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Cover Picture

GEOLOGIST AND CANEY CONCRETION

The photograph is of Hugh Dinsmore Miser, compiler of the 1926 and 1954 editions of the *Geologic Map of Oklahoma*.

Dr. Miser is shown on a concretion in the Delaware Creek Member of the Caney Shale. The locality is in a dredged cutoff of Jackfork Creek, just west of State Highway 99, in sec. 35, T. 3 N., R. 6 E., Pontotoc County. This is the locality from which E. B. Branson and M. G. Mehl obtained the conodonts described by them in 1940.

M. K. Elias named and described the Delaware Creek Member in 1956. The unit is a dark shale characteristically bearing large concretions (as large as 12 feet in diameter). Many concretions contain numbers of the cephalopod *Goniatites choctawensis*, a Meramecian index fossil. The Delaware Creek Member underlies the Sand Branch Member (Chesterian) and overlies the Ahlsoo Member, which is not clearly divided from the Delaware Creek. In the type section on Delaware Creek it is 270 feet thick. The "*Goniatites choctawensis* lentil" of Elias is typified by the area of the photograph and is the lowermost lentil of limestone concretions.

—C. C. B.

GEOLOGIC PUBLICATIONS BY OKLAHOMA ORGANIZATIONS

CARL C. BRANSON

As is the case in most states and countries, some geologic publications have started, ceased, changed names, and have otherwise caused confusion for bibliographers and librarians. Many change editors and mailing addresses, change format, frequency of publication, and method of printing. This article is an attempt to call attention to irregular Oklahoma publications in geology.

STATE AGENCIES

Territorial Survey

The oldest serial is the Biennial Report of the Department of Geology and Natural History Survey, Territory of Oklahoma. The Territorial Survey was founded in 1898 and was superseded by the Oklahoma Geological Survey in 1908.

The manuscript of the *First Biennial Report* was destroyed by fire. A report entitled *Advance Bulletin*, issued in 1902, which was to have been part of the first report, was an illustrated paper by J. W. Beede on the invertebrate fossils of the Whitchorse sandstone (now the Doe Creek Member of Marlow Formation).

The *Second Biennial Report* (for 1901-1902) was published in 1903 and contained three articles on geology, one on plants, one on birds, and one on snakes.

The *Third Biennial Report* (for 1903-1904), published in 1904, consisted of three geologic articles. No report was issued for 1905-1906.

Oklahoma Geological Survey

The Oklahoma Geological Survey was activated on July 25, 1908, under the directorship of C. N. Gould. The bulletin series was initiated immediately with the publication of Bulletin 1 in that year. Some subsequent bulletins did not correspond in numerical designation with the chronological order of publication and did not appear until years afterward; for example, Bulletin 4, *Coal in Oklahoma*, did not appear until 1926, and Bulletin 12, issued in 1927 and apparently planned for some other topic, was a crude reprint of U. S. Geological Survey Professional Paper 31. Bulletin 14 was issued in 1929. Bulletin 40, *Oil and Gas in Oklahoma*, was published in three volumes, volume 1 in 1928 and volumes 2 and 3 in 1930, but individual chapters were issued separately as they became available during the period 1926-1930.

Bulletins 54 and 56 were published by the University of Oklahoma Press in 1932 and few copies carry the bulletin number.

The bulletin series is now through Bulletin 113, but Bulletin 110 will probably not be issued until 1968.

The circular series is of shorter reports. Circular 1 was issued in 1908. Circular 4 was on trees and shrubs, and Circular 6 was on animal and plant life. Circular 70 was published on December 20, 1965, and Circular 72 on August 8, 1966. Circulars 71 and 74 will appear late in 1967.

The mineral-report series was begun in 1938 in mimeographed form (numbers 1-23). Later issues were printed by letterpress. The series ended in 1959 with Mineral Report 36.

Directors' biennial reports have been issued irregularly. The first report was in Bulletin 6 (1910), the second report was Part 1 of Bulletin 15 (1912), the third report was Part 1 of Bulletin 22 (1914). Directors' biennial reports were published in 1936, 1938, 1940, 1942, 1944, 1947, 1949, and 1955. The last of the series was the *Semi-Centennial Report, 1908-1958* (147 p., 1958).

Guide books have been of several types. Eleven mimeographed road logs of field trips were issued in 1925, 1926 (4), 1927 (4), 1928 (2). In 1929 the "Fifteenth Geological Field Conference" in the Arbuckle Mountains had a mimeographed 21-page guide book. The "Seventeenth Geological Field Conference" (1930) had a 14-page book, the "Eighteenth" (1930), 11 pages, the "Nineteenth" (1930), 14 pages.

In 1934 a 38-page book was issued for a trip in the Ada area. Five "Mineral Resources Field Trips" had guide books, issued in mimeographed form in 1930, 1945, 1946 (2), and 1950. A guide book of 9 pages was issued for an "industrial tour" in 1947.

The first formal guide book, Guide Book I (41 p.), was issued in 1953 with the Oklahoma City Geological Society. Others in the guide-book series are Guide Book II (1954, 41 p.) with the Oklahoma City Geological Society, Guide Book III (1955, 61 p.) with the Ardmore Geological Society, Guide Book IV (1956, 76 p.) with the Tulsa and Oklahoma City Geological Societies, and Guide Book V (1957, 58 p.) with the Panhandle Geological Society. Subsequent guide books and their years of publication are: VI, 1957 (220 p.); VII, 1958 (23 p.); VIII, 1959 (48 p.); IX, 1959 (31 p.); X, 1960 (28 p.); XI, 1963 (46 p.); XII, 1963 (95 p.); XIII, 1963 (139 p.); XIV, 1964 (48 p.); XV, to be issued in 1968; and XVI, 1966 (39 p.).

Control circulars were issued in mimeographed form as nos. 1-3, 1940-1941, to give results of the Oklahoma Geodetic Survey. These data were continued in Bulletins 58 and 61. The eastern half of the State was not surveyed.

The Survey issued a mimeographed periodical from 1941 to 1955 as *The Hopper*, volumes 1-15. Volume 1 had six numbers, 2 through 11 twelve numbers, 12 seven numbers, and 13 six numbers. *The Hopper* was superseded by the *Oklahoma Geology Notes*, with ten numbers annually in volumes 14 and 15, and thereafter, monthly through current volume 27.

The Survey issued in 1960 a *Guidebook, Paleobotanical Field Trip* for the American Institute of Biological Sciences, an edition limited to 100 copies.

Bureau of Geology

In 1923, when Governor Jack Walton cut off funds for the Survey, C. W. Shannon attempted to continue the work on a self-supporting basis with the Bureau of Geology. This organization published Bulletin 2, *Geology of the Stonewall Quadrangle*, in 1924; no Bulletin 1 appeared. Circulars 2 and 3 were published in 1924, but no Circular 1.

Shannon also started the *Bureau Monthly*, of which only volume 1, number 1 (1925) was published.

Department of Mines

The Department of Mines, Chief Mine Inspector, publishes annual reports containing much geological information. The last number received is the fifty-eighth annual report for the year ending December 31, 1966, issued in 1967.

Panhandle Agricultural Experiment Station

The *Panhandle Bulletin* was published monthly by Panhandle Agricultural and Mechanical College, Goodwell. Bulletin 38, May, 1932, was a report on water in Cimarron County, mainly ground water and its quality.

University of Oklahoma

A series of individual papers was issued as *The State University of Oklahoma, Research Bulletin*. The University Press printed the bulletins, of which numbers 3 and 4 (1910) were on geological subjects.

The *Proceedings of the Oklahoma Academy of Science* were also issued for some years as *University of Oklahoma Bulletins* (see *Oklahoma Academy of Science*).

The School of Geology and the Extension Division published proceedings of eight biennial geological symposia, with varying titles as follows:

- 1949. Subsurface Geological Symposium. 113 p.
- 1951. Second Subsurface Geological Symposium. 143 p.
- 1953. Proceedings of the Third Subsurface Geological Symposium. 94 p.
- 1955. Proceedings of the Fourth Subsurface Geological Symposium. 115 p.
- 1957. Proceedings of the Fifth Biennial Symposium on Subsurface Geology. 167 p.
- 1959. Proceedings of the Sixth Biennial Geological Symposium. 175 p.
- 1961. Proceedings of the Seventh Biennial Geological Symposium. 234 p.
- 1963. Proceedings of the Eighth Biennial Geological Symposium. 174 p.
- 1966. A ninth biennial symposium was presented, but no proceedings were published.

Oklahoma State University

The Engineering Experiment Station of Oklahoma Agricultural and Mechanical College published a report on clays and shales of Oklahoma, prepared jointly with the Oklahoma Geological Survey. This 251-page book appeared in 1932 as *Division of Engineering Publication*, volume 3, number 5 (also listed as *Engineering Experiment Station Publication 17*). A book of 474 pages on chemical analyses of the waters of Oklahoma was issued in 1942 as *Division of Engi-*

neering Publication, volume 12, number 1 (Engineering Experiment Station Publication 52).

State Department of Highways

The Research and Development Division has prepared and issued books, *Engineering Classification of Geological Materials*, on two of the eight highway divisions of the State. These were distributed in 1965 (Division Eight, 287 p.) and 1966 (Division Two, 356 p.).

Oklahoma Water Resources Board

Originally Water Resources Division of the Planning and Resources Board, the agency became the Water Resources Board in 1957. Bulletins have been published, Bulletin 4 in 1949, Bulletin 27 in 1965. No copies of Bulletins 1, 2, or 3 have been located. In 1965, the Board published *Ground Water in the Rush Springs Sandstone, Caddo County Area* as Publication 11.

GEOLOGICAL AND GEOPHYSICAL SOCIETIES

Oklahoma City Geological Society

Local geological societies sprang up and began publishing as early as 1930. The Oklahoma City Geological Society began issuing mimeographed guide books in 1930 (3), followed by *Highway Geology of Oklahoma* (1932, 67 p.) for the 17th Annual Convention of the American Association of Petroleum Geologists, and guide books of field trips in 1935 (as *Second Annual Outing*, a typed road log), 1936 (two trips), 1937, 1939, 1940 (14 p.), 1941, 1946 (17 p.), 1949 (17 p.), and 1950 (39 p.); those for 1953 and 1954 were published jointly with Oklahoma Geological Survey. In 1955 *Highway Geology of Oklahoma* was issued in cooperation with the Oklahoma Geological Survey and The University of Oklahoma (172 p.).

A guide book titled *Variations in Limestone Deposits* was issued in 1964 (92 p.), jointly with Oklahoma Geological Survey.

The Society issues the *Shale Shaker* monthly from September through June (10 issues yearly). Volume 1 appeared in 1950-1951. Papers published in the *Shale Shaker* through volume 14 have been reprinted with new pagination as *Shale Shaker Digest*, volumes I to IV, covering 1950-1955, 1955-1958, 1958-1961, 1961-1964.

In 1963 the society published *Oil and Gas Fields of Oklahoma, Reference Report, Volume 1*, in loose-leaf format.

Tulsa Geological Society

In 1932 the Tulsa Geological Society issued its *Summaries and Abstracts of Technical Papers* in 43 unnumbered pages. Publication was by the *Tulsa Daily World*. The subsequent issues have been called *Tulsa Geological Society Digest*, with volume numbering beginning in 1942 with volume 9; the series is now at volume 33.

The Tulsa Geological Society issued mimeographed guide books in 1941 (9 p.), 1941 (8 p.), and 1946 (17 p.). Letterpress guide books were published in 1947 (56 p.), 1951 (35 p.), and 1954 (57 p.), and in 1961 jointly with Fort Smith Geological Society (78 p.).

Ardmore Geological Society

The Ardmore Geological Society began its series of guide books in 1936 (five trips) and continued it with others in 1937 (two trips), 1938, 1940, 1946, 1948 (9 p.), 1950 (11 p.), 1952, 1954, 1956, 1957, and 1963 (51 p.), and in 1966 (50 p.) jointly with Oklahoma Geological Survey. In 1959 the society issued, jointly with the Dallas Geological Society, *The Geology of the Ouachita Mountains- a Symposium*, consisting of 208 pages and a 68-page field-trip guide book.

Shawnee Geological Society

The Shawnee Society held a field trip in 1938, but only typed guide books were issued; later in 1938 a mimeographed 12-page guide book for another trip was issued, jointly with Oklahoma Geological Survey. The society is now disbanded.

Okmulgee Geological and Engineering Society

The Okmulgee Geological and Engineering Society was founded in 1956, published *Geology of the Okmulgee District* in 1957, and then disbanded.

Geophysical Society of Tulsa

The *Proceedings of the Geophysical Society of Tulsa* have been published irregularly. Volumes 1 to 8 have appeared since 1953; volume 8 is for 1961-1964.

Oklahoma Academy of Science

The geology section of Oklahoma Academy of Science has issued dittoed guide books of trips held for its spring meetings. A more ambitious guide book of 9 pages was mimeographed in 1952 and was issued jointly with Gamma Chapter of Sigma Gamma Epsilon.

Oklahoma Academy of Science was formed in 1910 and first published its *Proceedings* in 1921. Earlier volumes contain many geologic articles; those since 1958 contain few. The current volume is numbered 47. From 1921 to 1928 the *Proceedings* volumes were also numbers of *University Studies*: no. 14 in 1921, no. 15 in 1922, no. 16 in 1923, no. 21 in 1925, and no. 22 in 1926. They were then included in the *University of Oklahoma Bulletin*, New Series, as no. 348 in 1927, as no. 409 and *Studies Series* no. 29 in 1928 (for 1927), as no. 410 and *Studies Series* no. 30 in 1928, and as no. 456 in 1929.

Sigma Gamma Epsilon

Sigma Gamma Epsilon, the honorary scholastic geologic fraternity, held five conferences on stratigraphy, on May 9, 1936, on May 8, 1937, on Nov. 4, 1939, on Dec. 7, 1940, and on March 14, 1942. Mimeographed proceedings were issued. Although the 1942 issue was headed *Seventh Annual Symposium*, only five conference proceedings have been located.

The fraternity sponsored field trips and published guide books in 1941, 1947, 1953, and 1959.

OTHER ORGANIZATIONS

Museum of the Great Plains

The Museum of the Great Plains (Lawton) is operated by the Great Plains Historical Association and issues the *Great Plains Journal* semiannually. Volume 6, number 2, appeared in July, 1967. The Museum issued a symposium titled *Domebo: A Paleo-Indian Mammoth Kill in the Prairie-Plains* in 1966. It also distributes a mimeographed newsletter, and volume 3, number 6 is dated April, 1967.

Oklahoma Historical Society

Chronicles of Oklahoma, the publication of the Oklahoma Historical Society, contains several geological articles and many other articles useful to geologists.

Gem and Mineral Societies

At present nine gem and mineral societies exist in the State. The Oklahoma Mineral and Gem Society issues *Sooner Rockologist*. Two numbers of volume 1 appeared in 1946, and volumes 1-4 (to Oct. 1950) were monthly. Volumes 5 through the present are in six numbers each, issued bimonthly.

The Tulsa Rock and Mineral Society issues a processed monthly journal titled *T-Town Rockhound*. The August, 1967, issue is volume 10, no. 8.

The Northern Oklahoma Gem and Mineral Society, Inc. (Ponca City), was organized in 1960 and issued at least four numbers of *Pebble City News*, the last in September, 1967.

Publications of local organizations are especially difficult to obtain. Many have small editions, go out of print quickly, and have no permanent address, so that even within the State libraries cannot be complete.

New Theses Added to O. U. Geology Library

The following Master of Science thesis was added to The University of Oklahoma Geology Library in October, 1967:

Subsurface stratigraphic analysis of the "Cherokee" group in north-central Creek County, Oklahoma, by Harold Wayne Hanke.

—L. F.

CHEMICAL ANALYSES BY X-RAY FLUORESCENCE

RAYMOND L. KERNS, JR.*

INTRODUCTION

Secondary x-ray-fluorescence techniques provide quick, precise, and nondestructive qualitative and quantitative chemical analyses. It is assumed that the reader is familiar with the fundamental theory concerning the generation and nature of x-radiation. The description and directions for operating the x-ray-fluorescence equipment used in this study are available in manuals supplied by Siemens America Inc. The following is intended as a discussion of the experimental technique designed to obtain reproducible results.

QUALITATIVE ANALYSIS

A qualitative analysis may be obtained by running an x-ray-spectrometer scan, which is similar to an x-ray-diffractometer scan. The spectrometer contains an x-ray tube that provides the primary excitation radiation. The x-ray beam is focused on the sample, which is in a fixed position, and the secondary radiation of the excited elements is collimated by means of a Soller slit onto an analyzing crystal, the interplanar spacing (d) of which has been precisely determined. The diffracted radiation is collimated by another Soller slit to the detector. Scans may run from 16 to 82 degrees 2θ on the Siemens vacuum spectrometer. Detection of K spectral lines for elements from magnesium (atomic number 12) to chromium (atomic number 24) may be done with the gypsum crystal ($d = 7.6 \text{ \AA}$); analyses of elements with atomic numbers larger than 24 may be obtained by using the lithium fluoride analyzing crystal ($d = 2.01 \text{ \AA}$). K-spectral-line detection of elements with atomic numbers larger than 29 (copper) is more satisfactorily accomplished with a scintillation counter because it has a higher quantum-counting efficiency for radiation of shorter wavelengths. A proportional counter is more efficient for detection of longer wavelengths.

A scanning rate of 1 or 2 degrees 2θ is generally suitable with a chart rate of 1 or 2 cm per minute, respectively. The baseline setting of the pulse-height analyzer should be at the limiting value of 0.5 volt for acceptance of radiation of all wavelengths; channel-width control should be removed from the circuit by flipping the toggle switch to integral. Attenuation is routinely set at 20, with the counter operated at 2,000 to 2,050 volts. The linear scale factor may be varied to keep the more intense peaks on the chart or to enhance the weaker peaks. Siemens recording panels also have a logarithm scale factor that is quite useful in spectrometer scanning.

Solutions of the Bragg equation ($n\lambda = 2d' \sin \theta$) for different angles of incidence (θ) and the d value of the analyzing crystal yield wavelength values for the spectral lines or, in this case, peaks. These may be compared with values of recorded wavelengths of the charac-

* Utah State University, Logan, Utah.

teristic radiation for various elements. This process is simplified through the use of charts constructed for various analyzing crystals having different interplanar spacings. These charts have the positions of the various characteristic radiations labeled along a 2θ scale.

QUANTITATIVE ANALYSIS

Spectrometer Method.—Semiquantitative data may be taken from the spectrometer scans obtained for qualitative chemical analyses. The first requirement is a set of suitable standards that contains accurately determined percentages of the chemical elements of interest in the range of the percentages being analyzed. By carefully preparing all standard and unknown samples uniformly and by running all scans at the same machine settings with a linear scale factor, the intensity of the peak for a particular element will be proportional to the percentage of the element present in the sample. A graphical plot of the percentage of the constituent in each standard against the K_α peak intensity above the background provides a curve from which percentages of the chemical constituents of the sample to be analyzed may be extrapolated on the basis of peak-height data.

Figure 1 represents a set of standard curves for silicate samples, for oxides of iron, titanium, calcium, potassium, silicon, and aluminum.

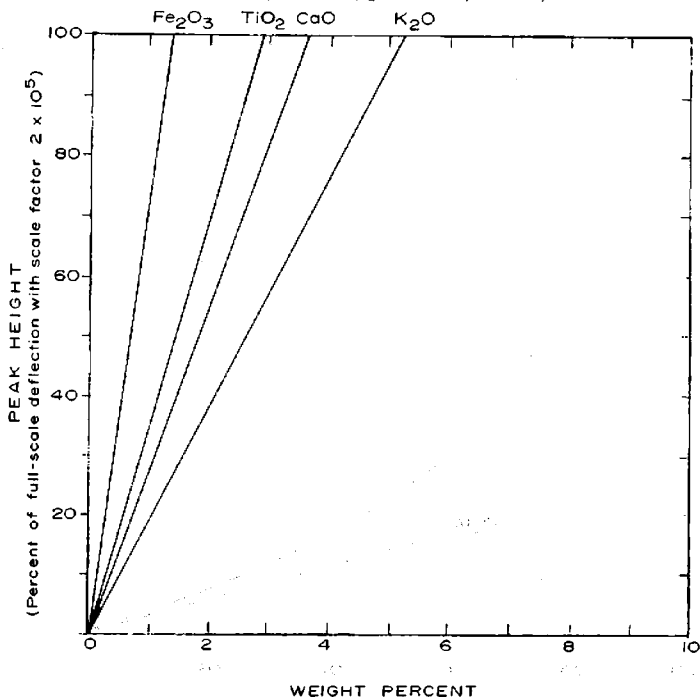


Figure 1. Relative-intensity curves determined by measuring heights of K_α peaks on spectrometer scans of selected silicate standards.

The intensities are relative to a full-scale deflection of 100 at a linear-scale-factor setting of 2×10^7 counts per minute. All curves were established with the gypsum analyzing crystal except that of iron, for which the lithium fluoride crystal was used. The scans were run at 1 degree 2θ per minute and a chart speed of 1 cm per minute. The percent of each oxide is plotted along the abscissa. This scale reads directly in weight percent oxide on a 105 °C dry basis. The pulse-height analyzer was operated on integral with a minimal 0.5-volt baseline setting. The detector was a flow-proportional counter operated at 2,050 volts with a P-10 gas (90% argon, 10% methane gas mixture) flow rate of 0.06 cfh. The Siemens Kristalloflex IV generator was operated at 35 kilovolts and 40 milliamps. The primary excitation radiation was provided by a chromium-target x-ray tube. The samples were prepared as pellets containing 10 percent polyvinyl alcohol (PVA) as a binding agent, mixed with 90 percent of the powdered sample and pressed at 15 tons per square inch on a Paul Weber press, using a 1.25-inch diameter Buehler die. Table I is a comparison of analyses obtained by measuring peak heights from spectrometer scans with analyses obtained by the more precise pulse-counting method described in the following section.

TABLE I.—COMPARISON OF QUANTITATIVE ANALYSES BY SPECTROMETER SCAN (A) AND BY PULSE COUNTING (B)

(All values are weight percent)

	SAMPLE 1		SAMPLE 2		SAMPLE 3		SAMPLE 4	
	A	B	A	B	A	B	A	B
SiO ₂	50.5	48.00	43.5	43.50	40.7	40.60	51.3	50.46
Al ₂ O ₃	17.5	16.82	13.0	12.92	9.70	9.85	19.5	18.69
Fe ₂ O ₃	7.14	7.08	7.35	7.20	9.10	9.24	6.51	6.58
CaO	0.80	9.74	0.70	0.66	1.59	1.52	0.90	0.88
K ₂ O	5.00	5.04	2.85	2.86	1.53	1.46	5.38	5.41
TiO ₂	0.25	0.24	0.27	0.26	0.30	0.31	0.25	0.24

Spectrometer-scan analyses are accurate enough for semiquantitative purposes, but, unless a qualitative analysis is necessary, the technique takes longer than the pulse-counting method. If a large number of samples is to be analyzed, the fast, more precise pulse-counting method should be used.

Pulse-Counting Method.—Precise quantitative chemical analyses may be obtained by using the pulse-counting method. This technique involves precise location of the maximum intensity of the spectral line. The detector voltage is operated on the plateau region of the counter for the particular wavelength involved (usually a K_{α} line), and the intensity is determined in counts per minute by taking preset time counts (usually 2 minutes in duration on the peak maximum). A more precise method involves step scanning at increments of 0.005 or 0.02 degrees 2θ , taking preset time counts at each successive step, and recording the maximum count as the peak plus background intensity. The background intensity is measured at some spectrometer setting close to the spectral line, but not at a position where the intensity may

TABLE II.—MACHINE SETTINGS FOR QUANTITATIVE CHEMICAL ANALYSES WITH A SIEMENS VACUUM SPECTROMETER

	Mg	Al	Si	K	Ca	Ti	Fe
Kilovolts	35	35	35	35	30	35	20
Milliamps	50	40	40	40	40	40	20
Counter Voltage	2200	2050	2025	1925	1925	1900	1900
Baseline	20.0	10.0	8.0	8.0	8.0	10.0	7.5
Channel Width	30.0	18.0	28.0	18.0	18.0	15.0	27.0
Attenuation	50	20	20	20	20	20	20
Peak Position (degrees 2θ)	81.24	66.65	55.99	28.59	25.63	20.92	57.46
Background Position (degrees 2θ)	79.50	69.00	57.50	31.00	22.50	22.50	55.00
Analyzing Crystal	Gypsum	Gypsum	Gypsum	Gypsum	Gypsum	Gypsum	Lithium fluoride

A flow-proportional counter was used with a gas flow of 0.06 cfm; the counter gas was a 90% argon-10% methane mixture.

be in part a measure of some other spectral line. Table II lists machine settings for seven of the more important elements found in silicate rocks. These settings will vary with a change of the x-ray tube, the detector used, and the age of the circuitry. Peak positions are to some extent a function of fine alignment and adjustment of the spectrometer, and may change during the time of a single series of operations. For this reason, the peak position should be checked by step scanning across it frequently.

For greatest precision, the following precautions should be observed.

1. Allow the machine to warm up for a minimum of 4 hours before beginning quantitative analyses, so that the circuit has time to stabilize.

2. Keep sample preparation and sample loading as consistent as possible. With a silicate sample, a binder, such as PVA, may be necessary; add an exact amount (usually 10%) to all samples and standards. Homogenize thoroughly and brickette at the same pressure. Use the same size of sample holder for all samples.

3. Be sure that the vacuum is sufficient before beginning the counting; a vacuum of 0.1 torr is sufficient and should be attained in 1 minute if the vacuum chamber is well sealed.

4. Check the spectral-line position frequently or measure intensities by step-scanning operations.

5. Peak intensities should not exceed the resolving capacity of the EIT counter tubes in the scaler circuit; the resolving capacity is approximately 12 microseconds, or 100,000 counts per minute (c/m). An excess of impulses will result in counting loss. By operating on the first binary ($\times 2$), counting rates up to 200,000 c/m may be tolerated; the maximum intensities that may be counted without loss is 400,000 c/m if the second binary ($\times 4$) is used. The accuracy of the EIT tubes may be checked by pushing the control check button and beginning the counting. This operation feeds a programmed impulse of 100,000 c/m into the scaler circuit and serves as a check. The control check button should then be released before continuing the analysis.

6. While counts are taken on samples to be analyzed, counts should also be made periodically on standard samples; a deviation of more than 10 parts per thousand (ppt) is extreme. If there is this great a deviation, check the peak location, counter voltage, PHA settings, and the energy distribution of the spectral line by means of the pulse spectroscopy. In most cases, extreme deviations in counts on standard samples are due to circuit instability from insufficient machine warm-up time or to drifting of the spectral-line position from thermal expansion of the spectrometer.

7. Plastic sample holders should be used for aluminum analyses; aluminum sample holders are suitable for analyses on all other elements.

If experimental technique is good throughout the analyses, the results will be precise. Analyses of the heavier elements, potassium through iron, may be reproduced to ± 2 ppt. The reproducibility of silicon analyses may be as high as ± 5 ppt, and ± 5 to ± 10 ppt may be obtained for aluminum and magnesium determinations.

Table III is a comparison of two analyses of Beavers Bend illite, one by the x-ray-fluorescence method, the other by the wet-chemical method. The wet-chemical analysis is that of J. A. Schleicher, reported in Mankin and Dodd (1963), made upon the same material used in the x-ray method.

TABLE III.—COMPARISON OF CHEMICAL ANALYSES
BY X-RAY-FLUORESCENCE AND WET-CHEMISTRY METHODS

(All values are weight percent)

	BEAVERS BEND ILLITE	
	X-RAY FLUORESCENCE	WET CHEMISTRY
SiO ₂	50.90	49.85
Al ₂ O ₃	23.10	23.68
Fe ₂ O ₃ *	6.79	6.60
FeO	-	1.87
MgO	1.79	1.86
CaO	0.11	0.12
K ₂ O	7.56	6.64
TiO ₂	1.30	1.40
Total**	91.55	92.02

* All iron analyzed by X-ray-fluorescence method reported as Fe₂O₃.

** Weight loss due to H₂O not included.

SAMPLE PREPARATION

Qualitative Analysis

The Siemens vacuum spectrograph is equipped with sample holders that accommodate solid or liquid samples. Chemical analyses of rock specimens are usually performed on solid samples. No detailed sample preparation is necessary if only a qualitative analysis is to be obtained. Fluorescence scans may be run on rock slabs, powder imbedded in paraffin, samples sedimented onto a glass slide, or pressed pellets of powdered samples. For quantitative analyses, only the pressed pellets are suitable. Rock slabs do not provide a representative sample because they generally are inhomogeneous, and sample quantity and thickness cannot be controlled in the other methods.

Quantitative Analysis

Pressed pellets or brickettes of rock samples may be prepared for quantitative analysis by the following method. The sample must be ground to a fine powder and homogenized. An 80- to 100-mesh size is usually small enough for clay materials. Rock samples with large mineral grains, such as found in igneous rocks, sandstones, and some carbonates, should be ground to as fine a size as possible. A 400-mesh screen is available with the Pitchford Uniform Particle Size Grinder. Homogenization may be achieved by shaking the ground sample on the Pitchford grinder for 12 seconds. Brickettes are prepared by pres-

sing the powdered material in a die on a mechanical press. A pressure of 15 tons per square inch is usually sufficient for dies up to 1.5 inches in diameter.

Binding Agent.—Pellets of pure material may be prepared, but ordinarily a binding agent must be added for a brickette that will withstand routine handling. Polyvinyl alcohol is ideal for this purpose. A 10 percent (by weight) addition of PVA is usually sufficient for clay materials; more coarsely crystalline materials may require as much as 20 percent. The x-ray-absorption and sample-dilution effects of PVA on the intensity of a particular spectral line were determined experimentally. Brickettes of the same clay material were accurately weighed and mixed with 1, 5, 10, 20, and 40 percent PVA. The intensities of the K_{α} lines of Al, Si, K, Ti, and Fe were measured several times and the deviations in intensity of the samples containing 5, 10, 20, and 40 percent PVA from that of the sample containing 1 percent were calculated in parts per thousand. Figure 2 shows graphically the variation in intensity of the K_{alpha} lines of several elements as a function of

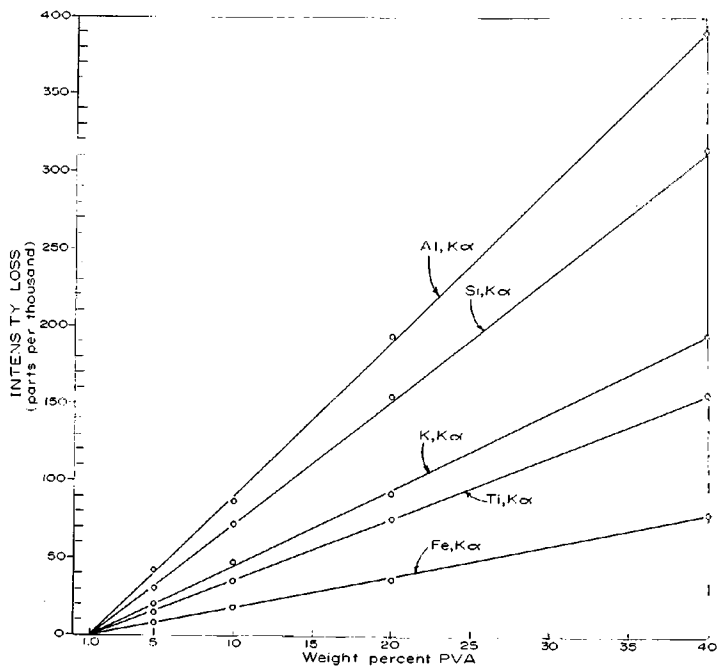


Figure 2. Loss of intensity of K_{α} spectral lines of selected elements as a function of percentage of polyvinyl alcohol (PVA) contained in sample. The slope of each line is the measure of the loss of intensity due to admixture of PVA. The slope values (ppt/%PVA - 1) are: Al 10, Si 8, K 5, Ti 4, Fe 2.

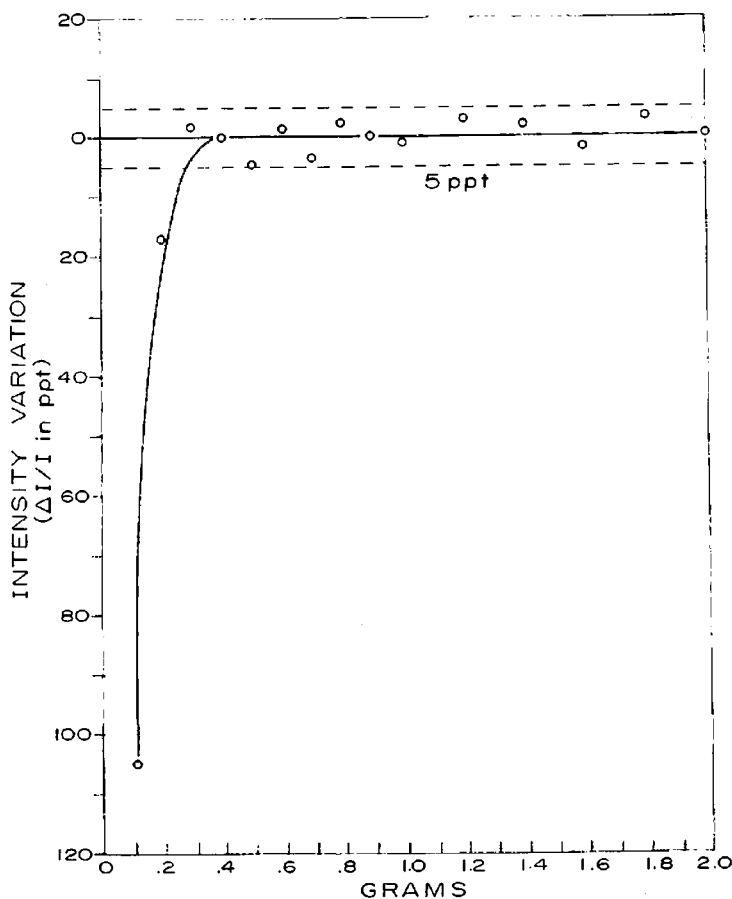


Figure 3. Variation of intensity of K_{α} spectral lines of iron as a function of sample thickness. Thickness is expressed as weight of powdered sample containing 10 percent polyvinyl alcohol compressed into 1-inch-diameter brickette under a pressure of 15 tons per square inch. The factor ΔI is the difference in intensity between the spectral line of the sample and that of the 2-gm standard (I).

weight percent PVA added to the sample. Counting losses (slope of line) range from 2 ppt/1% PVA for Fe- K_{α} to 10 ppt/1% PVA for Al- K_{α} . It is extremely important, therefore, to prepare all samples and standards with precisely the same amount of binding material.

Pressing.—The sample and PVA must be homogenized thoroughly before pressing. A total weight of 5 gms of mixture will ordinarily make a good brickette with dies 1 to 1.5 inches in diameter. The powder is poured into a die and the pressure brought up to 15 tons per square inch. If the die is equipped with a vacuum mechanism, enough pressure is applied to form a cake (about 1 ton), the air is evacuated from the die, and pressure is then reapplied until the 15-ton maximum is reached. The pressure should be released slowly to avoid cracking the pellet when removing it. Pressure must be applied more slowly with systems not equipped with a vacuum mechanism; it should be increased by 5-ton increments, followed by 5-minute periods to allow the air to escape.

Thickness.—Small samples of 1 gm or less may be made into useable brickettes by pressing a wafer of the material onto a pellet of PVA. The powdered sample plus PVA binder is weighed, mixed, and thoroughly homogenized, and the mixture is poured into the die and spread with a spatula so that it uniformly covers the bottom of the cylinder. Pressure (less than 1-ton load) is applied to form a cake, the pressure is released, and the ram is removed. About 4 grams of PVA is poured on top of the wafer, the ram is reinserted, and the sample bricketted in the usual manner. This technique results in a strong pellet of PVA coated with a veneer of sample. The wafer will eventually break away from the backing due to differential expansion and contraction, but most samples will remain intact for several weeks.

The primary x-radiation used to excite the elements in the sample, and thus produce the characteristic spectral lines, decreases in intensity as it penetrates the sample. The excited elements emit x-rays which also undergo absorption as they pass through the sample to the surface. The spectrometer is designed so that the intensity of the spectral line is measured as it is radiated from the surface on which the primary radiation is focused. The relative decrease in intensity of any monochromatic x-radiation may be predicted from the formula:

$$\frac{I_x}{I_0} = e^{-\left(\frac{\mu}{\rho}\right)\rho t}$$

where I_x is the intensity after absorption, I_0 is the intensity of the x-rays before absorption, e is the base of the natural logarithmic system, μ/ρ is the mass-absorption coefficient of a substance for a particular wavelength, ρ is the density of the substance, and t is the thickness of the substance penetrated (Cullity, 1956, p. 11). Theoretically, the relative reduced intensity of an x-ray beam I_x/I_0 will never reach zero except for a sample of infinite thickness. It is, however, controlled by a log function, so that the value decreases rapidly with increasing distance of penetration. To reproduce the intensity of a spectral line for a given amount of an element within a defined matrix, maintain a sample thickness that permits only intensity deviations within the limits of accuracy for the equipment and the technique. The precision

of quantitative chemical analyses by x-ray-fluorescence techniques is seldom better than ± 1 ppt.

Pellets of an illite clay were bricketted with 10 percent PVA. Total sample weights were measured starting at 0.1 gm and increased in 0.1-gm increments to 1 gm; additional samples were increased from 1 to 2 gms in 0.2-gm increments. All pellets were pressed in a 1-inch-diameter cylindrical die. The 2-gm sample was assumed to be a close approximation of an infinitely thick sample. Six analyses were made on each of the other samples. A deviation less than ± 5 ppt was taken as systematic error for the experiment. Deviations outside this range were considered as intensity deviations due to insufficient thickness.

Figure 3 is a plot of the results of the experiment. Deviations of intensity measurements for the various samples as compared to the intensity of Fe- K_{α} for the 2-gm sample are plotted (ordinate) against sample weights for the illite clay (abscissa). Appreciable deviations in intensity ($\Delta I/I$) are not encountered in samples of 0.3 gm or larger.

This experiment indicates that samples of less than 0.5 gm may be used for quantitative chemical analysis if they are bricketted in a 1-inch-diameter die. However, in practice, it is desirable to use samples weighing at least 1 gm because smaller quantities make the preparation of useable brickettes most difficult.

CONCLUSIONS

X-ray-fluorescence spectrometry is a precise, accurate, and non-destructive method of chemical analysis. Analyses may be performed quite rapidly, permitting handling of a large number of samples.

With the instrumental precision of x-ray-fluorescence spectrometry, the accuracy of the technique is limited only by the reliability of the chemical analyses of the standard samples and by the skill of the analyst.

References Cited

- Cullity, B. D., 1956, *Elements of x-ray diffraction*: Reading, Mass., Addison-Wesley Publishing Co., Inc., 514 p.
- Mankin, C. J., and Dodd, C. C., 1963, Proposed reference illite from the Ouachita Mountains, in *Clays and clay minerals*, vol. X: New York, Pergamon Press, p. 372-379.

Synopsis of Early Permian Vertebrates of Oklahoma

Now in press and shortly to be published is Oklahoma Geological Survey Circular 74, *Early Permian Vertebrates of Oklahoma*, by Everett C. Olson.

Dr. Olson, who has written several other reports published by the Survey, is vertebrate paleontologist at the Walker Museum, University of Chicago, and one of the foremost authorities on the Permian vertebrates of the Southwest.

Among his earlier Survey publications are Circular 59, *Permian Vertebrates from Oklahoma and Texas* (in part with Herbert Barghusen; 1962), and Circular 70, *New Permian Vertebrates from the Chickasha Formation in Oklahoma* (1965).

The forthcoming book is an attempt to collate all the known information regarding the occurrence of vertebrate remains in the Lower Permian of Oklahoma and to assess the stratigraphic implications of these occurrences in regard to the correlation of the Lower Permian of Oklahoma with that of Texas. About 45 collecting sites are described and their faunas listed and evaluated. The appendix of the book lists the cataloged specimens upon which the study was based and their depositories. The abstract is given below.

ABSTRACT

Remains of terrestrial Early Permian vertebrates were discovered in Oklahoma prior to 1900. Occasional finds have been made since that time and the Hennessey Formation was carefully explored by J. Willis Stovall. No other systematic collecting has been done and no comprehensive report on the vertebrates has been made. The study reported here represents an attempt to establish a sound base from which future work can proceed.

All sites discovered earlier have been revisited and, as possible, re-collected. A large number of new sites have been discovered. The general geology of the Lower Permian beds of Oklahoma is reviewed and revised to establish a context in which the vertebrate sites may be related. For each site a list of vertebrate genera and species, conditions of occurrence of the fossils, geological age, and, as far as possible, a measured section are given. A summary of the vertebrate fossils in each of the three producing areas, southwestern, south-central, and central and north-central Oklahoma, is given.

The pre-Hennessey Permian faunas have a close relationship to those of north-central Texas. The Hennessey vertebrates have affinities with those of the later Chickasha beds of Oklahoma and the San Angelo beds of Texas.

The book will comprise approximately 80 pages, 12 figures, and 3 plates. It can be purchased from the Survey for \$4.00, cloth bound, or \$3.00, paper bound.

Index to Geologic Mapping in Oklahoma

—Supplement 2 in Press

The second supplement to the *Index to Geologic Mapping in Oklahoma* is now in press and will be available shortly. Supplement 2 comprises Map I-B, Surface Mapping, 1901-1966, compiled by C. C. Branson, and Map VII, Subsurface Mapping, 1964-1966, compiled by Louise Jordan and J. F. Roberts.

The surface geologic index lists 90 published maps (outlined and numbered in black), those published in color indicated by an asterisk (*). The published maps listed are the best and most recent at scales of 1 inch = 2 miles (1:126,720) or larger; maps and parts of maps which have been superseded are not shown. Seventy-seven manuscript maps (outlined and numbered in red) are also listed, most of which were prepared for theses and dissertations by graduate students in geology at The University of Oklahoma. Some were done for reports by the Oklahoma Geological Survey, and many are available for inspection at the Geology Library of the University or at the Oklahoma Geological Survey.

The subsurface geology index lists 62 maps compiled between 1964 and 1966. Maps based on several different types of subsurface data are included: gravity; thickness or isopach; areal extent; magnetic; paleogeologic; structural or contour; and porosity, lithofacies, and other information.

Supplement 2, like the first supplement, is priced at \$1.00, and the original index is available for \$2.00; the index and either of the supplements may be purchased together, however, for \$2.50.

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