

SPECTROGRAPHIC EXAMINATION OF THE OCCURRENCE OF CERTAIN ALKALI ELEMENTS IN CALCITE MARBLES

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ABSTRACT

More than 100 samples of calcite marbles were analyzed spectrographically by the line width method for three alkali elements: sodium, potassium, and lithium. Sodium content varied from 0.001 to 0.067%, potassium content from <0.005 to 0.43%, and lithium content from none to 0.0018%. Rubidium was found only in four marbles in trace amounts. A geographical pattern was discernible. Statistical resolutions of the errors showed the film error to be somewhat greater than the analytical, and both errors combined were found to vary from one-half to one-fifth of the sampling error. In spite of pronounced scattering, a general potassium-sodium relationship of 5:1 was observed. Where potassium was 0.2% or higher, trace amounts of rubidium were detected.

INTRODUCTION

In the course of some exploratory examinations of marble samples from commercial quarry beds throughout the United States considerable variations in the sodium and potassium content were observed. It was thought that knowledge of the alkali content from a wide selection of samples might be helpful in some geological and weathering interpretations.

SPECTROGRAPHIC ANALYSIS

Spectrographic analysis is ideally suited to this problem for several reasons: (1) Four alkali elements (lithium, sodium, potassium and rubidium) are detectable in a single spectrographic exposure range. (2) A single sample can be completely analyzed in much less time than is required for a sodium determination by chemical methods. (3) Such small amounts of these alkalis were present in most of the samples that the use of chemical methods would not have been sufficiently sensitive.

The spectral phenomenon of self-reversal is particularly strong in the alkali elements and always enters the problem of analysis when more than ten times the detectable limit is present. Self-reversal, an effect which produces the so-called Fraunhofer or dark lines in the solar spectrum, is due to the absorption of some of the emitted light by the colder vapors surrounding arcs and flames. It causes the intensity of certain spectral radiations to be abnormally diminished. Consequently any concentrations determined from peak intensity measurements of such ab-

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sorbed lines will be low. Dilution of the samples down to a normally useable range would have entailed a great deal of survey work and subsequent errors for the large number of samples to be analyzed. The line width method has been used for various problems where self-reversal has been present (Coheur, 1946, Eastmond and Williams, 1948). In this method a trace of the line is made by a Leeds and Northrup microphotometer from which the line width at 60% transmission is measured and used as a function of the concentration present. This technique can be used over a concentration range of more than 2000 fold while the usual procedure is useful for about a 20 fold range.

ANALYTICAL PROCEDURE

A series of standards was made to contain 0.003%, 0.01%, 0.03%, 0.1%, and 0.3% sodium and potassium and 1/10 of those amounts of lithium. The base material was calcium carbonate precipitated from c.p. calcium nitrate solution and washed more than 30 times with hot, deionized water (Archibald, 1932). A residual correction method indicated that 0.001% sodium was present (Nachtrieb, 1950). This amount was compensated for when plotting working curves of log *line widths* vs. log *concentrations*. The presence of no other alkalis was detected in the calcium carbonate base.

Samples selected for analysis were crushed and ground to pass a 100-mesh bolting cloth sieve. High purity graphite electrodes, 6.3 mm. in diameter with 2 mm. deep center post craters, were packed level with standard or sample material and burned in a 300-volt direct current arc at 12 amperes for 60 seconds. Spectra were recorded by an Applied Research Laboratories two-meter grating spectrograph on Eastman Spectroscopic Film type I-L. A Wratten K-2 filter was placed at the slit to absorb the interfering radiations. The camera was positioned so that the following lines were recorded whenever they were present: sodium 5889.95 Å, lithium 6707.84, potassium 7664.90, and rubidium 7800.23. Cesium, which has a relatively poor sensitivity, has lines that occur beyond the wavelength range of the spectrograph at the camera setting for sodium. Consequently the presence of cesium was not sought.

OBSERVATIONS

Information was desired as to the magnitudes of the film and experimental errors and as to the size of these two errors as compared with the sampling error. To obtain the former, a large number of spectra were made of two different samples, and the statistical results of one sample, Vermont Imperial Danby marble, are shown in Table 1. The other sample, Tennessee Ross Pink marble, indicated comparable precision. The results and accompanying analyses of variance are given in Table 1.

TABLE 1. PRECISION OF DETERMINATIONS OF SAMPLE OF VERMONT
IMPERIAL DANBY MARBLE

<i>Sodium Analyses</i>				
	Film A	Film B	Film C	Film D
	0.0072	0.0064	0.0072	0.0072
	0.0092	0.0092	0.0086	0.0058
	0.0092	0.0090	0.0072	0.0072
	0.0092	0.0060	0.0078	0.0098
	0.0088	0.0092	0.0064	0.0072
<i>Film Averages</i>	0.0087	0.0080	0.0074	0.0074
<i>Sample Average</i>	0.0079 per cent sodium			
Analysis of Variance of Sodium Determinations				
Variance Associated with	Degrees of Freedom	Variance	F Ratio	1% Level Critical F Values
Films	3	0.00000180	2.03	4.5
Analyses	4	0.00000110	1.24	4.0
Experimental Error	29	0.000000886	—	—
<i>Potassium Analyses</i>				
	Film A	Film B	Film C	Film D
	0.074	0.060	0.067	0.058
	0.064	0.059	0.069	0.060
	0.078	0.060	0.078	0.064
	0.077	0.055	0.073	0.070
	0.079	0.055	0.069	0.064
<i>Film Averages</i>	0.074	0.058	0.071	0.063
<i>Sample Average</i>	0.067 per cent potassium			
Analysis of Variance of Potassium Determinations				
Variance Associated with	Degrees of Freedom	Variance	F Ratio	1% Level Critical F Values
Films	3	0.000285	4.0	4.5
Analyses	4	0.000033	0.46	4.0
Experimental Error	29	0.000072	—	—

In making an analysis of variance (Youden, 1951), the error associated with the four different films in Table 1 was calculated and found to be less than the critical F value in comparison with the experimental error at the one per cent confidence level for both sodium and potassium. The variance associated with the analyses was lower than the film variance; for potassium the low analytical F ratio reflects the much greater differences among the films for that element. The relative magnitudes of the F ratios show, with one chance in a hundred of being incorrect, that the errors are not large enough to be the result of chance and can be relied on to that extent.

Resolution of the errors was continued by investigating the sampling error. Thirty-seven samples of three calcite marbles were analyzed in triplicate or in duplicate and the magnitudes of the errors were established in terms of the standard deviations, as shown in Table 2. It is apparent that the sampling error was two to five times the film and analytical errors combined.

TABLE 2. RESOLUTION OF ERRORS FOR THREE CALCITE MARBLES

State	Name of Marble	Number of Samples	Number of Analyses	Element Found	Averages, Per Cent	Standard Deviations, Per Cent	
						Film + Analytical	Sampling
Alabama	Cream	12	24	Na	0.0060	0.00141	0.00280
				K	0.026	0.0038	0.0068
Georgia	Creole	12	36	Na	0.011	0.00083	0.0042
				K	0.015	0.0025	0.0138
Georgia	White	13	26	Na	0.0038	0.00118	0.00172
				K	<0.001	—	—

The samples were selected at random, in order to minimize bias, from a large number of freshly-quarried marble samples cut from three mutually perpendicular directions in the quarry beds. The trade names have been utilized for identification of the marbles since the color, grain size, and textural patterns associated with the names are adhered to quite closely by the industry. After intensive analyses to establish the magnitudes of the errors for the three marbles discussed above, the investigation was broadened to include as large a number of marble varieties as possible.

Duplicate determinations were made and averaged to furnish sample

TABLE 3. PER CENT ALKALI ELEMENTS IN VARIOUS CALCITE MARBLES

State of Origin	Name of Marble	Number of Sample	Potassium				Sodium				Lithium	
			Average	Standard Error	Low Sample	High Sample	Average	Standard Error	Low Sample	High Sample	Average	High Sample
<i>Alabama</i>	Cream	12	0.026	0.002	0.016	0.037	0.0060	0.0005	0.0031	0.0097	<0.0001	<0.0001
	Madre Cream	1	0.016	—	—	—	<0.001	—	—	—	<0.0001	—
	Madre Veined	1	0.042	—	—	—	0.0059	—	—	—	N.D.	—
	Madre Veined	1	0.46	—	—	—	0.030	—	—	—	0.0018	—
<i>Georgia</i>	Creole	12	0.015	0.007	<0.005	0.072	0.011	0.001	0.0074	0.022	<0.001	<0.001
	White	13	<0.001	—	—	—	0.0038	0.0005	0.0023	0.0074	N.D.	N.D.
	White Cherokee	3	<0.003	—	<0.003	<0.003	0.0092	0.0014	0.0065	0.0111	N.D.	N.D.
	Silver Gray	1	<0.005	—	—	—	0.0077	—	—	—	N.D.	N.D.
	Etowah	3	0.073	0.035	0.035	0.145	0.047	0.008	0.032	0.058	N.D.	N.D.
<i>Missouri</i>	Ozark Tavernelle	6	0.035	0.003	0.024	0.042	0.012	0.001	0.0096	0.015	<0.0001	<0.0001
	Ozark Veined	1	0.055	—	—	—	0.014	—	—	—	<0.0001	<0.0001
	St. Genevieve Rose	1	0.041	—	—	—	0.013	—	—	—	<0.0001	<0.0001
	St. Genevieve Golden Vein	1	0.019	—	—	—	0.019	—	—	—	<0.0001	<0.0001
<i>Vermont</i>	Imperial Danby	7	0.081	0.018	0.010	0.145	0.012	0.003	0.0030	0.027	0.0001	0.0001
	Standard White	3	0.17	0.01	0.16	0.18	0.0068	0.0027	0.0030	0.012	0.0001	0.0001
	Brocardillo	6	0.24	0.01	0.20	0.30	0.042	0.007	0.025	0.067	0.00072	0.00072
	Westland Cippolino	6	0.34	0.06	0.24	0.43	0.082	0.007	0.054	0.10	0.0011	0.0011
	Verdoso	1	0.40	—	—	—	0.027	—	—	—	0.0013	0.0013
	Metawee	1	0.093	—	—	—	0.068	—	—	—	0.0001	0.0001
	Pearl	1	0.21	—	—	—	0.018	—	—	—	0.0008	0.0008
	Clarendon Light Exterior	1	0.083	—	—	—	0.084	—	—	—	<0.0001	<0.0001
	West Rutland White Exterior	1	0.040	—	—	—	0.043	—	—	—	N.D.	N.D.
	Pittsford Italian	1	0.047	—	—	—	0.080	—	—	—	<0.0001	<0.0001
	Pittsford Valley	3	0.053	0.005	0.045	0.062	0.066	0.0005	0.0058	0.0078	N.D.	N.D.
	Neshobe	1	0.020	—	—	—	0.051	—	—	—	N.D.	N.D.
	Neshobe Gray	3	0.0083	0.0016	0.0023	0.018	0.016	0.001	0.0032	0.0070	N.D.	N.D.
West Blue	1	0.026	—	—	—	0.0058	—	—	—	<0.0001	<0.0001	
<i>Tennessee</i>	Ross Pink	3	0.014	0.002	0.0070	0.027	0.053	0.003	0.014	0.023	<0.0001	<0.0001
	Cedar Tavernelle	3	0.11	0.006	0.10	0.12	0.018	0.001	0.017	0.019	0.0002	0.0002
	Granox Quaker Gray	3	0.040	0.009	0.029	0.058	0.057	0.002	0.0016	0.022	0.0002	0.0002

N.D. = Not Detected.

means. When the values deviated from the mean by more than 25%, re-determinations were made and used. The results are tabulated in Table 3 for sodium, potassium, and lithium. The rubidium line 7800.23 Å indicated trace amounts in the spectra of only Alabama Madre Veined, Vermont Brocadillo, Vermont Westland Cippolino and Vermont Verdoso marbles. It is worth mentioning that the samples in which the potassium was 0.2% or higher also contained rubidium in detectable amounts. The confidence limits of the sample average can be obtained by multiplying the standard error as given in Table 3 by the desired confidence interval. The standard error was computed using the equation

$$s_{\bar{x}} = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n(n-1)}}$$

where

\bar{x} = arithmetic mean,

x_i = single sample,

n = number of samples.

It was observed, upon plotting the sample means of sodium vs. potassium on log-log paper, that there was a general relationship in which the potassium was for the most part five times greater than the sodium. Scattering was pronounced, however, and a few individual cases showed ratios varying between 0.5 and 50. A general geographical pattern was observed. The Georgia samples ran less than 0.01% sodium and very low in potassium, thus causing a strong divergence from the five to one ratio for potassium-sodium noted above. The Alabama marbles with one exception were quite low in sodium. Vermont samples in general showed a high concentration of alkali elements.

SUMMARY

Over 100 samples of calcite marbles have been analyzed for sodium and potassium by measuring the width of the spectral line. It was observed that the alkali content followed a pattern depending on the geographical origin. In general, where sodium was high, potassium showed a ratio of 5:1. Where potassium was above 0.2%, the presence of rubidium was observed in four cases.

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