale pyrolyzed by the Fischer assay method.

The objective of leaching spent shale with water was to determine the amounts of water-soluble sodium, aluminum, and silicon which may be released by spent shale. Nevens, Culbertson, and Hollingshead (1970) have reported data for H_2O leaching of spent shale from the Colony mine and the U.S. Bureau of Mines site, but they report no data concerning the mineral constitution of the raw shale.

Prior to the present study there appears to be no data published for the concentrations of Na_2O , Al_2O_3 , and SiO_2 released from pyrolyzed oil shale using either NaOH or KOH, although caustic leaching has been proposed for the commercial extraction of Al_2O_3 from pyrolyzed oil shale (Weichman, 1974).

Samples of analcime-bearing oil shale and analcime-free oil shale were obtained from two drill cores, one from the northwest edge, and one from the center of the Piceance Creek basin (fig. 1). Fifteen samples from each of the two drill cores (fig. 2) were analyzed by conventional Fischer assay analysis. Mineralogy of the raw and the spent (pyrolyzed) oil shale was determined for all samples by X-ray diffraction methods and the major minerals are indicated on figure 2.

Dawsonite is not the dominant mineral in any of these 30 samples, but is present as a minor constituent in three samples from core C176 and four samples from core C173. It is an abundant mineral in the two samples from the R-4 zone in core C173.

The major mineralogical changes which occurred as a result of Fischer assay pyrolysis for these 30 samples are summarized as follows:

- (1) The cell dimensions of analcime were reduced principally due to loss of water
- (2) Dawsonite was converted to an X-ray amorphous compound
- (3) Aragonite was converted to calcite

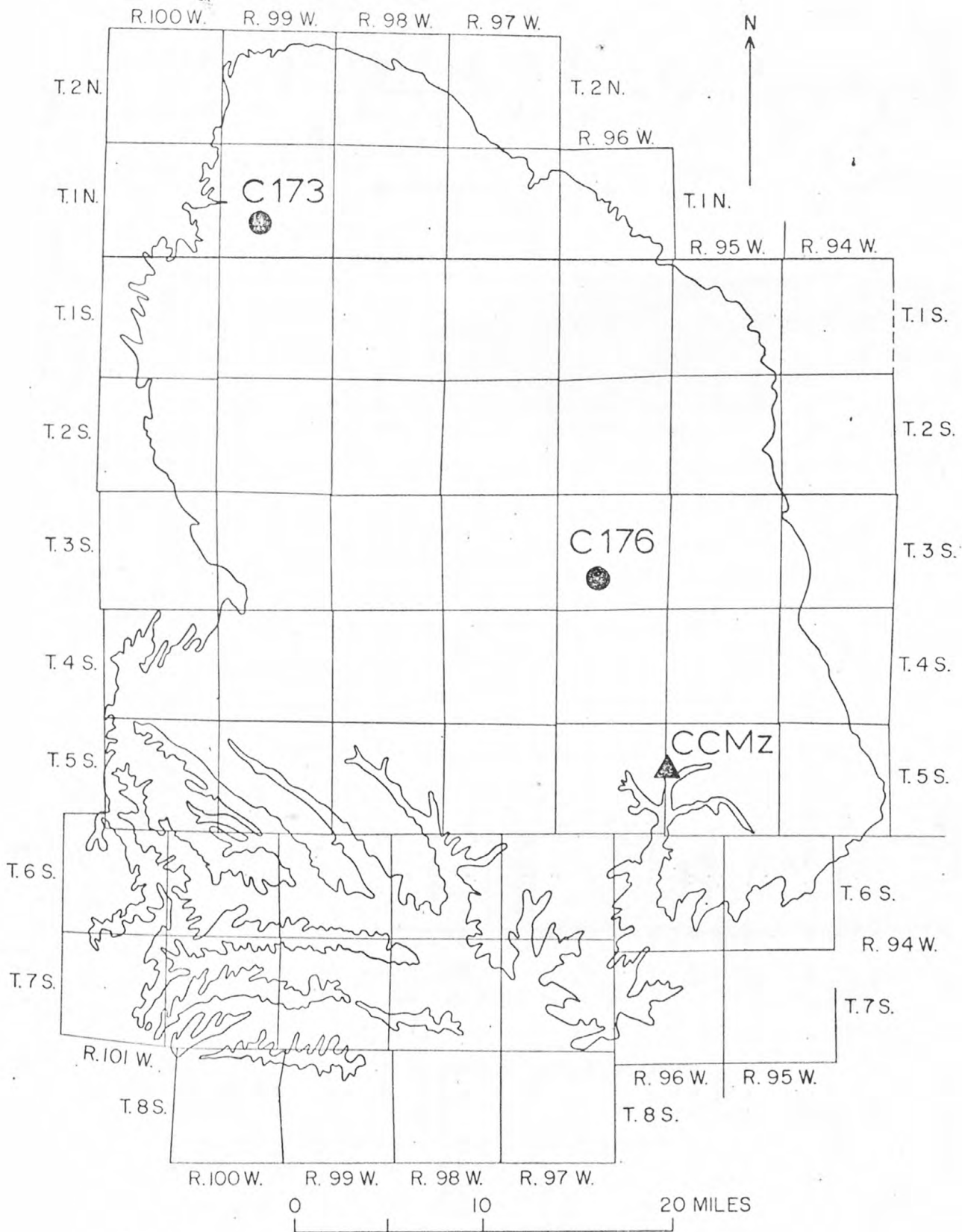


Figure 1.--Map showing the location of drill core samples studied and the outline of the Green River Formation in the Piceance Creek basin, Colorado. CCMz designates the location of a composite sample of the Mahogany zone at the Colony mine. (Modified from Donnell, 1961.)

Except for two samples containing aragonite, the composition and proportions of dolomite and calcite were not significantly modified during pyrolysis. The 10 \AA X-ray peak of samples containing illite and/or 10 \AA micas was not affected by pyrolysis.

For comparative purposes, a composite sample from the Mahogany zone at the Colony mine was studied. This composite sample contains detectable dawsonite and analcime which together constitute less than 3 weight percent, according to X-ray diffraction analysis.

SAMPLE PREPARATION, X-RAY DIFFRACTION, AND FISCHER ASSAY RESULTS

Samples of core C173 were obtained by cutting longitudinal segments from intact core. These segments ranged from 3.5 to 5.5 inches (9 to 14 cm) in length and were crushed in a jaw crusher prior to fine-crushing to minus 65 mesh. Splits from the raw shale were taken from each sample for X-ray diffraction studies, and the remainder was used for Fischer assay analysis. Raw shale samples of core C176 were generously provided by The Oil Shale Corp. All of those studied were from 1-foot (30.5 cm) intervals except for samples 1003.0 and 1012.0 which represent 3-foot (91.5 cm) intervals. Splits of these were extracted for X-ray diffraction studies and the remainder was used for Fischer assay analysis. Both raw shale and spent shale of the composite sample from the Mahogany zone from the Colony mine were kindly provided by The Oil Shale Corp., who also provided the Fischer assay data.

Samples separated for X-ray diffraction studies were pelletized and X-rayed using $\text{CuK}\alpha$ radiation for the 2θ range from 4° to 50° at a chart speed of $2^\circ 2\theta$ per minute with $4^\circ 2\theta$ equal to 1 inch. These samples were also X-rayed for the 2θ range from 25° to 36° at a chart speed of $1/4^\circ 2\theta$ per minute with $1^\circ 2\theta$ equal to 4 inches. This was done on both raw shale and spent shale in order to evaluate primary mineralogy and mineralogical changes which occurred due to pyrolysis. The relative abundances of major minerals shown on figure 2 are chiefly based on the most intense X-ray peak of each of these minerals in raw shale.

The 30 samples from cores C173 and C176 were assayed using the modified Fischer retort (Stanfield and Frost, 1949) and these results are shown in table 1.

Table 1.--Fischer assay data for oil-shale samples from cores C173, C176, and the composite sample of the Mahogany zone from the Colony mine. (Sample number corresponds to depth, in feet, of the top of the interval studied.)

<u>Drill core - C173</u>						
Sample no.	Oil gals./ton	Water gals./ton	Oil, wt. percent	Water, wt. percent	Spent shale wt. percent	Gas and loss, wt. percent
240.7	7.1	3.6	2.7	1.5	90.5	5.3
260.0	22.6	3.6	8.6	1.5	88.0	1.9
279.4	14.0	4.0	5.4	1.6	91.5	1.5
300.0	22.1	3.6	6.7	1.5	90.0	1.8
339.9	24.2	3.6	9.3	1.5	87.0	2.2
400.0	12.4	1.8	4.7	0.8	92.8	1.7
440.1	28.2	4.2	10.8	1.8	84.5	2.9
480.1	32.1	5.4	12.3	2.3	83.5	1.9
500.6	25.0	5.0	9.5	2.1	84.5	3.9
560.0	15.8	5.8	6.0	2.4	90.0	1.6
620.6	13.6	4.6	5.2	1.9	91.0	1.9
800.0	9.2	7.4	3.5	3.1	91.5	1.9
939.9	24.9	4.8	9.5	2.0	86.0	2.5
1141.0	28.4	4.8	10.8	2.0	84.0	3.2
1159.9	33.5	5.6	12.7	2.4	79.0	5.9

Table 1.--Fischer assay data for oil-shale samples from cores C173, C176, and the composite sample of the Mahogany zone from the Colony mine. (sample number corresponds to depth, in feet, of the top of the interval studied.)

Sample no.	Oil gals./ton	Water gals./ton	Drill core - C176			
			Oil, wt. percent	Water, wt. percent	Spent shale wt. percent	Gas and loss, wt. percent
784.0	27.3	2.6	10.5	1.1	86.0	2.4
806.6	23.1	2.0	8.8	0.8	88.0	2.4
817.6	35.7	4.6	13.4	1.9	80.5	4.2
852.0	52.3	4.3	19.8	1.8	73.5	4.9
860.0	25.4	3.2	9.6	1.4	86.5	2.5
∞ 865.5			Insufficient sample			
881.5	22.5	1.9	8.6	0.8	89.0	1.6
903.0	35.8	2.9	13.5	1.2	83.0	2.3
923.0	21.0	2.2	7.8	0.9	89.0	2.3
938.0	12.5	1.0	4.8	0.4	94.0	0.8
942.0	33.7	1.9	12.7	0.8	85.0	1.5
954.0	17.1	1.2	6.5	0.5	91.5	1.5
960.0	15.6	0.6	5.9	0.2	92.5	1.4
1003.0	22.3	1.9	8.5	0.8	89.0	1.7
1012.0	9.0	0.4	3.4	0.1	95.5	1.0

Table 1.--Fischer assay data for oil-shale samples from cores C173, C176, and the composite sample of the Mahogany zone from the Colony mine. (sample number corresponds to depth, in feet, of the top of the interval studied.)

Sample no.	Colony composite, Mahogany zone					
	Oil gals./ton	Water gals./ton	Oil, wt. percent	Water, wt. percent	Spent shale wt. percent	Gas and loss, wt. percent
Colony mine composite	32.3	3.4	12.2	1.0	83.7	2.6

Analyst: I. C. Frost

Analcime was detected by X-ray diffraction methods in 13 of the 15 samples from core C173, but it was not detected in any of the samples from core C176 (fig. 2). Two of the four samples containing dawsonite in core C173 also contain analcime. The occurrence of dawsonite and analcime together in samples from core C173 is in contrast with the results of Smith and Robb (1974, p. 98) for Colorado Core Hole No. 1 in which "analcime and dawsonite do not seem to exist together."

The relative abundance of analcime in samples from core C173 was determined by measuring the intensity of the 211 X-ray peak on pressed pellets. For the analcime-bearing samples, the concentration of analcime is estimated to be between 1 and 20 weight percent. This estimate is based on X-ray diffraction studies of these samples and comparing the intensity of the analcime 211 X-ray peak with oil-shale standards to which 5, 15, and 20 weight percent of analcime was added, respectively. Due to oil-shale matrix effects, the relative error in estimating analcime concentration may be as much as 10 percent.

EXPERIMENTAL PROCEDURE FOR LEACHING PYROLYZED OIL SHALE AND ANALYSIS OF LEACHATE SOLUTIONS

The pyrolyzed oil-shale samples were reground and remixed before the following extractions to insure homogeneity. Five 0.500-gram portions of each sample were weighed and transferred to separate 4-oz polyethylene bottles. One hundred ml of each leaching solution--H₂O, 0.1M NaOH, 0.1M KOH, 0.5M NaOH, and 0.5M KOH--were added to successive bottles. The excess air was removed from the bottles by squeezing so the liquid came up to within 3/8 inch of the top. The cap was then screwed on tightly and the bottles placed on their sides in a pan, containing about 1/2 inch of boiling water, on an oscillating hot plate. The bottles were placed so their axes were parallel to the direction of oscillation of the hot plate for more thorough agitation. In addition, the pan was covered and live steam passed over the bottles. Heating and agitating in this manner was continued for 2 hours. Occasional checks were made to see that all of the water did not evaporate from the pan and that excessive pressure did not build up in any of the bottles. After the digestion,

the bottles were removed from the bath, the covers loosened, and allowed to cool to room temperature. They were then centrifuged at about 2,000 rpm for 5 minutes. A 50-ml portion of each leachate was decanted into a nalgene graduated cylinder. This was poured through a long stemmed plastic funnel into a 100 ml volumetric flask, to which had been added enough 6% v/v HCl to neutralize the added base and to provide an acidity comparable to that of the S1 and A1 blank and standard used. The total amounts of the acid added for the various leachate solutions were as follows:

<u>Leach solution</u>	<u>Amount of 5% HCl added to each 100 ml vol. flask</u>
H ₂ O	13.8 ml
0.1M NaOH or 0.1M KOH	26.8 ml
0.5M NaOH or 0.5M KOH	50.0

The sample solutions were diluted to 100 ml volume with water and mixed. The solutions were analyzed for their Na₂O, SiO₂, and Al₂O₃ content by the methods described below.

Sodium was determined by atomic absorption spectrophotometry. The instrumental parameters recommended in Analytical Methods for Atomic Absorption Spectrophotometry by Perkin Elmer Corp., Norwalk, Conn., were used. The solutions from the water leaches generally were not diluted; however, in some cases dilutions of 5 ml in 25 were made to attain an optimum concentration for solutions containing considerable sodium. The KOH extracts were diluted 10 to 25 fold to minimize the interference of the potassium ions and still use the range of the instrument where optimum precision is attained. SiO₂ and Al₂O₃ were determined colorimetrically by methods described by Brannock and Shapiro (1962). To read at the optimum concentration, aliquot sizes were varied from 2 to 10 ml. The results of all these experiments for the 31 samples are given in table 2.

RESULTS OF LEACHING PYROLYZED OIL SHALE

H₂O solvent.--For the hot distilled water leachate from spent shale the amounts of Na₂O ranged from less than 0.01 to 1.78 weight percent. Samples containing dawsonite and analcime yielded the highest amounts of

Table 2.--Concentration of elements extracted from 0.5000 g of Fischer assay spent oil shale by 100.0 ml of hot solvent. [Concentration expressed in weight percent of spent shale.]

Sample No.	Element	Solvent				
		H ₂ O	0.1M NaOH	0.1M KOH	0.5M NaOH	0.5M KOH
C173-240.7	(Na ₂ O	0.09*	--	1.08*	--	1.60*
	(SiO ₂	0.24*	1.09*	1.93	0.95*	2.19
	(Al ₂ O ₃	0.04*	0.36	0.58*	0.51*	0.98*
C173-260.0	(Na ₂ O	0.09*	--	0.72*	--	1.02*
	(SiO ₂	0.25*	1.28*	1.68*	1.48*	1.93*
	(Al ₂ O ₃	0.04*	0.17*	0.29	0.48*	0.80*
C173-279.4	(Na ₂ O	0.10*	--	0.78*	--	1.44
	(SiO ₂	0.28*	1.26*	1.50*	1.46*	1.68*
	(Al ₂ O ₃	0.04*	0.24*	0.45*	0.48*	0.87*
C173-300.0	(Na ₂ O	0.08	--	1.14	--	0.89
	(SiO ₂	0.20	1.62	2.0	1.43	1.45
	(Al ₂ O ₃	0.03	0.05*	0.33*	0.38	0.57
C173-339.9	(Na ₂ O	0.08*	--	1.00*	--	1.50*
	(SiO ₂	0.24*	0.74*	1.85*	1.74*	2.38*
	(Al ₂ O ₃	0.06*	0.82	0.42*	0.94*	1.15*
C173-400.0	(Na ₂ O	0.02*	--	0.93*	--	0.22*
	(SiO ₂	0.12*	0.68	0.36*	0.98	0.54*
	(Al ₂ O ₃	0.04*	0.09*	0.05*	0.17*	0.08*
C173-440.1	(Na ₂ O	0.08*	--	1.00	--	1.44
	(SiO ₂	0.24	1.10	2.5*	1.35	2.33*
	(Al ₂ O ₃	0.08	0.37	0.78	0.70*	1.08
C173-480.1	(Na ₂ O	0.18	--	1.61	--	1.99
	(SiO ₂	0.28	1.30	3.74	1.92	3.71
	(Al ₂ O ₃	0.53	0.44*	1.15	0.78	1.38
C173-500.6	(Na ₂ O	0.09*	--	1.58	--	1.96*
	(SiO ₂	0.26	1.96	3.8	2.4	4.1*
	(Al ₂ O ₃	0.06	0.68	1.04*	1.44	3.9
C173-560.0	(Na ₂ O	0.14	--	1.82	--	2.8
	(SiO ₂	0.38	1.56	2.26	1.54	3.83
	(Al ₂ O ₃	0.09	0.72	0.93	0.97	1.81
C173-620.6	(Na ₂ O	0.12	--	1.40	--	1.80
	(SiO ₂	0.34	1.42	2.8	1.89	3.6
	(Al ₂ O ₃	0.11	0.56	1.06	0.92	1.49
C173-800.0	(Na ₂ O	0.38*	--	1.61	--	2.02
	(SiO ₂	0.36*	3.03*	4.0	4.2	5.6
	(Al ₂ O ₃	0.09*	0.90	1.19	1.49*	2.4

Sample No.	Element	Solvent				
		H ₂ O	0.1M NaOH	0.1M KOH	0.5M NaOH	0.5M KOH
173-939.9	(Na ₂ O	0.45	--	1.00	--	1.49
	(SiO ₂	0.34	1.88	2.8	2.7	4.1
	(Al ₂ O ₃	0.08	0.57	0.86	0.89	1.25
173-1141.0	(Na ₂ O	0.74	-	1.22	-	1.44
	(SiO ₂	0.05	0.42	0.72*	1.24	1.16
	(Al ₂ O ₃	0.37	0.88	1.03*	1.01	1.22
173-1159-9	(Na ₂ O	1.78	--	2.5	-	2.4
	(SiO ₂	0.01	0.29	0.17	0.61*	.27
	(Al ₂ O ₃	0.87	3.24	3.36	2.99	2.98
Colony mine composite	(Na ₂ O	0.18	--	0.34	--	0.54*
	(SiO ₂	0.03	0.49	0.52	0.69	0.90
	(Al ₂ O ₃	0.10	0.30	0.38	0.48	0.44
176-784.0	(Na ₂ O	0.07	--	0.23	--	0.34
	(SiO ₂	0.11	0.51	0.34	1.05	0.46*
	(Al ₂ O ₃	0.06*	0.08	0.09	0.18	0.05
176-806.6	(Na ₂ O	0.06	--	0.16	--	0.28*
	(SiO ₂	0.14*	0.66*	0.60	0.64*	0.60*
	(Al ₂ O ₃	0.14*	0.52*	0.45*	0.62*	0.60*
176-817.6	(Na ₂ O	0.09	--	0.98	--	0.41
	(SiO ₂	0.16	0.83	0.98	1.64	1.15
	(Al ₂ O ₃	0.15	0.60	0.67	0.96	0.82
176-852.0	(Na ₂ O	0.63	--	1.39	--	0.86
	(SiO ₂	0.05	0.36	0.23	0.80	0.36
	(Al ₂ O ₃	0.32*	1.05*	1.05*	1.02*	1.04
176-860.0	(Na ₂ O	0.23	--	0.42	--	0.56
	(SiO ₂	0.02	0.60	0.36	0.58	1.11
	(Al ₂ O ₃	0.19	0.32	0.32	0.36	0.44
176-865.5	(Na ₂ O	0.21	--	0.37	--	0.45
	(SiO ₂	0.05	0.42	0.27	0.77	0.32
	(Al ₂ O ₃	0.23	0.42	0.44	0.45	0.34

Sample No.	Element	Solvent				
		H ₂ O	0.1M NaOH	0.1M KOH	0.5M NaOH	0.5M KOH
76-881.5	(Na ₂ O	0.02	--	0.10*	--	0.25
	(SiO ₂	0.08	0.73	0.62	0.75	0.78
	(Al ₂ O ₃	0.12	0.12	0.11	0.30	0.25
76-903.0	(Na ₂ O	0.06	--	0.16	--	0.33
	(SiO ₂	0.06	0.49	0.40	0.39	0.70
	(Al ₂ O ₃	0.10	0.15	0.12	0.20	0.12
76-923.0	(Na ₂ O	<0.01	--	0.07*	--	0.23
	(SiO ₂	0.09	0.88	0.65	0.82	0.99
	(Al ₂ O ₃	0.15	0.62	0.54	0.77	0.67
76-938.0	(Na ₂ O	<0.01	--	0.08	--	0.45
	(SiO ₂	0.06	0.33	0.29*	0.38	0.32
	(Al ₂ O ₃	0.02	<0.02	<0.02	0.03	0.03
76-942.0	(Na ₂ O	0.02	--	0.12	--	0.23
	(SiO ₂	0.13	0.11	0.44	0.85	0.48
	(Al ₂ O ₃	0.03	0.31	0.12	0.48	0.14
76-954.0	(Na ₂ O	0.02	--	0.09	--	0.20
	(SiO ₂	0.08	0.36	0.21	0.53	0.21
	(Al ₂ O ₃	0.03	0.04	0.04	0.11	0.06
76-960.0	(Na ₂ O	0.01	--	0.08	--	0.22
	(SiO ₂	0.10	0.59	0.24	0.80	0.39
	(Al ₂ O ₃	0.02	<0.02	<0.02	0.08	<0.02
76-1003.0	(Na ₂ O	0.02	--	0.09	--	0.23
	(SiO ₂	0.12	0.77	0.33	1.22	0.37
	(Al ₂ O ₃	0.06	0.11*	0.06	0.27	0.06
76-1015.0	(Na ₂ O	<0.01	--	0.06	--	0.18
	(SiO ₂	0.16	0.80	0.37	0.94	0.43
	(Al ₂ O ₃	0.07	0.10	0.03	0.41	0.12

* Indicate⁵ the figure is an average of two determinations.

Analysts: Wayne Mountjoy and I. C. Frost.

extractable Na_2O . Two samples which contained the greatest amounts of dawsonite, and which were free of analcime, yielded 0.74 and 1.78 weight percent of Na_2O . In contrast, three samples from core C173 which contained the greatest amounts of analcime, and which were free of dawsonite, yielded 0.12, 0.38, and 0.45 weight percent of Na_2O . Analcime-bearing samples free of dawsonite yielded from 0.08 to 0.45 weight percent of Na_2O . Samples free of detectable dawsonite and analcime yielded from less than 0.01 to 0.09 weight percent of Na_2O . The composite sample from the Mahogany zone at the Colony mine yielded more Na_2O than the highest value reported by Nevens, Culbertson, and Hollingshead (1970) in their study of pyrolyzed shale from the Mahogany zone at the Colony mine. However, this is expected because of the lower temperatures and smaller volumes of solvent used in their studies.

Amounts of SiO_2 ranged from 0.01 to 0.38 weight percent and were distinctly higher in those samples which contained analcime. The four samples containing the largest concentrations of analcime yielded 0.34 to 0.38 weight percent of SiO_2 . Conversely the smallest amounts of SiO_2 were obtained from dawsonite-bearing samples which were free of analcime and these ranged from 0.01 to 0.05 weight percent of SiO_2 . Samples free of both dawsonite and analcime yielded between 0.06 and 0.16 weight percent of SiO_2 , which is intermediate between the low values obtained for dawsonite-bearing samples, and the high values for analcime-bearing samples, respectively.

Amounts of Al_2O_3 ranged from 0.02 to 0.87 weight percent and the highest values were for dawsonite-bearing samples. However, all dawsonite-bearing samples did not consistently yield more Al_2O_3 than samples which were free of dawsonite. The values of Al_2O_3 obtained for the Colony composite sample are more than 200 times greater than the values of 2 ppm (Al) reported by Nevens, Culbertson, and Hollingshead (1970), but this is undoubtedly due to the different conditions of extraction.

Weight percent proportions of Al_2O_3 , SiO_2 , and Na_2O extracted from all samples are shown on a ternary diagram on which the compositions of analcime and dawsonite are illustrated (fig. 3). This illustration shows that both analcime and dawsonite contribute to the amounts of Na_2O

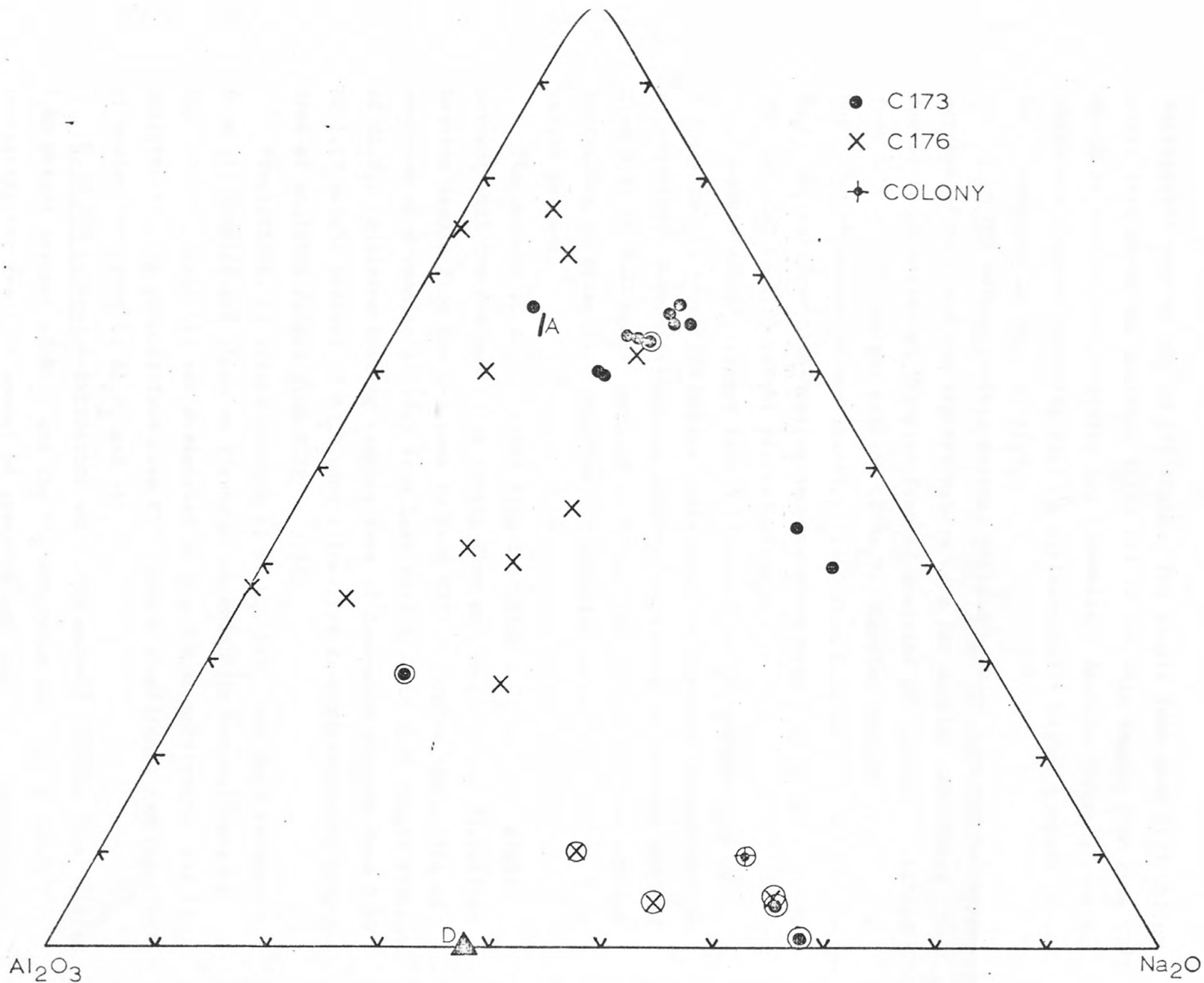


Figure 3.--Weight percent proportions of Al₂O₃, SiO₂, and Na₂O extracted from spent shale with H₂O. A designates the composition of analcime and D designates the composition of dawsonite. Circled symbols indicate samples which contain dawsonite according to X-ray diffraction analysis of raw shale.

extractable from pyrolyzed oil shale. The sample from core C173 which plots just above the analcime field (A) is the only sample from core C173 which is free of both analcime and dawsonite. Analcime-bearing samples which are free of dawsonite yield a preferentially higher proportion of Na_2O , compared to SiO_2 and Al_2O_3 .

0.1M KOH solvent.--This solvent yielded between 0.06 and 2.5 weight percent of Na_2O and the highest values were for samples containing dawsonite or analcime. Samples free of analcime and dawsonite yielded from 0.06 to 0.98 weight percent of Na_2O . Samples containing analcime, but in which dawsonite was absent, yielded from 0.72 to 1.61 weight percent Na_2O , whereas dawsonite-bearing samples which were free of analcime yielded 0.37 to 2.50 weight percent of Na_2O .

Amounts of SiO_2 ranged from 0.17 to 4.0 weight percent and the highest values were from samples containing the greatest concentrations of analcime. Dawsonite-bearing samples containing no analcime yielded from 0.17 to 0.72 weight percent of SiO_2 . The SiO_2 yield from samples containing no detectable analcime or dawsonite ranged from 0.2 to 0.98 weight percent.

The amounts of Al_2O_3 ranged from less than 0.02 to 3.36 weight percent with the maximum value coming from an analcime-free dawsonite-bearing sample from the R-4 zone in core C173. Samples containing no analcime or dawsonite yielded from less than 0.02 to 0.67 weight percent of Al_2O_3 . Analcime-bearing samples free of dawsonite yielded from 0.29 to 1.19 weight percent of Al_2O_3 and values for dawsonite-bearing samples free of analcime ranged from 0.32 to 3.36.

Proportions, by weight percent, of Al_2O_3 , SiO_2 , and Na_2O extracted from all samples are shown on figure 4, on which the compositions of analcime and dawsonite are designated by A and D, respectively. The 12 analcime-bearing samples from core C173 show a significant contribution of sodium, compared to Al_2O_3 and SiO_2 .

0.5M KOH solvent.--Extraction with this solvent yielded from 0.18 to 2.80 weight percent of Na_2O and the highest value was from a sample containing the greatest amount of analcime and only minor dawsonite. Samples in which both dawsonite and analcime were absent yielded from 0.18

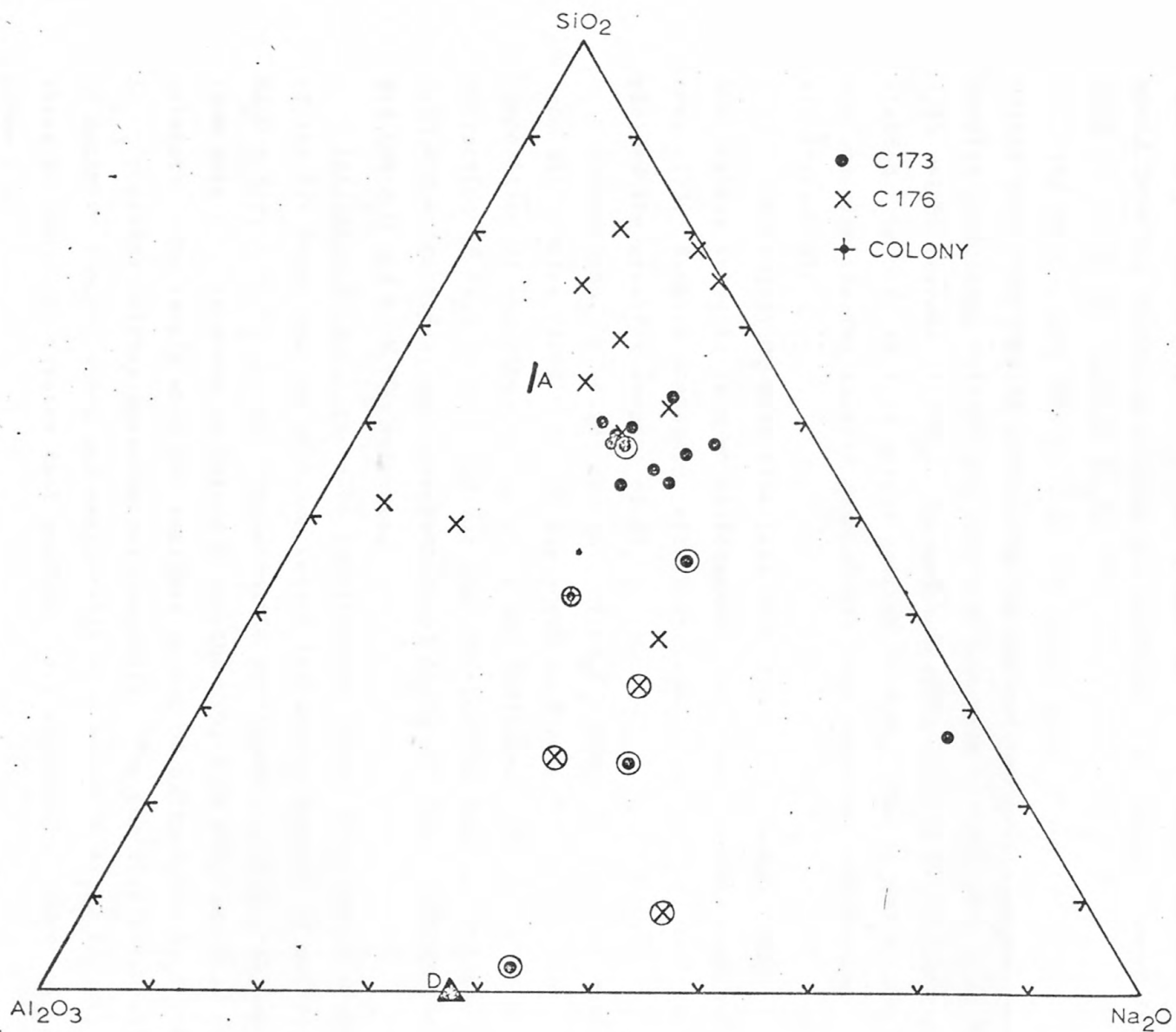


Figure 4.--Weight percent proportions of Al₂O₃, SiO₂, and Na₂O extracted from spent shale with 0.1M KOH. A designates the composition of analcime, and D designates the composition of dawsonite. Circled symbols indicate samples which contain dawsonite according to X-ray diffraction analysis of raw shale.

to 0.45 weight percent of Na_2O . The analcime-bearing and dawsonite-free samples yielded from 0.89 to 2.02 weight percent of Na_2O , whereas the yield from the dawsonite-bearing and analcime-free samples ranged from 0.45 to 2.4 weight percent Na_2O .

The SiO_2 ranged from 0.21 to 5.6 weight percent and the highest values were from samples containing the highest concentration of analcime. Samples containing neither analcime nor dawsonite yielded from 0.21 to 1.15 weight percent of SiO_2 . Dawsonite-bearing samples free of analcime yielded from 0.27 to 1.16 weight percent of SiO_2 . The higher values from the analcime-bearing samples demonstrate that analcime contributes significant SiO_2 .

Values for Al_2O_3 were from less than 0.02 to 3.9 weight percent and the highest value is from an analcime-bearing dawsonite-free sample from core C173. Samples containing either analcime or dawsonite, or both, yielded the greatest amounts of Al_2O_3 .

Proportions, by weight percent, of Al_2O_3 , SiO_2 , and Na_2O extracted from all samples using 0.5M KOH are shown on figure 5, on which the composition of analcime and dawsonite are indicated. Preferential extraction of Na_2O is observed for analcime-bearing samples, but the 0.5M KOH extracted a higher proportion of Al_2O_3 for these samples than did the H_2O and 0.1M KOH solvents.

Influence of analcime.--The relationship of the relative intensity of the 211 X-ray peak of analcime versus the weight percent of extractable $\text{Na}_2\text{O} + \text{SiO}_2 + \text{Al}_2\text{O}_3$ for all nondawsonitic pyrolyzed oil-shale samples from core C173 is shown on figure 6 for the H_2O , 0.1M KOH, and 0.5M KOH solvents. The sample with the smallest amount of extractable $\text{Na}_2\text{O} + \text{SiO}_2 + \text{Al}_2\text{O}_3$ contains neither analcime nor dawsonite. The positive correlation of analcime concentration and extractable $\text{Na}_2\text{O} + \text{SiO}_2 + \text{Al}_2\text{O}_3$ for all three solvents illustrates that analcime is a significant source of these three elements.

Extractable Al_2O_3 and SiO_2 .--Amounts of Al_2O_3 and SiO_2 extracted from spent shale using 0.1M NaOH and 0.5M NaOH are shown for 30 spent shale samples on figure 7. In the case of the 0.1M NaOH solvent, only five of the 30 samples have more extractable Al_2O_3 than SiO_2 , whereas

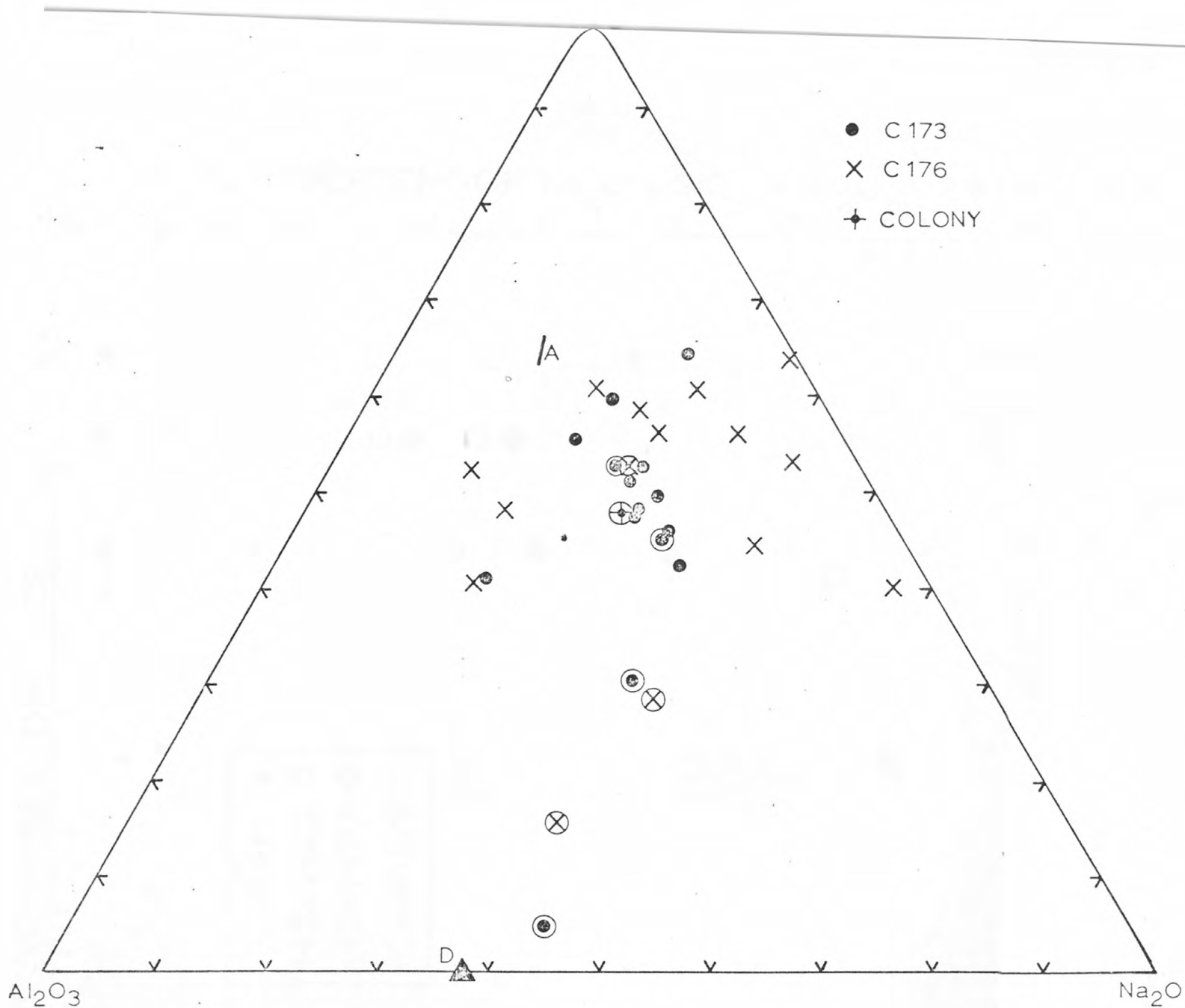


Figure 5.--Weight percent proportions of Al_2O_3 , SiO_2 , and Na_2O extracted from spent shale with 0.5M KOH. A designates the composition of analcime, and D designates the composition of dawsonite. Circled symbols indicate samples which contain dawsonite according to X-ray diffraction analysis of raw shale.

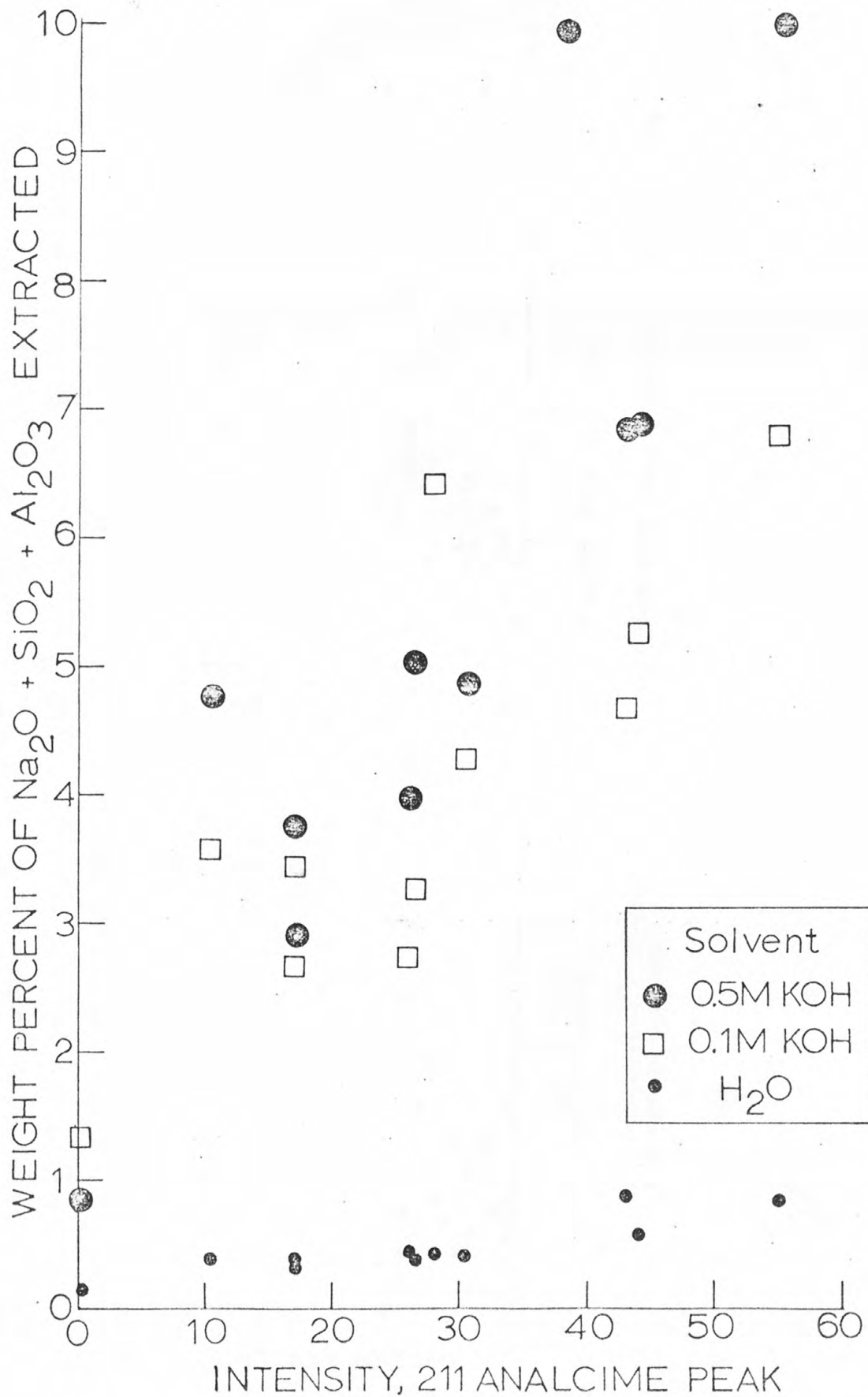


Figure 6.--Contribution of analcime to the amount of $\text{Na}_2\text{O} + \text{SiO}_2 + \text{Al}_2\text{O}_3$ extractable from non-dawsonitic spent shale from core C173. Analcime 211 peak intensities determined on raw shale samples.

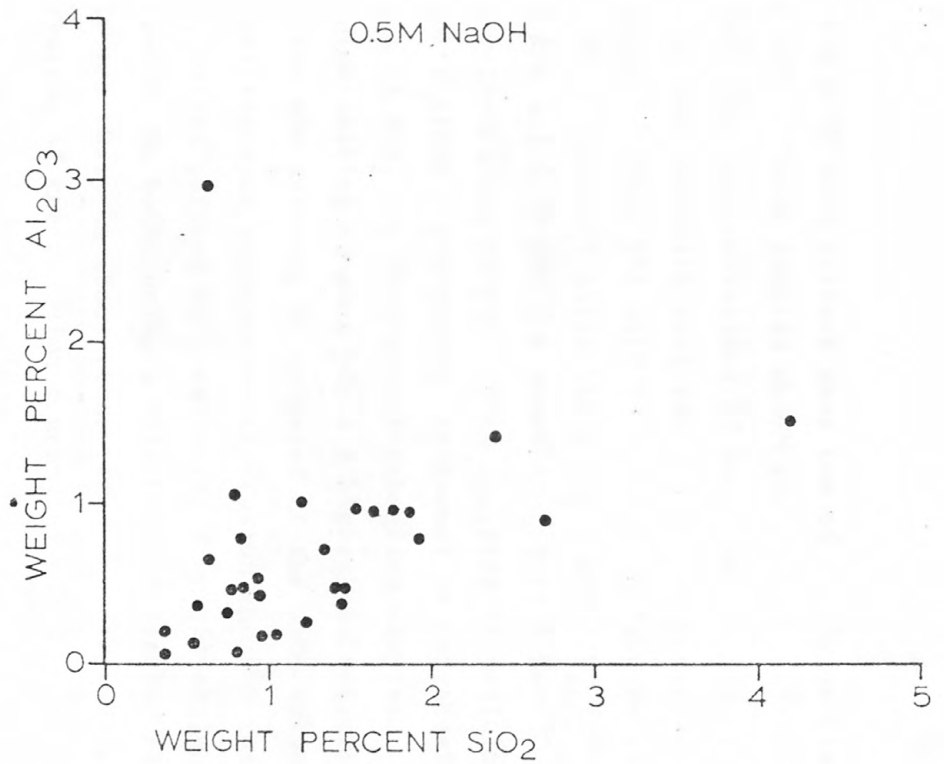
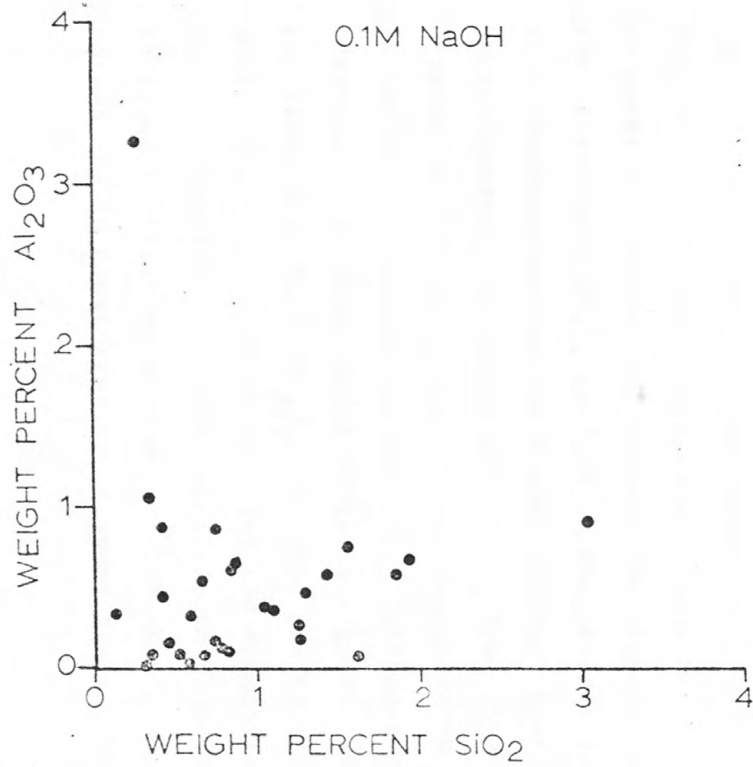


Figure 7.--Relations of Al_2O_3 and SiO_2 extracted from 30 spent shale samples from core C173 and C176 using 0.1M NaOH and 0.5M NaOH.

for the 0.5M NaOH solvent only two of the 30 samples yield more Al_2O_3 than SiO_2 . Those samples which yield the highest amounts of SiO_2 contain high concentrations of analcime, and in general the analcime-bearing and dawsonite-free samples yield more than twice as much SiO_2 as Al_2O_3 for both the 0.1M NaOH and 0.5M NaOH solvents.

The amounts of extractable Al_2O_3 and SiO_2 from spent shale using 0.1M KOH and 0.5M KOH are shown on figure 8 for 30 samples. Only dawsonite-bearing samples which are free of analcime yield Al_2O_3 concentrations which exceed the amount of extractable SiO_2 . The highest values of SiO_2 are from analcime-bearing samples. In general, the analcime-bearing samples yield a higher concentration of SiO_2 than Al_2O_3 from the KOH solvent, as compared to the NaOH solvents. Figure 9 shows the relations of analcime concentration and the ratio of weight percent Al_2O_3 /weight percent SiO_2 extracted from oil shale containing analcime, dawsonite, or both, using a mild caustic leach. For samples containing analcime, there is about three times as much SiO_2 extracted as Al_2O_3 regardless of the analcime concentration.

DISCUSSION OF RESULTS AND CONCLUSIONS

Analcime contributes significantly to the amount of Na_2O , Al_2O_3 , and SiO_2 extracted from pyrolyzed oil shale when it is leached with either water or alkaline solutions. The highest concentration of caustic extractable Al_2O_3 is 3.36 weight percent in a sample which contains dawsonite as the third most abundant mineral. The value of 3.36 weight percent of extractable Al_2O_3 from this spent shale sample corresponds to 7.58 weight percent of dawsonite in the raw shale. This sample yields 12.7 weight percent (33.5 gallons per ton) of oil.

Pyrolyzed oil shale which contains significant analcime will release several times more Na_2O , Al_2O_3 , and SiO_2 due to leaching by water than oil shales which are free of analcime and dawsonite. After pyrolysis of dawsonite-bearing oil shale, significant quantities of Na_2O and Al_2O_3 are released by leaching with water. These mineralogical considerations are noteworthy in consideration of spent shale disposal.

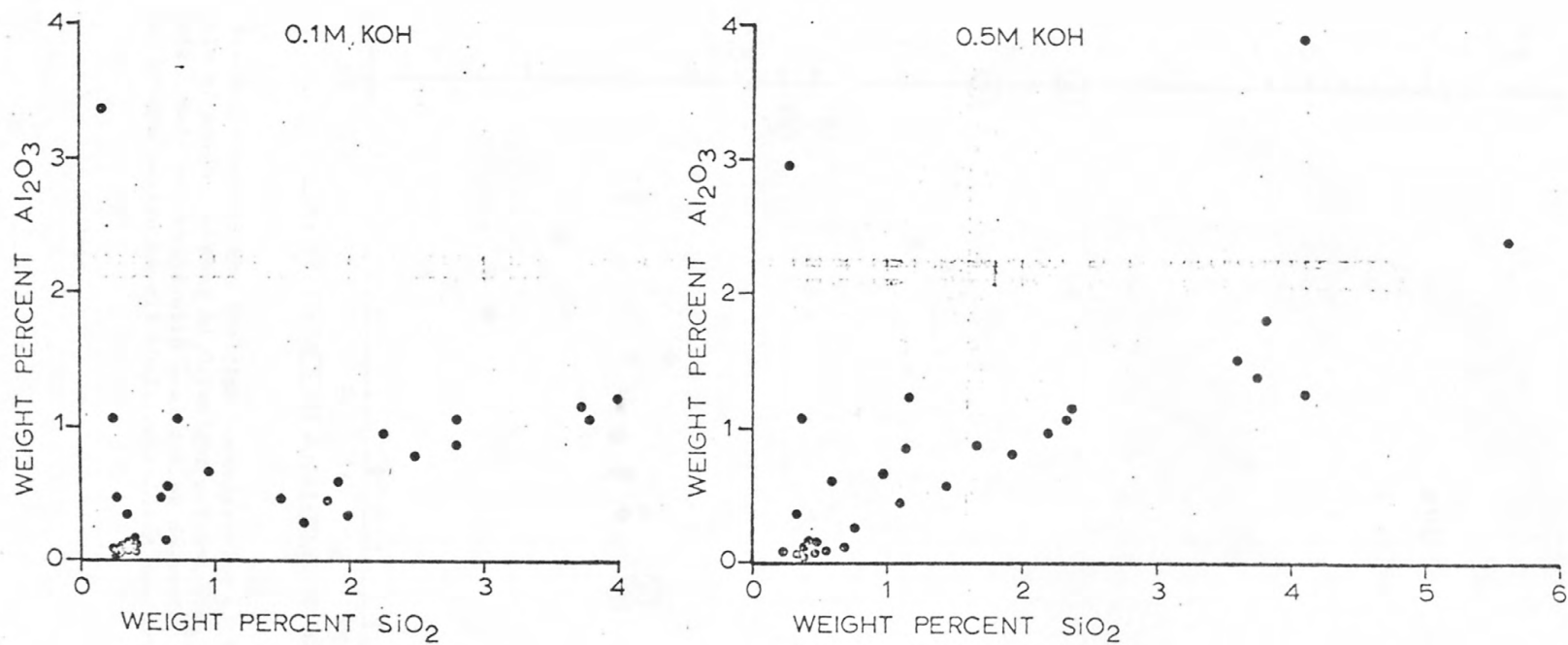


Figure 8.--Relations of Al₂O₃ and SiO₂ extracted from 30 spent shale samples from C173 and C176 using 0.1M KOH and 0.5M KOH.

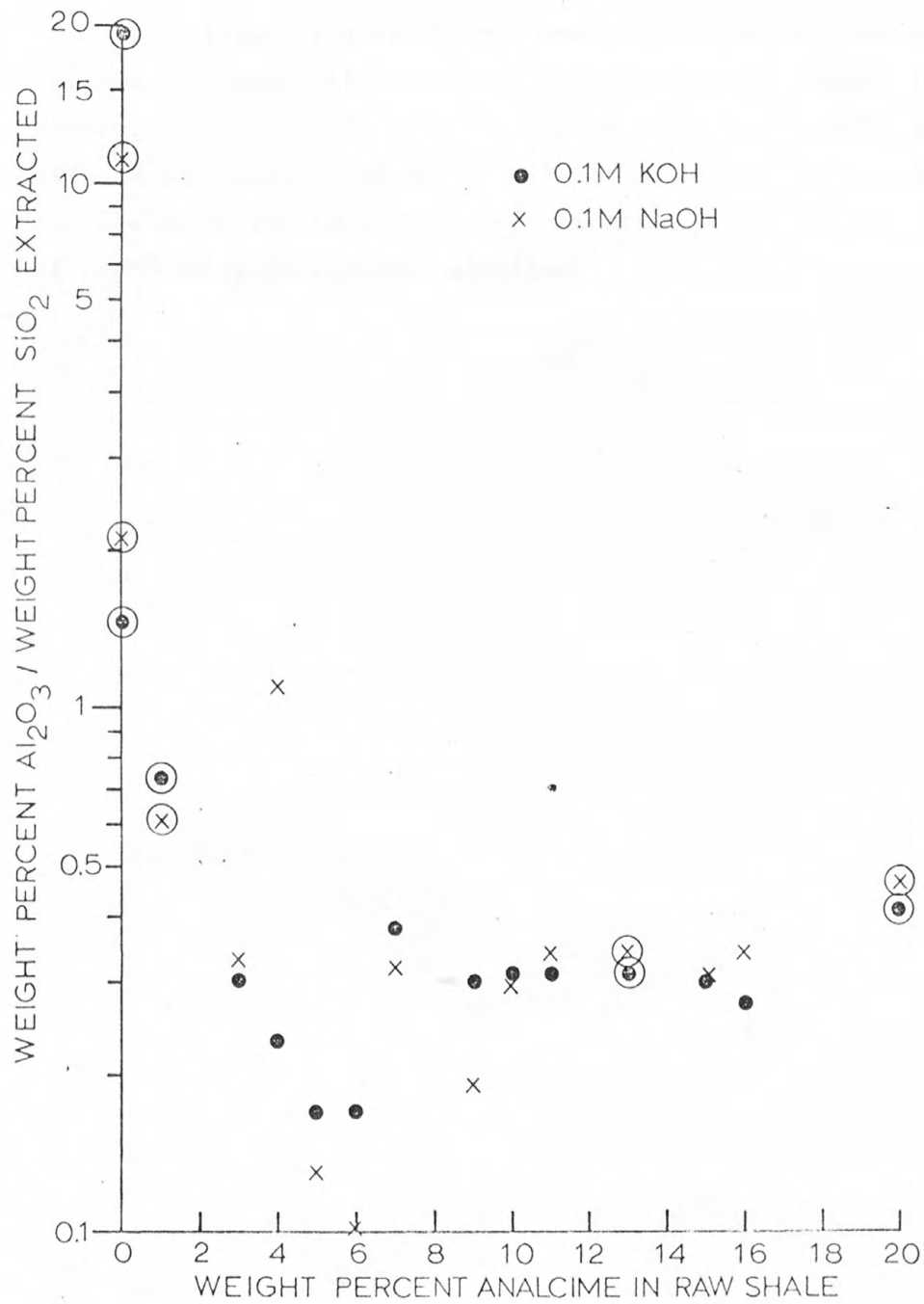
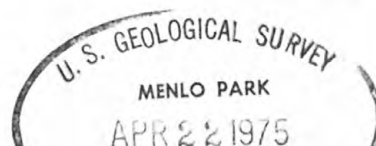


Figure 9.--Relations of the analcime concentration of raw oil shale to the ratio of weight percent Al_2O_3 /weight percent SiO_2 extracted from spent shale. Only oil shale with analcime or dawsonite is shown. Circled data points designate oil shale containing dawsonite.

If analcime is present in dawsonite-bearing oil shales, caustic leaching of these oil shales after pyrolysis will result in high concentrations of SiO_2 in the leachate which may inhibit or prohibit efficient extraction of Al_2O_3 from the leachate. Therefore, careful consideration should be given to oil-shale mineralogy in the assessment of potentially extractable aluminum.

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