Short Papers on Research in 1966

Edited by Doris E. Zeller

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This collection of six papers is the first published "Short Papers on Research" instituted in 1967 as a part of the Reports of Studies series in the Bulletin. The papers present scientific and economic results of work by members of the State Geological Survey of Kansas during the calendar year 1966.

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ERNEST E. ANGINO

Distribution of Iron in Recent Carbonate Sediments

ABSTRACT

Iron showed a strong covariance with insoluble (in H_2O_2, $HC_2H_3O_2$, and H_2O) material present in Recent carbonate sediments from Vieques Passage, Puerto Rico. The insoluble fraction, making up about 11 percent (range 8-17) of the sediment, carries approximately 83 percent (range 70-98) of the total iron present in the sediment. The mean Fe concentration of the samples was 0.48 percent with a range of 0.08 to 1.0 percent and a σ of 0.16.

The concentrations of trace and minor elements found in carbonate rocks are a function of the element concentrations present in: (1) solid solution in the carbonate minerals, (2) detrital minerals, (3) accessory authigenic precipitates, (4) noncarbonate skeletal material, (5) organic matter, (6) phases formed during diagenesis, and (7) elements absorbed upon all these materials. A given trace or minor element present in a carbonate rock is frequently distributed among components formed at different times in the history of the sediment by differing mechanisms. Evaluation of the minor element content of each of the components is difficult and the attempt has not often been made. The percentage distribution of the respective fractions of the trace and minor elements in carbonate rocks is imperfectly known at present. If we hope to understand the distribution patterns of trace and minor elements in ancient sediments, we must start with an understanding of those processes at work in Recent sediments. It was the purpose of this study to examine the distribution of Fe in Recent carbonate sediments taken from the Vieques Passage area of eastern Puerto Rico (Fig. 1).

Vieques Passage lies between Puerto Rico on the west and Vieques Island on the east. The area of investigation lies between 65°36′ and 65°46′W and 18°08′ and 18°14′N. Vieques Passage is a relatively shallow body of water ranging up to 15 fathoms in depth. All of the

samples used in this investigation were from depths of less than 12 fathoms (Fig. 1).

Excepting tidal currents to the south of Playa de Naguabo, coastal and nearshore currents flow in a general northeasterly direction under the influence of the general shoreline configuration and the north Equatorial Current (Kaye, 1959). Representative physical properties of water in the area are: Salinity, 35.39‰; Cl, 1959 mg/l; Ca, 402 mg/l; water temperature, 28.5°C; and pH, 8.05.

FIGURE 1.—Location map of study area. Dots represent sample locations. The 3 and 5 fathom lines (3F and 5F) are indicated.

The major portion of the Recent carbonate sediments consists of the remains of carbonate-secreting organisms. Carbonate precipitation from sea water plays a minor part. Skeletal debris is largely composed of aragonite, low Mg-calcite, and high Mg-calcite. Sediment size distribution with depth shows a strong bimodal pattern indicating poor sorting. Mean grain size generally increases down the core. The bimodal pattern is thought to be the result of chemical solution of the fine-grained portion causing the sediments to be skewed towards the coarse fraction (Sommer, *et al.*, 1964). Montmorillonite is present in significant amounts only in those sediments containing less than 90 per-

cent $CaCO_3$ and was found only in the near-shore samples; kaolinite is more common in deeper water samples. Iron was found to vary with both the clay and insoluble fractions. A weak covariance between iron content and water depth was noted.

The association of iron with the clay minerals clearly affects the distribution of iron in these sediments. Montmorillonite has greater adsorptive properties than kaolinite. Montmorillonite might be adsorbed by or adsorb some part of any iron hydroxide and be forced out of suspension. The chemical state of iron necessary for ionic substitution into clays is incompatible with the forms bonded to hydroxide. Iron apparently follows the clay in essentially constant proportions. Most of the iron is probably brought to the site of clay mineral deposition as part of an $Fe(OH)_3$ sol. It could be returned to the ionic state at or near the sediment interface by the acid effect of large amounts of organic material, and subsequently could enter the clay mineral lattice.

As has been noted, in most studies of the trace, minor, or major element concentrations in carbonate rocks, little attention has been paid to the relative concentrations of the elements in the various components that make up a carbonate sediment. This problem has been discussed by Hirst and Nicholls (1958), Hirst (1962a, b), and Angino (1964), but generally the study of element fractionation has been avoided. If the minor and trace element content of a sediment is ever to be of real value in reconstructing paleoecologic conditions, then consideration must be given to differentiating between the elemental content of the respective fractions making up the sample (*i.e.* water soluble, H_2O_2 soluble, acetic acid soluble, carbonate, and insoluble). However before this possibility can be attained, it will be necessary to give greater attention to a study of the trace element content of the various components making up a rock unit. With such analyses we may then be able to delineate more distinctly some of the detailed environmental conditions prevailing during the deposition of carbonate sediments.

The major carbonate minerals, calcite and aragonite, take few trace elements into solid solutions; only Sr, Mn, Ba, Pb, and Fe are likely to be present in significant amounts.

Four fractions were examined in this study. A water-soluble fraction was obtained by washing 1-2 g of sediment (ground to pass a 150-μ screen) in a 150-ml beaker with 100 ml of doubly distilled deionized water with constant stirring for 24 hours. The solution was then allowed to stand for 12 hours and the supernatant separated by centrifugation (or vacuum-filtration) and analysed by atomic absorption spectrometry for iron.

For the organic (H_2O_2-soluble) fraction, 75 ml of 10 percent H_2O_2 was added to 1 to 2 g of crushed sample (150-μ), placed in a 150-ml beaker and allowed to set for 4 hours with frequent stirring. This solution was separated by centrifugation and analysed for Fe.

In a study of the acid soluble fraction a 9:1 v/v water-acetic acid solution was used to dissolve the carbonate and the sample allowed to set for 2 to 4 hours prior to separation of the supernatant.

A total analysis for iron was obtained by dissolving a 1- to 2-g sample in 5 ml 48 percent HF and 5 drops concentrated H_2SO_4, and heating at 100°C to dryness. This step was repeated three times and the solution transferred to a 250-ml erlenmeyer flask using 200 ml of hot 9:1 v/v water/HCl. If a black residue remained, it was taken up in H_2O_2 and analysed for Fe. The sum of the Fe content of the other three fractions subtracted from the total gives the Fe content in the insoluble fraction. A total determination was also made for manganese. All iron and manganese determinations were made on a Perkin-Elmer 303 atomic absorption spectrometer using the 2483Å and 2803Å lines of Fe and Mn respectively and an air-acetylene flame. Except for a slight interference caused by Ca molecular absorption, no other interferences were noted.

The well known strong covariance of iron and manganese is shown by the insoluble content of the Recent carbonate sediments from the Vieques Passage area (Fig. 2). As might be
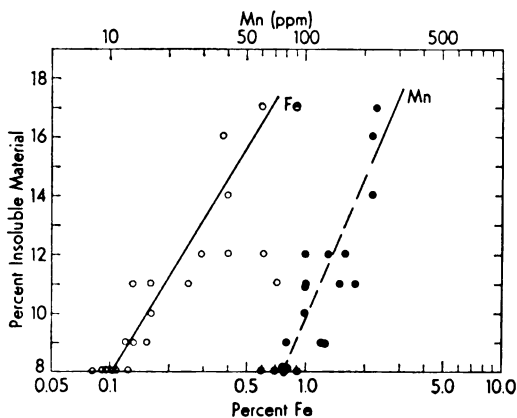

FIGURE 2.—Covariance of iron and manganese with percent insoluble component in the sample. The trend lines were visually fitted. Data from Sommer, *et al.* (1964).

expected, the Fe/Mn ratio is relatively constant (range 7-44). Further evidence of the pronounced concentration of Fe in the acetic acid insoluble fraction is shown in Fig. 3. Although making up only about 10.9 percent of the sample, the insoluble fraction carries approximately 83 percent of the Fe present in the sediment. Similar data for the other fractions are summarized in Table 1.

TABLE 1.—Percent iron in each fraction of carbonate samples from Vieques Passage.

Fraction	Percent of sample (range)	Fe content as percent of total sample	Mean Fe, %
Insoluble	8-17	70-98	83
Acetic acid soluble (carbonate)	83-92	2-30	15.8
H₂O₂ soluble (organic)	0-< 1	0.02-2	0.86
Water soluble	0-<0.1	0.06-1.2	0.45

The mean iron content, based on a total Fe analysis of all the samples was 0.48 percent (4800 ppm) with a range of 0.08 to 1.0 percent and a σ of 0.16.

It is obvious that although the insoluble fraction makes up no more than 8-17 percent of the carbonate sediment, it carries 70-98 percent of the Fe. Although aragonite comprised 89-97 percent of the carbonate fraction, no association of Fe content with either aragonite or calcite was noted.

To use the figures for the absolute concentration of Fe in these carbonate sediments to
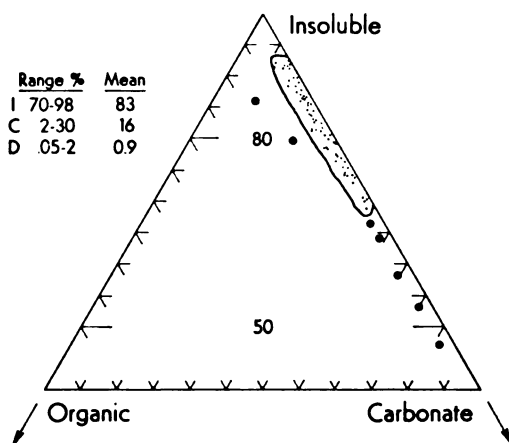
FIGURE 3.—Ternary diagram showing extreme fractionation and concentration of iron in the insoluble component of the sample. *I*, *C*, and *O* indicate insoluble, carbonate, and organic fraction. Large dots represent those few data that did not fall within the indicated field.

make any predictions about environmental conditions prevailing during the deposition of these sediments would be difficult. To attempt to make predictions about the paleoenvironment of ancient carbonate sediments based solely on the absolute concentration of Fe (or any other trace element) in those sediments would be meaningless with the present state of our knowledge of those factors controlling trace element distribution in carbonate sediments.

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RONALD G. HARDY
MAYNARD P. BAULEKE
ALLISON L. HORNBAKER

Photoelectric Beneficiation of Rock Salt

ABSTRACT

A dry method for upgrading rock salt that can be adapted to salt mine processing is highly desirable. A photoelectric method based on the differences in light transmission through pure halite and contaminated halite is described. In laboratory tests using this method 92 percent rock salt was upgraded to 98.5 percent.

Kansas salt, as mined, consists of halite, halite-anhydrite, halite-shale, and halite-anhydrite-shale fragments. The contaminants, shale and anhydrite, are the major contributors to a lower NaCl content. An analysis of a Kansas commercial rock salt is given in Table 1.

TABLE 1.—Composition of rock salt, Reno County, Kansas.

Acid insolubles (shale)	0.165%
Iron oxide	0.012%
Calcium sulfate	2.744%
Calcium chloride	0.010%
Magnesium chloride	0.293%
Sodium chloride (by difference)	96.776%
	100.000%

From a cost standpoint it is highly advantageous to be able to upgrade this rock salt by some dry method that is adaptable to present processing procedures. With salt of 98 to 99 percent NaCl content, a larger market is available.

Because there are some slight differences in the physical characteristics of halite and anhydrite (Table 2) a number of procedures attempting to separate halite and anhydrite based on these differences have been investigated. These procedures include variations in crushing and screening techniques, centrifugal and drop-bounce methods, and density difference separation. None of these gave sufficiently good, consistent results to really warrant consideration as plant-scale operations.

A procedure based on differences in halite and anhydrite diathermancy has been developed to separate these two materials. In essence, this technique calls for exposing the salt-anhydrite mixture to radiant heat of the proper wavelength and allowing the mixture to spread on a high speed endless belt coated with heat-sensitive resin. Halite, with greater ability to transmit radiant heat, does not become as warm as anhydrite, and thus, does not adhere to the resin. The net result is a separation due to preferential adherence. This method can be incorporated into a production operation and has already performed satisfactorily in some salt mines. However, thermoadhesive field tests with Kansas salt did not result in the desired improvement.

Industrial use of photoelectric cells for sorting by color, size, or transparency led to the development of this technique as a means of separating clear grains of halite from those clouded with anhydrite or shale. Accordingly,

TABLE 2.—Physical properties of halite and anhydrite.

	Chemical composition	Hardness	Specific gravity	Index of refraction	Transparency	Tenacity	Fracture	Specific heat at 200° C. BTU/lb
Halite	NaCl	2.0-2.5	2.1-2.6	1.544	Transparent-translucent	Brittle	Conchoidal	.393
Anhydrite	CaSO₄	3.0-3.5	2.7-3.0	1.571-1.614	Transparent-opaque	Brittle	Irregular	.239

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a preliminary series of tests using a very simple photoelectric method gave positive results in upgrading Kansas salt (Fig. 1).
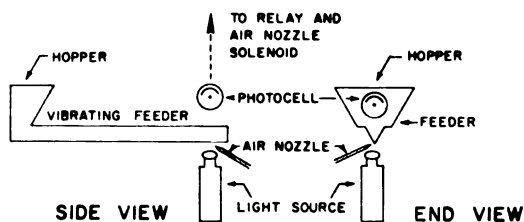

FIGURE 1.—General arrangement of feeder, photoelectric cell, and air nozzle. Feeder has 1/16″ slot for light to pass through. Air jet also goes through same slot.

Essentially, the system consists of a means of feeding a single layer of salt particles ($<$ .375″ to $>$ .125″) between a light source and a photoelectric cell. The cell is connected through a relay to a solenoid-activated air valve to which a fine nozzle is attached. As long as the grains of halite are clear, the cell does not actuate the air valve. A dimming of the light due to anhydrite or shale causes immediate actuation of the air valve, and in turn, the nozzle blows the impure grain out of the stream. The system performs excellently, and by varying the speed of feed and light intensity, a wide range in separation pre-

ciseness is available. Results using this method are given in Table 3.

TABLE 3.—Photoelectric grading of a Kansas salt.

	As received		After treatment	
KGS sample	NaCl content, %	Acid insolubles, %	Acid insolubles, %	NaCl content, %
10	92.0	0.400	0.072	98.59
19	96.0	0.165	0.091	98.00
21	96.0	0.165	0.049	98.78
22	92.0	0.400	0.070	98.49

Speculating on the "after treatment" NaCl content, the data indicate that the top percentage obtainable by this method probably is in the order of 99 percent.

Several areas of study are immediately suggested to determine whether or not this technique is operationally feasible on a plant scale. These include evaluations of photoelectric cells, sources of illumination, and circuitry. Also, experiments should be carried on to determine optimum salt particle sizes, methods of conveying salt to and away from classification, and handling of rejected salt. This all implies that an optimum method of scanning the salt will also be determined.

Manuscript received November 2, 1966.

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O. KARMIE GALLE
ERNEST E. ANGINO

Determination of Calcium and Magnesium in Carbonate and Silicate Rocks by Atomic Absorption

ABSTRACT

Two wet chemical methods for the determination of calcium and magnesium were adapted to atomic absorption analysis. Experimental work was carried out with four National Bureau of Standard samples and reagent-grade calcium carbonate. Results from the wet chemical methods and the instrumental method were compared and found to be in reasonable agreement. The effect of four common acids ($HClO_4$, HCl, HNO_3, and H_2SO_4) on the analytical sensitivity of Ca and Mg by atomic absorption was also tested. Perchloric acid provides the greatest sensitivity and H_2SO_4 the least. Nitrate was found to interfere with the determination of Ca and Mg, but it can be eliminated by the addition of Sr or NH_4Cl.

The method for putting carbonate and silicate samples into solution so that determinations of other elements can be made in addition to Ca and Mg is relatively simple and straightforward and involves the adaptation of two separate methods described by Hillebrand, *et al.* (1955). One method consists of treating a weighed and dried sample with 48 percent HF, evaporating to dryness, putting the residue into solution with HCl, separating the R_2O_3 group by precipitation with NH_4OH, and determining the Ca and Mg on the filtrate. This is a standard method for treatment of silicate samples. The other method consists of an initial step of separating the silica by dehydration with $HClO_4$ and then precipitating the R_2O_3 from the filtrate of the silica separation. The R_2O_3 precipitation and the Ca and Mg determination are the same from this step on. The second method is used routinely on all carbonate samples in the analytical laboratories of the Kansas State Geological Survey and has an advantage over the first method in that it allows an SiO_2 determination on the same sample on which all of the major elements are determined. If a silica determination is not desired as a preliminary step on carbonate samples,

they may be treated with HF as described in the first method.

The filtrate and washings from the R_2O_3 precipitation are evaporated so that appropriate dilutions can be made and the Ca and Mg determined by atomic absorption. The dilutions used depend upon the size of the original sample (for silicates, a 1.0-g sample is a minimum amount) and the amount of Ca and Mg present. The R_2O_3 filtrate from a silicate sample is evaporated down to 250 ml. A 25-ml aliquot is then taken and diluted four times. If the Ca and Mg content is extremely low (less than 0.5 percent) no dilution is necessary. In the case of carbonates where large amounts of Ca and Mg are present, the original sample size is of some importance. If Si, Fe, and Al are to be determined on the same sample, a 2-g sample is needed because of the small amounts of these elements normally present in carbonates. If Ca and Mg are the only determinations to be made, a smaller sample size may be used and the later dilutions adjusted accordingly. For a 2-g sample, the R_2O_3 filtrate is put into a 1 liter volumetric flask and made up to the mark. A 10-ml aliquot is then taken and diluted 50 times. The above dilutions were adequate to allow readings to be taken on the middle part of the calibration curve. However, dilutions can be adjusted for individual samples or to meet the specific needs of a particular laboratory.

All determinations were made using the 4226Å and 2853Å lines of Ca and Mg respectively. It was found that the best concentration range for Ca analysis was 1-25 ppm. Because of the extreme sensitivity of Mg to atomic absorption analysis, the concentration range used was 0.1-3.0 ppm.

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The instrument used for this work was a Jarrell-Ash Model 82-516 atomic absorption-flame emission spectrophotometer equipped with a "Hetco" (high efficiency, total consumption) burner. The width of the entrance and exit slits on the Ebert-mount monochromator were 100 and 150 μ respectively. A Westinghouse multi-element hollow-cathode tube containing Ca, Mg, Al, and Li was used. The tube was operated at a current of 5 ma; the photomultiplier, an R106, was operated at 480 v. An air-hydrogen flame was used with the best sensitivities obtained at air and fuel pressures of 12 and 10 psi respectively.

A series of National Bureau of Standard samples were run along with reagent-grade calcium carbonate and a dolomite sample supplied by the G. Fredrick Smith Chemical Company. Table 1 shows a comparison of results obtained by atomic absorption with values given on analysis certificates for each NBS standard. The

TABLE 1.—Comparison of values obtained by atomic absorption method with values given for several standards. An agreement of 0.20 percent was determined to be acceptable.

Sample no.	Ca, %		Mg, %	
	NBS Value	At. Abs.	NBS Value	At. Abs.
National Bureau of Standards 76	0.19	0.14	0.35	0.19
National Bureau of Standards 81	0.04	0.02	0.01	0.01
National Bureau of Standards 102	1.64	1.88	0.13	0.05
National Bureau of Standards 1A	29.53	29.95	1.32	1.44
G. Fredrick Smith 400	21.79	21.70	12.98	13.01
CaCO₃*	40.04	39.96	0.00†	<0.10 ppm

* Reagent-grade CaCO₃.

† Some Mg present, but listed as sulfate. Therefore an exact value is not known.

results obtained with the atomic absorption method were close enough to the listed values to allow a reasonable confidence in the method.

Interferences due to Al, SiO_2, PO_4^{-3}, and SO_4^{-2} are well documented in the literature (Trent and Slavin, 1964; Sprague, 1963). The treatment of silicate samples with HF and the separation of silica with $HClO_4$ in the carbonate samples was used to eliminate silica as a possible interfering element. The R_2O_3 precipitation was used to minimize any aluminum and phosphate interference. Sulfate was present in very small quantities in the samples, but it was felt that it would cause no interference problems. With one exception, no problems with interferences were noted when the same acid was

used to put the standards and the samples into solution.

Commercial atomic absorption standards supplied by the Fisher Scientific Company were used in the initial phases of the work on the methods discussed. Working curves made from these standards were used to obtain the first Ca and Mg results from the NBS standards. The initial values were approximately twice those listed on the analysis certificate. A check for the common interferences was made but no interferences were found. The standards used for the working curves were made up by dissolving $CaCO_3$ and Mg-metal in dilute HNO_3. The effect of acid upon the sensitivity of Ca and Mg was observed next. Standards were made up from $CaCO_3$ and Mg-metal using HCl as the dissolving agent. The NBS samples were rerun, and the results compared with those listed on the analysis certificate and found to be acceptable.

The next step was to note the effect of different acids upon the sensitivity of Ca and Mg to atomic absorption analysis. A series of Ca and Mg standards were made up using four different acids ($HClO_4$, HCl, HNO_3, and H_2SO_4) and separate working curves plotted for each acid. The results for Mg do not show as wide a difference between curves as does Ca, but the same effect is present (Fig. 1, 2). Because of the known effect of sulfate ions on Ca and Mg, a
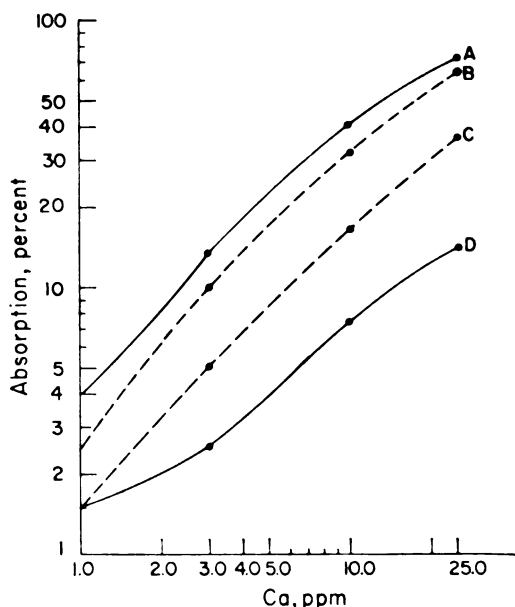

FIGURE 1.—Comparison of calibration curves for calcium made up from four different acids. *A*, $HClO_4$; *B*, HCl; *C*, HNO_3; and *D*, H_2SO_4.
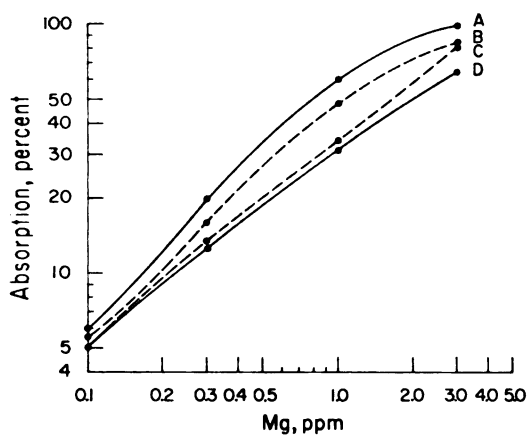
FIGURE 2.—Comparison of calibration curves for magnesium made up from four different acids. *A*, HClO₄; *B*, HCl; *C*, HNO₃; *D*, H₂SO₄.

check for nitrate interference seemed reasonable. To determine whether we were actually getting nitrate interference, three sets of Ca standards were made up. One set of standards was made up from the HNO_3 solution. Another was made up from an HCl solution of $CaCO_3$ to which 100 ppm nitrate had been added. The nitrate was obtained from a solution of primary standard KNO_3. A third set of standards was made up using a solution of $Ca(NO_3)_2$ in water. The results showed that nitrate reduced the sensitivity of Ca to atomic absorption in terms of percent absorption by 2.5 percent at 1 ppm to 10 percent at 25 ppm when compared with an HCl solution of Ca. Figure 3 shows a comparison of Ca and Ca with nitrate added. The curves of the standards made up from $Ca(NO_3)_2$ and $CaCO_3$ in HNO_3 are essentially the same as the curve shown in Figure 3, but for the sake of simplicity in this presentation only the curve with 100 ppm nitrate is shown. The curves shown were run with the recorder set on the 0-10-mv scale. It is apparent from the curves that to determine Ca in amounts less than 1 ppm with nitrate present a scale expansion technique is necessary. However, with an HCl solution of Ca, it was possible to detect Ca in amounts of 0.1 ppm without scale expansion. Figure 3 also shows a comparison of the absorption of Mg and Mg with 100 ppm nitrate added. Again, the difference is not as great as
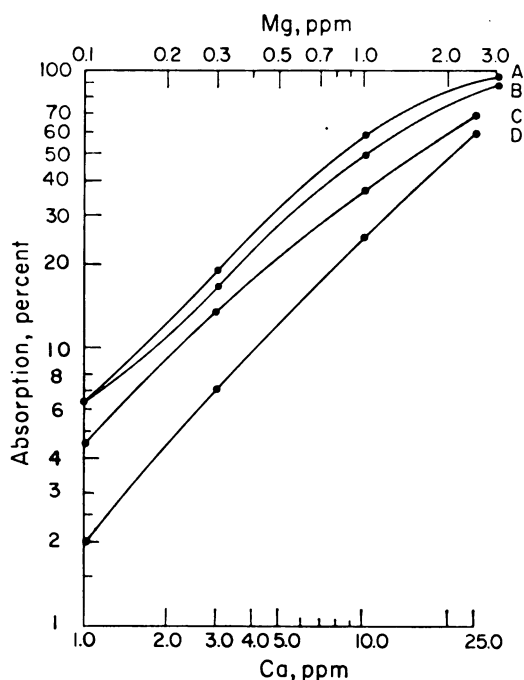

FIGURE 3.—Comparison of calibration curves for calcium and magnesium. *A*, Mg; *B*, Mg + 100 ppm NO₃; *C*, Ca; *D*, Ca + 100 ppm NO₃.

with Ca, but the loss of sensitivity is apparent. Additional work showed that nitrate present in amounts as little as 10 ppm produced some interference effects. The interference effects of nitrate were not difficult to eliminate. Strontium added in the amount of 1500 ppm and NH_4Cl in concentrations of 1000 ppm were effective in eliminating nitrate interference.

It is not known at this time why nitrate interferes with the determination of Ca and Mg. Other workers have reported nitrate interference, but presently no explanation for this interference is known. Although nitrates do interfere, the interference is not difficult to overcome and will not cause any great analytical problems. It is also apparent that even though several types of acid may be used to put Ca and Mg into solution, if the ultimate sensitivity is desired, the choice is limited to $HClO_4$.

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WALTER E. HILL, JR.

Copper in Redbeds of South-Central Kansas

ABSTRACT

A study was made of the copper content of the Ninnescah Shale and the Milan Dolomite Member of the Wellington Formation in south-central Kansas. Five east-west sampling traverses were made across the outcrop in a four-county area. Channel samples numbering 411 were analyzed by x-ray spectroscopy for copper. The copper, as the mineral malachite, was found to be the highest (6.65 percent Cu as the metal) in the Runnymede Sandstone Member of the Ninnescah Shale in Harper County, Kansas.

Geologists who have worked on the Permian redbeds in south-central Kansas have reported malachite ($CuCO_3 \cdot Ca(OH)_2$) associated with dolomite and with some of the shales and sandstones in the area (Swineford, 1955), (Norton, 1939), (Moore, 1951, p. 40). More recently Ham (1964) has reported commercial reserves of copper-bearing shale in a geologically higher unit (Flowerpot Shale) of the Permian redbeds in southwestern Oklahoma.

The Milan Dolomite Member, which is the topmost bed of the Wellington Formation (Permian), is the lowest unit studied. The Milan is approximately 52.7 feet thick at the type locality in section 30, T 32 S, R 3 W, and is composed of five thin, shaly dolomite beds 1-9 inches thick separated by 4-42.3 feet of banded and mottled red and gray-green blocky shale. Malachite is usually found on the laminations of the gray shale found under each thin dolomite bed and in the vugs and cracks in the basal part of the dolomite bed. This is the only copper mineral identified to date in the outcrops investigated.

The overlying Ninnescah Shale is predominantly red shale with gray-green spots and cracks, but it also contains discrete beds of red and gray-green shale. Secondary deposits of gypsum are found as crack fillings and as thin laminae that weather out differentially along the bedding planes of the shale. At some locations gypsum geodes and septarian concretions are relatively abundant. Locally, a thin discontinuous dolomite is found in outcrops of the Ninnescah Shale. The upper member of the Ninnescah Shale is the Runnymede Sandstone described by Norton (1939), who reported malachite in this unit in the vicinity of Runnymede, Harper County, Kansas. The Runnymede is a gray to white shaly, silty, sandstone that is often powdery on weathered outcrops.

Five east-west traverses were made from the outcrop of the Milan Dolomite Member across the Ninnescah Shale to the Runnymede Sandstone Member (Fig. 1), and samples were taken from available outcrops. Where no outcrops were available samples were augered from exposed bedrock, which permitted fresh samples to be taken from a depth of 2-2.5 feet in shale from relatively flat graded road cuts.

Samples were taken on the basis of vertical footage and change of lithology from the outcrops. Lithology changes could not be clearly seen in the auger samples and here samples were
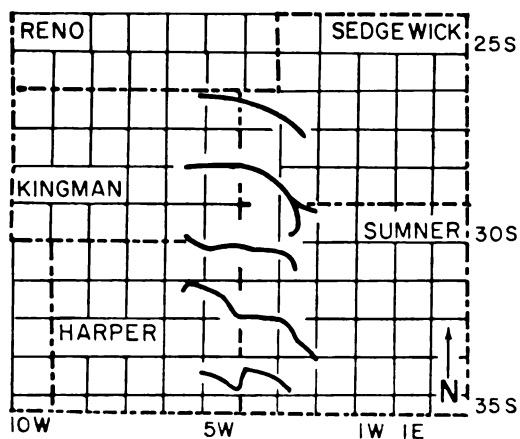

FIGURE 1.—Sampling traverses across the Ninnescah Shale and the Milan Dolomite Member of the Wellington Formation in south-central Kansas.

taken on a footage basis only. Of the entire suite of samples most were representative of lithologies less than one foot in vertical thickness. Thicker units in the shale were broken into 12″ channel samples.

The 441 samples taken were dried, crushed, and ground to pass a 250-μ screen and analyzed for copper content on a GE XRD-6 x-ray spectrograph using a LiF analyzing crystal and tungsten target x-ray tube. The x-ray spectrograph was made available for this study through the courtesy of the Geology Department of the University of Kansas. Copper standards were made up with both dolomite and clay matrices in order to simulate the range of geologic materials likely to be encountered. Plots of the standards in both matrices were linear and nearly superposed in the range from 0.05 to 10.0 percent Cu, indicating no major interferences resulting from the matrix differences.

The field observations and analytical results rapidly delineated several facts: (1) Copper was not present in concentrations exceeding 0.05 percent in any of the red, oxidized parts of the shales of the Milan Dolomite Member or of the Ninnescah Shale. Copper concentrations exceeding this value were found only in some of the gray-green shales, some of the dolomites, and in the silty, shaly Runnymede Sandstone Member; (2) The gray shales in the Ninnescah Shale were found to contain < 0.05 percent Cu; (3) The emplacement of the malachite is controlled by porosity, and it is deposited in the cracks and parting planes of the shales associated with dolomite beds and in cracks, vugs, and parting planes of the basal part of the dolomite strata; (4) The Cu has been carbonate precipitated from solution in the shale, dolomite, and sandstone; (5) Low porosity dolomite strata are usually very low in Cu content; (6) As pointed out by Swineford (1955), strontianite is also associated with the malachite in the Milan Dolomite Member; (7) The lower carbonate strata that overlie a shale sequence usually contain the highest amounts of Cu.

The anomalously high Cu in this area is concentrated in the outcrops of the Milan Dolomite Member and the Runnymede Sandstone Member. The highest concentrations found in percent by weight of copper as the metal are:

Milan Dolomite Member	*Runnymede Sandstone Member*
.31% Cu in dolomite .69% Cu in shale for 107 samples of Milan Dolomite and intercalated shales.	6.65% Cu (in a 3″-bed of siltstone) for 34 samples of Runnymede Sandstone and associated thin dolomites and gray shales.

Significantly high concentrations of Cu (up to 6.6 percent in one sample) are present at least surficially in the lower Milan Dolomite Member and Runnymede Sandstone Member of the lower part of the Permian redbeds. Additional investigation of the copper-rich zone both on the outcrop and in the subsurface appears warranted. If the copper-rich zones identified have sufficient areal extent with a favorable overburden ratio, they may warrant commercial exploitation.

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EDWIN D. GOEBEL

Age of Mississippian Rocks in a Core From Northwestern Kansas

ABSTRACT

Conodonts recovered from a core from extreme north-western Kansas indicate an age of late Osagian and late early Meramecian for Mississippian rocks from 5,265 to 5,365 feet. Parts of the *Taphrognathus varians-Apatognathus?* Assemblage Zone and the *Gnathodus texanus-Taphrognathus* Assemblage Zone are recognized from this interval.

Eighty conodont specimens representing eight genera, three species, and several unnamed representatives of four additional genera were recovered from the J. O. Farmer No. 1 Wagner well (C SW SW, sec. 5, T 2 S, R 40 W, Cheyenne County, Kansas). The core was taken for the Continental Oil Company. The well, drilled from an elevation of 3,523 feet above sea level, was cored from 5,148 to 5,365 feet across the Pennsylvanian-Mississippian boundary. Scouting information placed the top of the Mississippian at 5,264 feet, and the top of Cambro-Ordovician (Arbuckle) rocks at 5,470 feet.

Part of the core from 5,264 feet to 5,365 feet (carbonate and chert-carbonate rocks) was slabbed and half of the core was dissolved in dilute acetic acid. The distribution and abundance of conodonts recovered from this core were plotted (Table 1).

The conodonts indicate that these rocks in extreme northwestern Kansas are of late Osagian and late early Meramecian age. Parts of the *Taphrognathus varians-Apatognathus?* Assemblage Zone and the *Gnathodus texanus-Taphrognathus* Assemblage Zone, both of the Valmeyeran of Illinois (Collinson, *et al.*, 1962), are recognized in this Kansas conodont fauna.

Taphrognathus sp. and *Gnathodus* sp. are the most abundant conodonts in the fauna followed by *Neoprioniodus tulensis.* Few gnathodid conodonts were recovered above 5,300 feet and *Taphrognathus* is common from 5,266 to

5,300 feet. Below 5,300 feet *Gnathodus* dominates the conodont fauna and *Taphrognathus* is absent.

According to Collinson, *et al.* (1962), the base of the *Taphrognathus varians-Apatognathus?* Assemblage Zone of the type locality in the Upper Mississippi River Valley, which includes the Warsaw Limestone, the Salem Limestone, and the lower part of the St. Louis Limestone, is marked by the oldest occurrence of *Apatognathus?* and the common occurrence of *Taphrognathus varians.* The upper boundary of the zone is marked by the youngest regular occurrence of *Taphrognathus* sp., the oldest occurrence of abundant *Apatognathus?,* and the oldest common occurrence of *Cavusgnathus* sp. Collinson, *et al.* (1962), state that the *Gnathodus texanus-Taphrognathus* Assemblage Zone coincides with the boundaries of the Keokuk Limestone.

Rexroad and Collinson (1965) demonstrated a similarity between the Keokuk fauna and the Warsaw-Salem fauna in species present, but dissimilarity in proportions of species present. *Gnathodus texanus* dominated Rexroad and Collinson's Keokuk collection, making up 78 percent of the fauna, and *Taphrognathus* constituted only 7 percent of the fauna. In the Warsaw *Gnathodus* represented 44 percent of the specimens and *Taphrognathus* 20 percent of the specimens. In the Salem *Gnathodus* represented 3 percent and *Taphrognathus* 58 percent of the specimens. Thompson and Goebel (1963) and Thompson (1965) reported a distribution of Meramecian conodonts in the Warsaw and Salem rocks of Kansas similar to the distribution found at the type localities.

Unidentifiable fragments of conodonts were recovered from the core interval ranging from 5,305 to 5,335 feet. Study of this part of the

TABLE 1.—Distribution and abundance of conodonts recovered from the J. O. Farmer No. 1 Wagner core (sec. 5, T 2 S, R 40 W) Cheyenne County, Kansas. Numbers indicate identifiable specimens recovered. Dashed line indicates interval of high chert content in core.

Depth below surface, feet	Gnathodus sp.	G. texanus	Hibbardella sp.	Ligonodina sp.	Lonchodina sp.	Magnilaterella sp.	Neoprioniodus sp.	N. tulensis	Spathognathodus sp.	Taphrognathus sp.	T. varians
5260	..	..	..	..	..	..	..	..	..	..	..
65	..	..	..	..	..	..	..	..	..	..	..
70	..	..	..	3	2	1	1	3	..	6	6
75	..	..	..	5	1	2	1	1	1	..	8
5280	..	..	..	..	(core lost)	..	..	..	..	..	..
85	..	..	..	..	..	..	..	..	..	..	..
90	1	..	..	1	1	1	..	..	..	..	..
95	..	..	2	..	..	1	..	1	..	..	1
5300	..	..	..	..	..	1	..	1	1	1	..
05	1	1	..	..	1	1	..	..	..	..	..
10	..	..	..	..	..	..	..	..	..	..	..
15	..	..	..	..	..	..	..	..	..	..	..
5320	..	..	..	..	..	..	..	..	..	..	..
25	..	..	..	..	..	..	..	..	..	..	..
30	..	..	..	..	..	..	..	..	..	..	..
35	..	..	..	..	..	..	..	..	..	..	..
5340	..	1	..	..	..	..	..	..	..	..	..
45	..	..	..	..	..	..	..	..	..	..	..
50	..	6	1	1	..	..	..	..	..	..	..
55	..	6	..	..	..	..	..	..	..	..	..
5360	..	3	1	..	..	..	..	..	..	..	..
65	..	3	..	..	..	..	..	..	..	..	..

(Left margin labels: MERAMECIAN STAGE for rows 5260–05; ? between 05 and 10; OSAGIAN STAGE for rows 10–65.)

core, which is transitional from a dominance of *Gnathodus* to a dominance of *Taphrognathus*, yielded few specimens. This interval is composed of cherty dolomite and dolomitic chert and the residues make up 60-80 percent of the rock by weight. The Osagian-Meramecian boundary falls at the top of this interval. However, some scouting data indicate that the youngest Mississippian rocks in the Wagner core are the Warsaw Limestone (Meramecian) starting at 5,267 feet. The top of the Osagian rocks was designated at 5,320, and the top of Kinderhookian rocks at 5,368 feet.

The conodont fauna from 5,340 to 5,365 feet indicates late Osagian age only. The fauna in the upper part of the core studied, from 5,265 to 5,300 feet, indicates late early Meramecian age.

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GARY F. STEWART

Jointing in Upper Pennsylvanian Limestones in Northeastern Kansas

ABSTRACT

Joint sets were examined in the Plattsmouth and Leavenworth limestone members of the Oread Limestone and in the Ervine Creek and Rock Bluff limestone members of the Deer Creek Limestone. These joint sets trend about N 60° E and N 35° W, respectively. The long, planar northeast-trending shear joints are more common than the short, rough-surfaced northwest-trending tension joints. Short, planar north-trending joints also are present in these beds.

Joints are abundant in limestone beds of northeastern Kansas, but they have received little examination and have not been well described. This study is concerned with the general character and distribution of joints in four members of the Shawnee Group (Virgilian, Upper Pennsylvanian) in parts of Douglas, Shawnee, Jefferson, Osage, and Atchison counties, Kansas.

Well-jointed limestones were examined at 10 localities (Fig. 1), mainly in highway cuts. Most

FIGURE 1.—Map of northeastern Kansas showing approximate locations of exposures studied.

of the joints are vertical. This study was concentrated on the trends and interrelations of the joint sets, and the effects of lithology on development of joints. Only well-defined joints were studied, in an effort to eliminate fractures that could have been developed by human activity, *e.g.*, blasting for highway construction.

Trends of joints are shown by strike-frequency diagrams (Fig. 2, 3, 4, 5). Radial scales differ (cf. Fig. 2 and 3), so that diagrams constructed from only a few measurements can be easily compared by inspection with those constructed from many measurements.

The Ervine Creek Limestone Member of the Deer Creek Limestone and the Plattsmouth Limestone Member of the Oread Limestone where examined are about 10 and 15 feet thick, respectively. These members are gray, weathering buff, fossiliferous, and are wavy-bedded with thin shale partings. Small northeast- and northwest-trending joints cut thin single beds of these members, but dominant joints trend about N 60° E to N 65° E (Fig. 2, 3). The northeast-trending joints are long, planar, and distinct and cut completely through these multiple-bedded members. Northwest-trending joints are short, irregular fractures that generally trend about N 30° W and commonly do not penetrate the entire thickness of the Ervine Creek and Plattsmouth. Northeast-trending joints are more abundant than northwest-trending joints (Fig. 2, 3).

The Rock Bluff Limestone Member of the Deer Creek Limestone and the Leavenworth Limestone Member of the Oread Limestone are single beds about 2 feet thick and are bluish-gray, fossiliferous, hard, and brittle. The dominant joints in these units trend about N 55° E (Fig. 4, 5), are abundant, long, and planar, and many faces have feather-fracture markings.
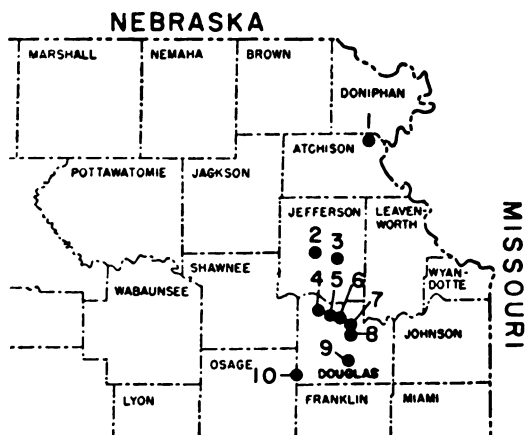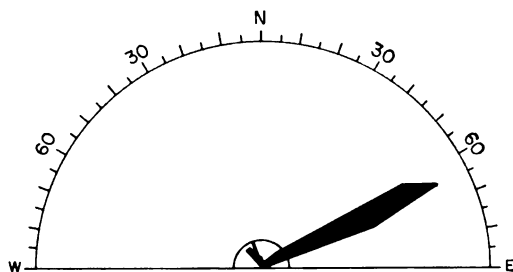
FIGURE 2.—Strike-frequency diagram of the Ervine Creek Limestone Member of the Deer Creek Limestone. Total number of observations is 244, of which 199 trend northeastward. Radius of small semicircle represents 10 observations.
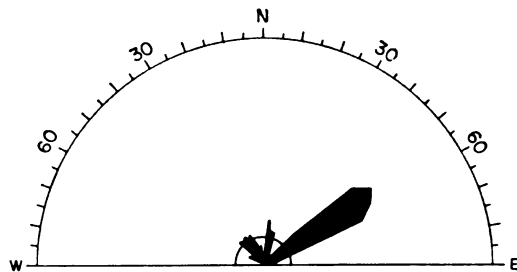

FIGURE 4.—Strike-frequency diagram of the **Rock Bluff** Limestone Member of the Deer Creek Limestone. Total number of observations is 350, of which 205 trend northeastward and 48 trend almost north. Radius of small semicircle represents 10 observations.
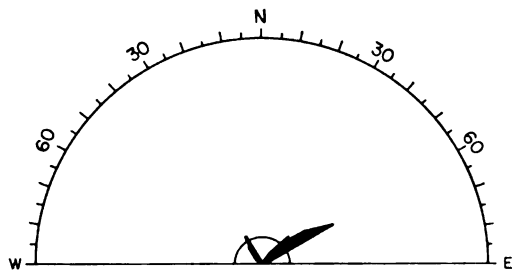

FIGURE 3.—Strike-frequency diagram of the Plattsmouth Limestone Member of the Oread Limestone. Total number of observations is 59, of which 46 trend northeastward. Radius of small semicircle represents 5 observations.
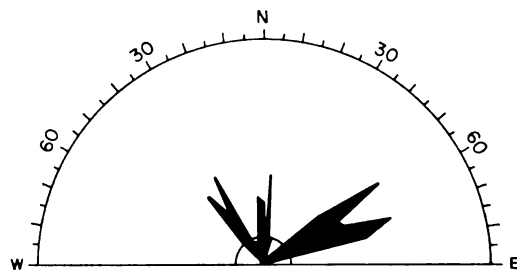

FIGURE 5.—Strike-frequency diagram of the Leavenworth Limestone Member of the Oread Limestone. Total number of observations is 228, of which 113 trend northeastward and 49 trend northward. Radius of small semicircle represents 5 observations.

Northwest-trending joints are not as abundant, and they trend about N 30° W to N 40° W. They commonly extend only from one northeast-trending joint to the next, and their surfaces generally are quite rough. Both the Rock Bluff and Leavenworth contain a set of short, smooth-surfaced, north-trending joints that are tightly closed, and many of the joints do not entirely penetrate the beds. At some places, joints that are smooth and unweathered parallel joints that are marked by solution channels and joints that are coated with calcium carbonate. Figures 4 and 5 show orientations of joints measured in the Rock Bluff and Leavenworth limestones.

The northeast-trending sets of joints in the Ervine Creek, Plattsmouth, Rock Bluff, and Leavenworth members are clean-cut in both single- and multiple-bedded units. They account for 64 percent of 881 observations and occur as a single set in each unit studied. In the single-bedded Rock Bluff and Leavenworth members, feather-fracture markings are commonly developed on faces of the northeast-trending joints. In contrast, northwest-trending joints have

rough surfaces in both types of limestone, and these sets make up only 25 percent of the measurements. They are not as straight as northeast-trending joints, and few of them have feather-fracture markings or completely penetrate the multiple-bedded limestones. North-trending joints generally are short, smooth-sided, and tightly closed. They make up 11 percent of all the joints measured in this study.[1]

Northeast-trending joints in these four limestone units are similar to a set of joints in Paleozoic rocks in parts of New York and Pennsylvania. These joints, described by Parker (1942, p. 395-397), are dominantly vertical, have plane surfaces, and cut many kinds of rock, including cross-bedded rocks, rocks deformed during deposition, conglomerate pebbles, and even hard concretions in shales. The joints are numerous, locally consistent in trend, and some joint surfaces have feather-fracture markings. Parker concluded that these are shear joints.

[1] North-trending joints probably make up more than 11 percent of the joints in the Rock Bluff and Leavenworth. Locally they are more abundant in the Leavenworth than even northeast-trending joints. Because most of these occur as short, tightly closed cracks in the rock, bearings of only the largest and most distinctive of them were measured.

Feather-fracture markings, similar to those present on many northeast-trending joints in the Rock Bluff and Leavenworth, were studied by Roberts (1961) in rocks of South Wales, Great Britain, that range in age from Devonian to Jurassic. Roberts concluded that feather-fracture markings seem to be restricted to surfaces of shear joints, although the process of feather-fracturing appears to be a tension phenomenon. Roberts showed that small shears could be enlarged by tensional forces during release of stored energy, with feather-fracture markings being produced in the process. Hence, northeast- and northwest-trending joints in the Ervine Creek, Plattsmouth, Rock Bluff and Leavenworth limestone members seem to be shear and tension joints, respectively.

Results of this study show only the general nature of jointing in four rock units of northeastern Kansas. A detailed study of jointing in limestones of this region should yield a great deal of evidence as to the genesis of the jointing in these rocks. Some of the points discussed below merit special consideration.

If northeast-trending joints are, in fact, shear joints, then perhaps other rocks of Pennsylvanian age in this area may contain two sets of shear joints rather than the single set observed in the four limestone units included in this study. North-trending joints have only been briefly discussed in this paper. They resemble shear joints, but as pointed out previously, they are common only in the Rock Bluff and Leavenworth and are not as well developed as northeast-trending joints. Unweathered joints in the Rock Bluff and Leavenworth parallel joints that show definite evidence of weathering, indicating that jointing has occurred at different times. These fresh joints have been observed in road cuts where they presumably were caused by lateral expansion of the limestone. If this interpretation is correct, then the Rock Bluff and Leavenworth limestones should contain directional zones of weakness that are likely to become the locations of joints when stresses on the rock are properly oriented. The common termination of tension joints at points of contact with shear joints also could be evidence of a difference in ages of joints, with shear joints being the older of the two sets.

EXPOSURES STUDIED

Locality 1.
SE ¼ sec. 2, T 5 S, R 20 E. East and west sides of road cut on Kansas Highway 7, 4.1 miles north of Atchison, Atchison Co., Kansas. Ervine Creek and Rock Bluff limestone members.

Locality 2.
NW ¼ sec. 32, T 9 S, R 18 E. Exposure along south-facing slope at southeast corner of cemetery at Ozawkie, Jefferson Co., Kansas. Rock Bluff Limestone Member.

Locality 3.
NE ¼ sec. 5, T 10 S, R 19 E. North side Kansas Highway 92, about .25 mile west of Oskaloosa, Jefferson Co., Kansas. Ervine Creek and Rock Bluff limestone members.

Locality 4.
SW ¼ sec. 15, T 12 S, R 18 E. North side Kansas Turnpike, 0.2 mile east of Bridge No. 253, Douglas Co., Kansas. Ervine Creek and Rock Bluff limestone members.

Locality 5.
NW ¼ sec. 20, T 12 S, R 19 E. North side Kansas Turnpike, 4.1 miles west of West Lawrence Interchange, Douglas Co., Kansas. Slope facing westward, about 0.1 mile east of small, southward-flowing stream. Plattsmouth Limestone Member.

Locality 6.
NW ¼ sec. 21, T 12 S, R 19 E. North side Kansas Turnpike, 3.3 miles west of West Lawrence Interchange, and 0.8 mile west of Baldwin Creek, Douglas Co., Kansas. Plattsmouth and Leavenworth limestone members.

Locality 7.
NW ¼ sec. 35, T 12 S, R 19 E. Exposure at residence of Oscar Rojas, southeast corner 9th Street and Pamela Lane, Lawrence, Douglas Co., Kansas. Leavenworth Limestone Member.

Locality 8.
NE ¼ sec. 2, and NW ¼ sec. 1, T 13 S, R 19 E. Exposure on both sides of Iowa Street, 0.2 mile south of intersection with 15th Street, Lawrence, Douglas Co., Kansas. Leavenworth Limestone Member.

Locality 9.
NE ¼ and SE ¼ sec. 2, T 14 S, R 19 E. Exposure along west side U.S. Highway 59, 0.1 mile north of Pleasant Grove, Douglas Co., Kansas. Plattsmouth and Leavenworth limestone members.

Locality 10.
NE ¼ sec. 3, and NE ¼ sec. 4, T 15 S, R 17 E. Exposures along south side U.S. Highway 50 N, 2.7 and 1.8 miles east of Overbrook, Osage Co., Kansas. Rock Bluff Limestone Member.

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