

SHORT PAPERS ON RESEARCH IN 1970

Bulletin 202, Part 1

Edited By Jo Anne Crossfield

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Lawrence, Kansas 1971*

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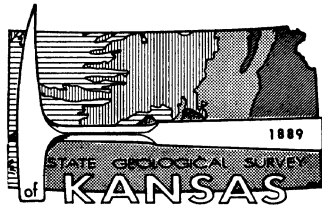
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BULLETIN 202, PART 1

Short Papers on Research in 1970

Edited by
Jo Anne Crossfield

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Short Papers on Research in 1970

This collection of papers continues the series begun in 1967 as a part of the *Reports of Studies* in the Bulletin. The papers present scientific and economic results of work by members of the State Geological Survey of Kansas and others during the calendar year 1970.

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Ubiquity of Hexahydrate in Kansas

ABSTRACT

Field and laboratory observations indicate that the efflorescences of magnesium sulfate widely distributed in Kansas are hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), not epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Epsomite occurs only as a transitional phase in the formation of hexahydrate.

Hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$) that occurs in Kansas from an underground storage area near Atchison was first identified by this author using the X-ray diffraction method (Tien and Waugh, 1970). Another phase of magnesium sulfate, epsomite or epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), that has long been known to have wide distribution in Kansas (Mudge, 1881) was also found in the underground storage area. Both field and laboratory evidence indicates that hexahydrate is formed by dehydration of epsomite, which is not stable under laboratory conditions (temperature above 20°C , relative humidity below 70 percent), and that reported wide distribution of epsomite in Kansas is questionable.

On a field trip to central and western Kansas in the winter, the author noted that white efflorescences were very common on the surface of the outcrops (Fig. 1). Samples were collected and kept in airtight



FIGURE 1.—Hexahydrate on the surface of Carlile Shale (Upper Cretaceous), NE sec. 3, T 11 S, R 17 W, Ellis County, Kansas.

¹ Department of Geology, East Carolina University, Greenville, North Carolina 27834. Manuscript received August 18, 1970.

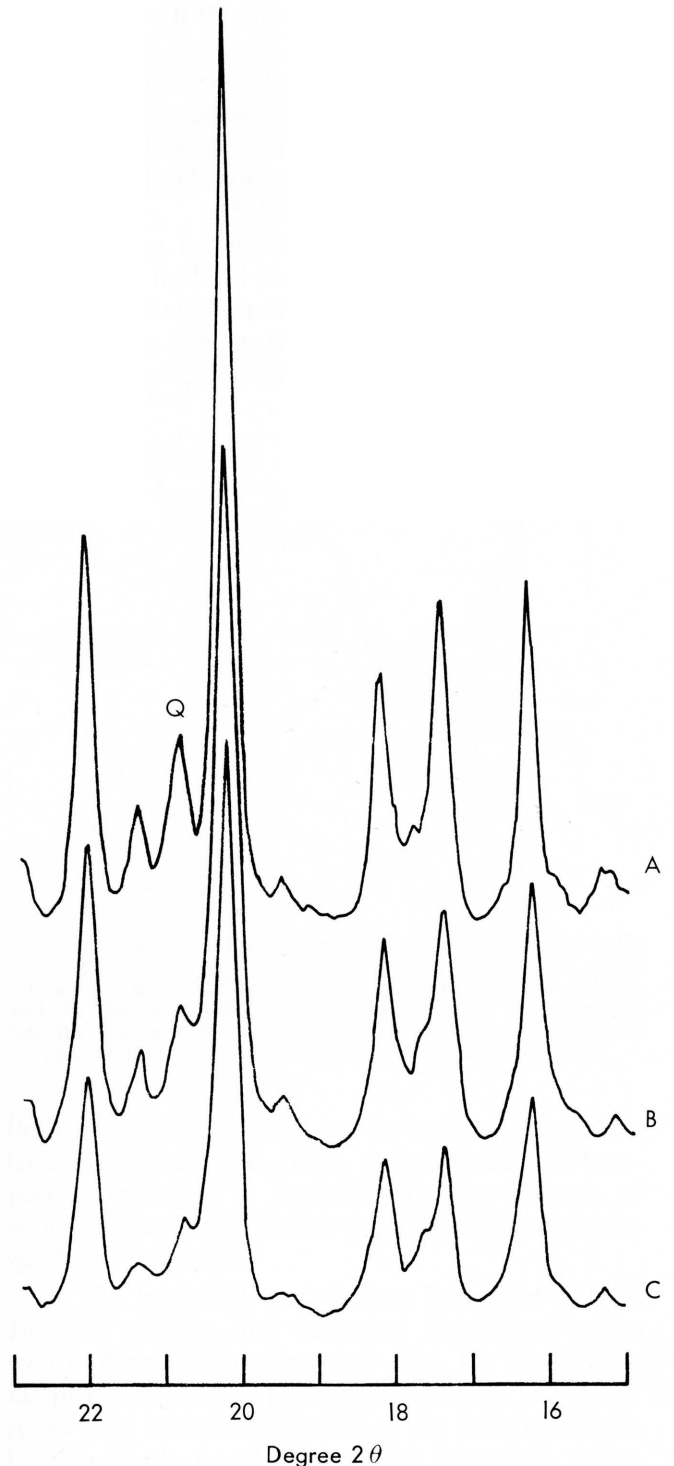


FIGURE 2.—X-ray diffraction patterns for hexahydrate from selected outcrops: (A) Carlile Shale (Upper Cretaceous), NE sec. 3, T 11 S, R 17 W, Ellis County, Kansas; (B) Argentine Limestone (Upper Pennsylvanian), NW sec. 9, T 13 S, R 22 E, Johnson County, Kansas; (C) Toronto Limestone (Upper Pennsylvanian), NW sec. 22, T 14 S, R 18 E, Douglas County, Kansas; (Q) quartz reflection.

jars to prevent dehydration and analyzed by the X-ray diffraction method as soon as they were brought into the laboratory. It was found that all the samples collected were hexahydrate. No trace of epsomite was detected. Samples of white efflorescences were also collected from various places in eastern Kansas during the summer. X-ray diffraction data for these samples also indicated that hexahydrate was the only phase of magnesium sulfate present (Fig. 2).

The origin and the occurrence of epsomite and hexahydrate has been discussed by Tien and Waugh (1970) on the basis of the evidence obtained from the studies of the underground storage area and from the laboratory. Additional observations from the surface

of outcrops confirm the conclusion that epsomite occurs only as a transitional phase in the formation of hexahydrate from solutions. The efflorescences of magnesium sulfate so widely distributed in Kansas are hexahydrate, which, therefore, is a common mineral in the State.

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Preliminary Report: Morphological Variation of Ostracoda from the Yankee Tank Creek Drainage Basin, Douglas County, Kansas

ABSTRACT

Thirty-three samples that contained ostracodes were collected by weekly sampling of each of nine ponds for a four-week period in June and July of 1969. Measurements of eight characters from the right valves of 317 specimens of *Cypridopsis vidua* were analyzed with a two-level nested analysis of variance. Statistically significant ($P < 0.001$) geographic variation was shown by all eight characters, whereas only one character showed significant temporal variation. Samples from ponds at higher elevations contributed most to the variation, and it is suggested that ponds with high elevations may have more heterogeneous environments.

The ostracode species *Cypridopsis vidua* is abundant in farm ponds in the Yankee Tank Creek drainage basin of Douglas County, Kansas, where the Environmental Geology Section of the Kansas Geological Survey is coordinating a survey of many aspects of the environment. The purpose of the research described herein is to begin investigation of the hypothesis that carapace morphology of *C. vidua* varies consistently with environmental parameters and thus may be developed as an indicator of long-term environmental changes. The first phase of the research involves establishing patterns of geographic and temporal variation. The Yankee Tank Creek drainage basin (Fig. 1) is well suited for such a study, not only because of the work of the Kansas Geological Survey there, but also because it includes more than 30 farm ponds that are likely habitats for *C. vidua*. The watershed is also the site of the upland sanitary landfill of the City of Lawrence and thus may be subjected to pollution at some time in the future.

Cypridopsis vidua was selected for study because of its nearly ubiquitous distribution in ponds and streams of the drainage basin and because, as a species with very broad geographic distribution, it has been included in many environmental studies both in North America and Europe. It is hoped that relationships between carapace morphology and environment will be found as a result of later phases of this research and that they will be applicable to the species wherever it occurs. Furthermore, *C. vidua* reproduces en-

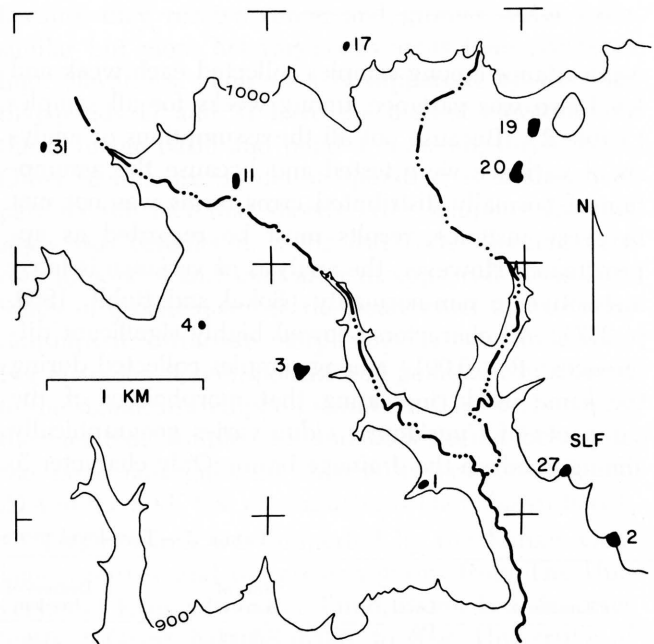


FIGURE 1.—Map of the Yankee Tank Creek drainage basin showing the locations of the ponds sampled, the location of the sanitary landfill (SLF), permanent and intermittent streams, and the 900- and 1000-foot contours. Pond 27 was sampled, but no *Cypridopsis vidua* were found presumably because effluent from the sanitary landfill had polluted the pond.

tirely parthenogenetically, and no males of the species have ever been found. Thus, statistical study of carapace morphology is facilitated by the absence of sexual dimorphism, which is pronounced among many species of ostracodes.

In the four-week period from June 6 to July 3, 1969, 33 samples that contained *Cypridopsis vidua* were collected from nine ponds (Fig. 1). Ponds were sampled each week. From these samples, 317 ostracodes were measured for each of the eight characters listed in Table 1 and illustrated in Figure 2. Where possible, ten specimens were measured from each sample. These specimens have been deposited with The University of Kansas Museum of Invertebrate Paleontology as specimens 1,007,570 through 1,007,886.

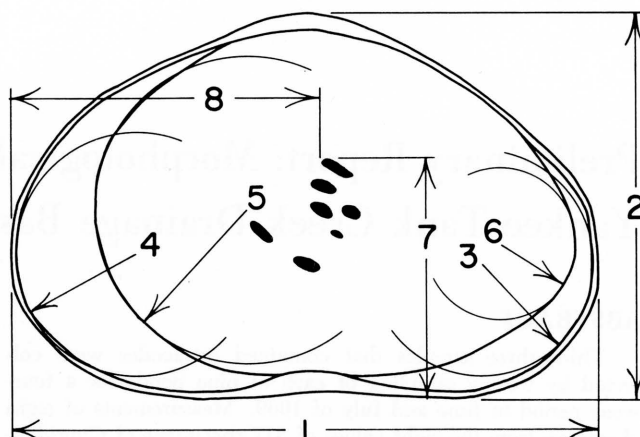
Data for each character were analyzed by a two-level nested analysis of variance in which level one

¹ Department of Geology, The University of Kansas, Lawrence, Kansas 66044. Manuscript received October 14, 1970.

TABLE 1.—Characters measured (see Fig. 1).

Character 1	Length of right valve
Character 2	Height of right valve
Character 3	Radius of curvature of posterior outline
Character 4	Radius of curvature of anterior outline
Character 5	Radius of curvature of anterior inner margin
Character 6	Radius of curvature of posterior inner margin
Character 7	Distance from venter to top of muscle scar pattern
Character 8	Distance from anterior margin to front of top adductor muscle scar

was variance among samples collected each week and level two was variance among weeks for all samples (Table 2). Because not all the assumptions of analysis of variance were tested and because the assumption of normally distributed error terms was not met in every instance, results must be regarded as approximate. However, the analysis of variance is fairly insensitive to non-normality (Sokal and Rohlf, 1969, p. 377). All characters showed highly significant differences ($P < 0.001$) among samples collected during the same week, indicating that morphology of the carapaces of *Cypridopsis vidua* varies geographically among ponds in the drainage basin. Only character 5,

FIGURE 2.—Right valve of *Cypridopsis vidua* showing the eight characters measured.

diameter of the anterior inner margin, showed significant difference of morphology ($P < 0.01$) from week to week, that is, temporal variation.

Details of the results of Student-Newman-Keuls (SNK) *a posteriori* tests will be presented in a later paper. Results for character 1, length, are shown in Table 3 and more or less summarize results from all

TABLE 2.—Two-level nested analysis of variance tables.

Character	Level	Sum of squares	Degrees of freedom	Mean square	F-test	Variance components (percent)
1	2	0.00	3.0	0.00	0.11 N.S.	-----
	1	0.12	29.0	0.00	13.40 ***	60.48
	0	0.09	28.9	0.00		46.74
2	2	0.00	3.0	0.00	0.36 N.S.	-----
	1	0.04	29.0	0.00	7.30 ***	41.16
	0	0.05	28.9	0.00		62.62
3	2	0.00	3.0	0.00	0.20 N.S.	-----
	1	0.01	29.0	0.00	2.62 ***	14.78
	0	0.02	28.6	0.00		87.58
4	2	0.00	3.0	0.00	2.16 N.S.	6.12
	1	0.00	29.0	0.00	7.11 ***	36.53
	0	0.00	28.9	0.00		57.35
5	2	0.01	3.0	0.00	4.92 **	9.07
	1	0.02	29.0	0.00	2.24 ***	10.40
	0	0.08	28.6	0.00		80.53
6	2	0.00	3.0	0.00	1.76 N.S.	2.31
	1	0.01	29.0	0.00	2.91 ***	16.24
	0	0.03	28.7	0.00		81.45
7	2	0.00	3.0	0.00	0.28 N.S.	-----
	1	0.02	29.0	0.00	6.30 ***	36.99
	0	0.03	28.8	0.00		66.90
8	2	0.00	3.0	0.00	0.91 N.S.	-----
	1	0.00	29.0	0.00	5.68 ***	32.94
	0	0.07	28.8	0.00		67.50

TABLE 3.—Results of Student-Newman-Keuls *a posteriori* test. Sample numbers indicate the pond number followed by the week during which the sample was collected.

Sample number	Nonsignificant subsets
4-2	
31-5	
4-5	
4-3	
31-4	
31-3	
4-4	
2-5	
31-2	
1-3	
2-4	
19-4	
20-2	
19-3	
2-3	
19-2	
1-4	
19-5	
11-5	
3-5	
20-5	
3-4	
20-4	
3-3	
1-5	
11-2	
11-3	
20-3	
17-5	
11-4	
17-3	
17-4	
17-2	

tests. Note that all samples from pond 4 are in nonsignificant subsets that do not include samples from pond 3 and pond 17. The differences cannot be easily interpreted. It was originally hypothesized that elevation of the ponds might correlate highly with environmental and, hence, morphological differences.

Geological formations in the area comprise alternating, nearly horizontal limestone and shale members all with maximum thickness of less than 15 feet. Ponds at lower elevations would in general receive (1) runoff from streams crossing a greater variety of substrates, and (2) groundwater from more members, thus representing greater lithologic variety. Insofar as environmental conditions in the ponds are affected by surface and ground water, ponds with low elevation could be expected to show greater homogenization because they receive runoff and ground water from similar but more heterogeneous areas than ponds at high elevations. This idea is supported by the fact that ponds 17 and 31 have the highest elevations in the drainage basin and pond 4 is among the highest. Other factors are no doubt operative as is shown in part by the fact that shortly after sampling for this study was completed, living ostracodes became very rare in pond 4 and soon after disappeared altogether. Study of geochemistry of the pond water and its relationships to ostracode morphology is now underway. For character 5, both pond 4 and pond 20 contributed to the significant temporal variation. This is shown by the fact that samples 4-2 and 20-2 do not belong to the same nonsignificant subsets as samples 4-5 and 20-4 in the SNK test of character 5 (not shown here).

This research was supported by the Kansas Geological Survey and by research grants from The University of Kansas Research Fund, Biomedical Sciences Support Grant No. FR-07037 to The University of Kansas, and the Wallace E. Pratt Research Fund of the Department of Geology. I am indebted to Richard B. Koepnick, Robert Evans, and John C. Waters for their help with the research. H. Meade Cadot read the manuscript and contributed to its improvement.

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MAYNARD P. BAULEKE

Incipient Expansion in Kansas Volcanic Ash

ABSTRACT

Expansion in a volcanic ash shard starts wherever the temperature-viscosity conditions are optimum for expansion.

A fully expanded volcanic ash shard is a mass of sealed bubbles. When viewing such material one cannot answer the questions: Where does the expansion start in the shard? Does it start at the edge and work inward or does it start at random locations?

During our experimental studies of expanding volcanic ash we found that the fully expanded ash could be separated from the nonexpanded ash by mixing with water and stirring. The fully expanded ash would float to the top; the remainder would sink to the bottom. In the sink portion were found a number of shards in which there was incipient expansion, but the shards had not expanded enough to lower the bulk density to less than that of water.

Shards that had just begun to develop an expanded structure could be separated under a microscope. Photographs of these shards are shown in Figure 1. The assumption that the expansion starts from the edge and moves inward is supported by bubble formations observed in many shards, but in some shards the expansion started in the middle at random locations. One can interpret this to mean that the shard contains an internal pore structure sealed by a thin cap of glass that reaches its softening point before that of the rest of the shard. The expanding gas inside the pore starts to push against the surface, causing the bubble to form. Even along the edge, where there is discrete bubble formation, there is evidence that a sealed capillary structure exists inside the shard.

Expansion begins at any location on the shard where the temperature is favorable to formation of viscous deformation accompanied by expansion of confined gas. When temperature conditions are uni-

form across the piece, expansion begins where the glass is thinnest.

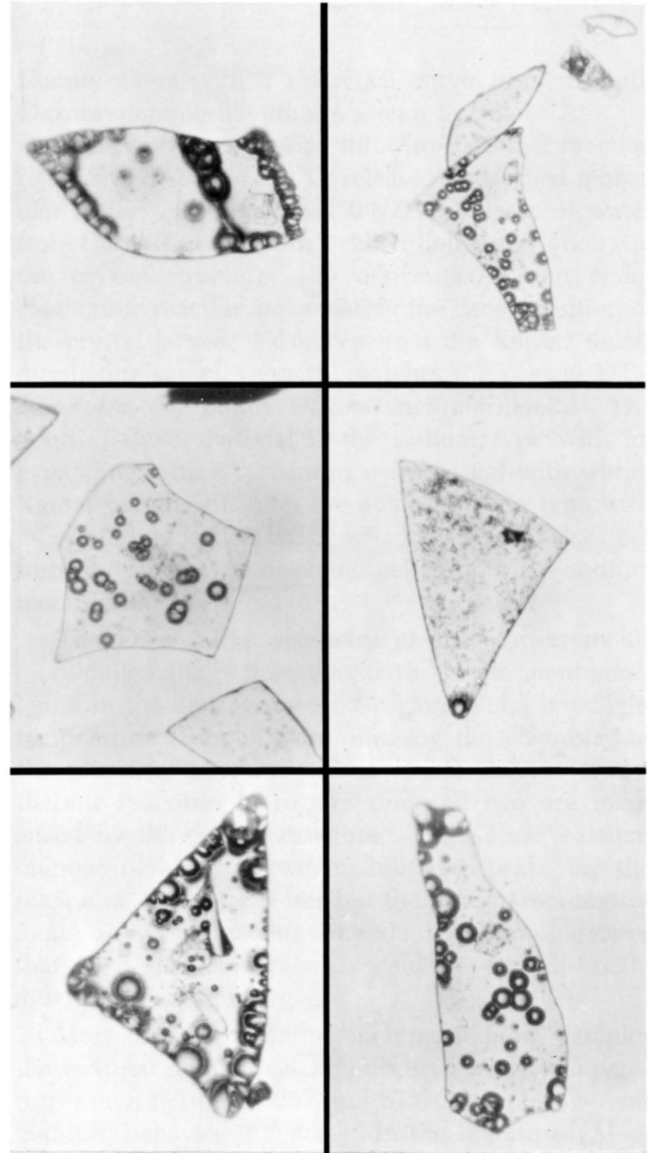


FIGURE 1.—Volcanic ash shards showing various stages of incipient expansion. 250×

Differential Thermal Analysis (DTA) Study of Kansas Montmorillonitic Clays from Phillips and Wallace Counties

ABSTRACT

Differential thermal analysis (DTA) curves of Kansas montmorillonites will most likely be those of an "abnormal" montmorillonite. No sample showed the single dehydroxylation reaction peak at 725°C of a normal montmorillonite. The predominant dehydroxylation reaction occurred at 525°C, although, especially in samples from Phillips County, two dehydroxylation peaks at 525° and 675°C were often present in a sample. Most curves had the typical two-peak endothermic water loss reactions in the 100-200°C range associated with calcium montmorillonite. Caliche (calcium carbonate) was a common impurity in Wallace County materials. All were very low in organic matter. Based on fired color, Wallace County material has a higher iron content than material from Phillips County.

The geology of the Kansas montmorillonite clay deposits in Phillips and Wallace counties has been adequately described by Ives (1960). Large, non-contaminated samples were obtained by drilling 24-inch holes at the sample locations listed in Table 1. The drill bucket was emptied every 12-14 inches of hole depth up to a maximum depth of 42 feet. Only the montmorillonitic clay zones were sampled.

Many of the Wallace County deposits were of the pocket and channel type. A good deposit would be drilled, yet 50 feet away no montmorillonite would be found. Phillips County deposits appeared to be more continuous across the region.

Earlier X-ray studies by the clay mineralogist of the State Geological Survey identified the clay mineral present as of the montmorillonite type (Paul Franks, personal communication, 1960). The purpose of this study was to compare the thermal decomposition behavior of the two deposits. A DTA was run on each sample collected. The 10-mg pellet sample method (Tien and Bauleke, 1970) was used in conjunction with the microsample holder in a STONE-TRACOR¹ Model 220 differential thermal analyzer. Care was exercised to eliminate impurities in these very small samples.

Representative data curves of the 24 samples from Phillips County and the 32 samples from Wallace

TABLE 1.—Sample locations.

Ranch	Phillips County		Wallace County	
	Location		Ranch	Location
Adee	Sec. 11, T 1 S, R 18 W		Abraham-	
O'Neill	Sec. 10, T 1 S, R 18 W		son	Sec. 19, T 12 S, R 41 W
Smith	Sec. 25, T 1 S, R 20 W		Swartz	Sec. 30, T 12 S, R 41 W
			Craft	Sec. 29, T 12 S, R 41 W

County along with a reference curve from a South Dakota montmorillonite are shown in Figure 1.

A curve can be divided into three distinct reaction regions: (1) below 200°C, release of adsorbed molecular water; (2) between 400-800°C, release of water from the loss of OH ions (called dehydroxylation) in the crystal structure; (3) above 800°C, an endo-exothermic reaction representing the decomposition of the crystal lattice. No curve from the Kansas montmorillonite samples exactly matches the normal DTA curve for the South Dakota montmorillonite. The South Dakota material is the sodium type with an expanding lattice that forms a stable gel with water. Kansas montmorillonites are of the calcium type with an expanding lattice, but reaction with water does not form the same type of stable gel as does the sodium montmorillonite.

The DTA curve geometry of the Kansas montmorillonites differs from the South Dakota montmorillonite in the first and second regions. The last high-temperature reaction, controlled by the chemistry of the minerals, is quite similar in all curves. Endothermic reactions in regions one and two are influenced by the crystal structure. The Kansas calcium montmorillonite has two endothermic peaks for the release of molecular water but the sodium montmorillonite shows only one. The double peak indicates that the molecular water is held by two distinctly different bonding energies.

Most of the Kansas montmorillonite samples showed that dehydroxylation occurred in the temperature range between 525° and 675°C. Such low-temperature behavior is reported in the literature (MacKenzie, 1964, p. 230) and given the name "abnormal" montmorillonite.

¹ Mention of companies or products is not to be considered an endorsement.

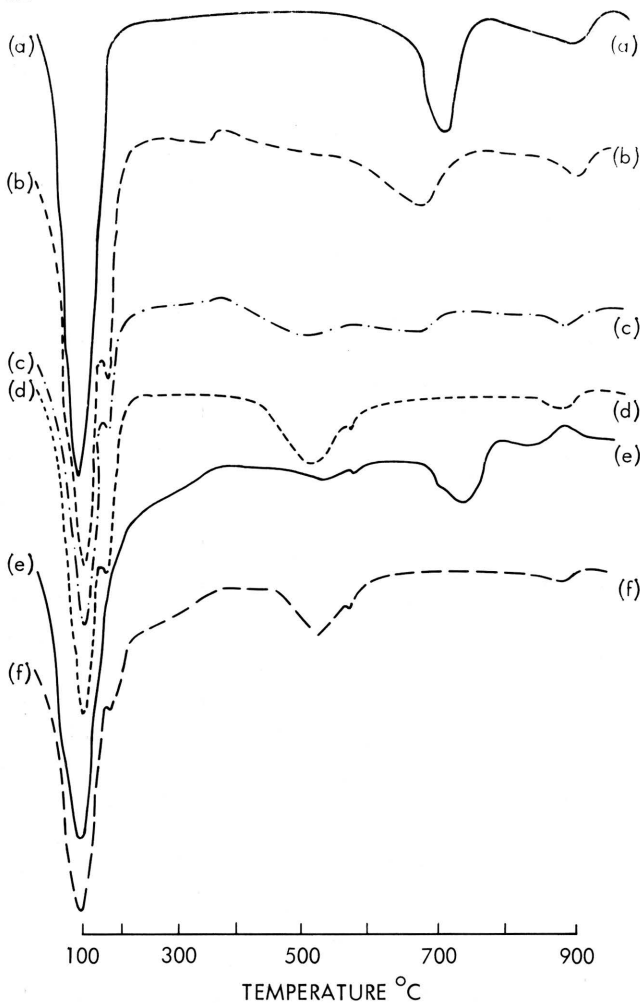


FIGURE 1.—DTA curves (10 mg; heating rate 20°C/min.; recording speed 0.2 in/min.; amplification 150 microvolts). (a) South Dakota montmorillonite, A.P.I. sample H-27. (b) Phillips County, Smith ranch. (c) Phillips County, Smith ranch. (d) Phillips County, O'Neill ranch. (e) Wallace County, Abrahamson ranch, caliche decomposition at 750°C. (f) Wallace County, Craft ranch.

X-ray diffraction does not appear to distinguish between the two different types of structure, only DTA detects the difference. But because DTA detects this difference, the DTA curve for an "abnormal" montmorillonite can very often be misinterpreted as being that of an illite structure. Therefore, DTA curves should not be used as the sole identifier of montmorillonite or illite clay minerals. A summary of the frequency of normal-"abnormal" patterns for Kansas montmorillonite samples is given in Table 2.

The term "normal" (above) means that there was only one distinct peak at 675°C. Thermal decomposition may have begun as low as 400°C, but only the peak or minimum on the curve was measured.

No sample from Wallace County showed evidence of the presence of only normal montmorillonite. Of

TABLE 2.—Type of DTA pattern.

County	Normal %	"Abnormal" %	Mixed %
Phillips	17	25	58
Wallace	0	92	8

the Phillips County samples, 17 percent showed normal behavior, and 58 percent showed a behavior indicative of a mixture of both types of minerals. By contrast, the Wallace County material showed normal reaction in only 8 percent of the samples and it was always associated with the "abnormal" material.

It is postulated (Hill, 1953) that the "abnormal" thermal behavior is caused by some random-type disorder within the crystal lattice. If so, one might ask these questions: Is this disorder a step in the decomposition process of volcanic ash? Is the crystal structure of the Kansas montmorillonite approaching that of the Wyoming-South Dakota montmorillonites? Has the Kansas montmorillonite been altered due to the weathering sequence? At present, the answers are not known.

Deposits from both Phillips and Wallace counties are relatively free from organic matter as shown by the small amount of exothermic activity between 300° and 500°C. No Phillips County sample contained calcium carbonate disseminated throughout the montmorillonite sample, yet 40 percent of the Wallace County sample had a recognizable calcium carbonate decomposition peak at 750°C. All samples having this characteristic peak also reacted with dilute hydrochloric acid. Small lumps of white caliche were found in Wallace County material. Some areas of Phillips County are also reported to contain caliche (A. Hornbaker, personal communication, 1969).

Interestingly, when the calcium carbonate decomposition peak was present (which must mean that an abundance of calcium ions was available to any groundwater), the distinct second dehydration peak occurring at 180°C had been transformed into a broad change-of-slope area. This occurred with all samples in Wallace County having the calcium carbonate peak; when the calcium carbonate decomposition peak was absent the second dehydration peak was present.

Quartz as an impurity was often present as shown by the small endothermic reaction at 575°C in curves d, e, and f of Figure 1. Some samples in Phillips County were found to be free from quartz. Fired color ranged from buff to red, depending upon the iron and caliche contents.

Ives (1960) reported that Kansas calcium montmorillonite could easily be converted to sodium montmorillonite by boiling in a saturated sodium chloride (NaCl) solution. A DTA curve prepared after boiling showed the thermal decomposition to be that of a normal montmorillonite. This was difficult to accept.

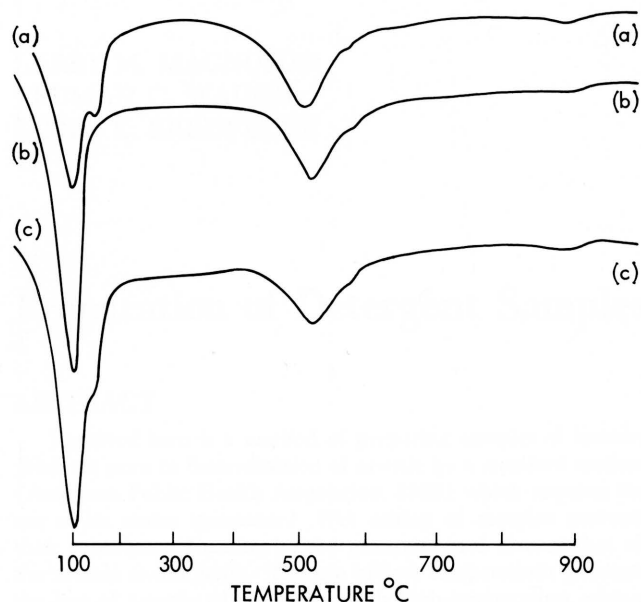


FIGURE 2.—DTA curves showing the effect of exchangeable ions. DTA parameters same as Figure 1. (a) Untreated montmorillonite, Phillips County, O'Neill ranch. (b) Boiled one-half hour in saturated sodium chloride. Second dehydration peak gone at 150°C . (c) Sodium saturated montmorillonite of curve b boiled one-half hour in saturated calcium chloride. Note the return of the 150°C endothermic inflection. The remainder of the curve beyond 200°C was unaffected by the boiling in either saturated solution.

Why should a reaction essentially affecting only the base-exchange cations on the outside of the clay mineral particle affect the manner in which the interior OH ions were bonded into the structure?

The experiment was repeated selecting a sample that showed only the "abnormal" 525°C endothermic peak. The sample was sodium saturated by boiling in a saturated sodium chloride solution for one-half hour, then the DTA curve was produced. The sodium-produced montmorillonite was then boiled in a saturated calcium chloride solution for one-half hour to return it to the calcium-saturated condition and a DTA curve was produced. Results are shown in Figure 2.

The only alteration in the sodium-saturation curve was the elimination of the second dehydration peak, producing the single-peak geometry typical of montmorillonite. An inflection point typical of calcium montmorillonite returned to the curve after resaturation with the calcium ions. There was no shift of the 525°C endothermic reaction peak.

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Preparation of Detergent Samples for Determination of Arsenic

ABSTRACT

Reported here is a method of preparing samples of laundry products prior to determination of arsenic by a standard method (American Public Health Association, 1965) which requires the use of an arsine generator.¹ Wet ashing of samples prevents their subsequent foaming in the generator and assures that all the arsenic is inorganic. The use of low temperatures prevents the loss of arsenic which occurs with high-temperature ashing.

The procedure of preparation is as follows:

1. Accurately weigh 0.1 to 3 gm of sample into a 125-ml flask and cover with a minimum of concentrated H_2SO_4 .
2. Digest resulting mixture at $100^\circ C$ until thoroughly charred.
3. Add 25 ml of concentrated HNO_3 and reflux solution until color is discharged.
4. Reduce solution to near its original volume by heating on a hot plate. Care must be taken to avoid reducing the volume to the point that SO_2 evolves; however, no brown fumes should still be evolving. If blackening occurs, an indication of incomplete ashing, Steps 3 and 4 must be repeated.
5. Cool sample, add 5 ml of 30-percent hydrogen peroxide, cover flask, and heat until effervescence ceases.
6. Add 25 ml of concentrated HCl and reduce solution to near its original volume. Repeat this step until no nitric oxide is evolved, usually three times.
7. Add 25 ml of water and again reduce solution to

near its original volume, subsequently cooling and diluting solution to 50 ml. The sample is now ready for the standard method.

The weight of sample in Step 1 must contain between 5 and 20 micrograms of arsenic for proper use of the standard method. This weight may be determined by emission spectrography (Waugh, personal communication, 1970) or trial and error. Use of a minimum of H_2SO_4 in Step 1 is necessary to prevent later overheating in the arsine generator. Reduction of volume to the point that fumes of H_2SO_4 form causes significant loss of arsenic. Step 5 aids in the removal of NO_3^- in Step 6. NO_3^- causes results that are too low. Step 7 eliminates an excess of HCl which also causes overheating in the arsine generator.

In all the detergents analyzed in this laboratory, the concentrations of metals which interfere with the determination were too low to affect results.

We found a coefficient of variation of 3.5 percent for the preparation and standard method combined; this increased to 12 percent when samples were taken from different parts of the detergent box. The difference between standards of As_2O_3 subjected to the preparation described here and duplicates determined directly by the standard method was less than 2 percent. W. J. Traversy (personal communication, 1970) of the Canadian Department of Energy, Mines and Resources reported a mean recovery of 98 percent from spiked samples and a coefficient of variation of 11 percent using our procedure.

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¹The Fisher No. 1-405 arsine generator has been found satisfactory for the purpose, Cat. 70.
Manuscript received October 26, 1970. Accepted for publication November 3, 1970.

LARRY M. MAGNUSON
O. KARMIE GALLE

Determination of Suspended Silica by Atomic Absorption

ABSTRACT

Described is a method for analyzing small quantities of suspended silica, either airborne or suspended in water. The silica is entrapped on a membrane. The membrane is ashed and the silica fused with Na_2CO_3 and dissolved in water. The quantity of silica is determined by atomic absorption.

The following steps are used in preparing samples:

1. Transfer membranes and silica to platinum crucibles and add 5 ml of 50-percent (V/V) H_2SO_4 to each.
2. Heat crucibles on a hot plate until fuming ceases.
3. Heat crucibles on a Meeker burner until all carbon is oxidized.
4. Fuse sample with 0.5 g Na_2CO_3 by heating at full flame on the Meeker burner. Heat until a clear melt results.
5. Cool crucibles, add 10 ml of water, and set aside overnight.
6. Dilute contents of crucibles to 100 ml in plastic volumetric flasks. The contents are quantitatively transferred to the flasks by washing the crucibles first with water, then 1 ml of 8 N NaOH, and then again with water.
7. Transfer resulting solutions to 4-ounce polypropylene bottles, cap bottles lightly, and digest on a steam bath for 1 to 2 hours. The solution can be stored indefinitely at this point; but, the

digestion must be repeated before proceeding with the analysis if they are stored. The measurement by atomic absorption should be made 30 minutes to 3 hours after digestion of the solutions.

Care must be exercised at all steps to avoid loss of silica or contamination. HF cleaning of all platinum and plastic prevents contamination from those sources. Keeping the samples covered at all times prevents airborne contamination. All reagents should be silica free, and use of glassware should be avoided.

Atomic absorption analysis is performed with a nitrous oxide-acetylene flame using the 2516 Å line of silicon. A standard curve is prepared using standards containing 100 to 0.3 ppm Si. A new curve should be prepared after every 10 samples.

The range of the method is 20 to 0.6 mg SiO_2 . This may be extended by dissolving the fused sample in a greater or lesser volume of water. However, if the amount of silica is much less than 0.6 mg, a colorimetric analysis should be performed or another method more sensitive than atomic absorption should be used.

The standard deviation based on 20 samples of 10-mg quartz was 0.5 mg, and the standard deviation based on 20 samples of 1-mg quartz was 0.06 mg. Recovery was 98 to 99 percent in both cases. After storage for three weeks recovery dropped to 90 percent but was restored to 98 to 99 percent after digestion on the steam bath for 1 hour.

Preliminary Studies of Stable Carbon Isotopes in Selected Kansas Shales

ABSTRACT

Ratios of stable carbon isotopes were measured on chemical fractions of four Kansas shales. Content of organic carbon and relative abundance of chemical fractions were also determined. Relationships and meaning of the data are discussed.

Distribution of stable isotopes of carbon is a geochemical parameter often used to indicate environment of deposition, relationships between petroleum and source rocks, and extent of *in situ* alteration of organic molecules. For a recent review see Degens (1969). Samples studied in this investigation were the Sharon Springs Shale Member (Upper Cretaceous), Graneros Shale (Upper/Lower Cretaceous), and the Heumader and Heebner Shale Members (Upper Pennsylvanian). Brief descriptions of these shales are given in Zeller (1968).

Shales were collected at the following localities in Kansas:

Sharon Springs Shale Member (outcrop)—Center of sec. 36, T 13 S, R 40 W, Wallace County

Graneros Shale (roadcut)—Center of southern line of sec. 31, T 14 S, R 10 W, Ellsworth County

Heumader Shale Member—U.S. Army Underground Storage Facility, Atchison

Heebner Shale Member (roadcut)—Northwest corner of sec. 5, T 16 S, R 18 E, Franklin County.

The samples were crushed in a jaw crusher and ground to a fine powder in an oscillating tungsten carbide mill (Siebtechnik). Powdered samples of shale were weighed and exhaustively extracted with chloroform-methanol and finally with chloroform only. Ultrasonic energy was used to aid extraction procedures. Total extracts were weighed and saponified overnight in 0.5N KOH in methanol. Non-polar fractions were extracted with hexane and subsequently chromatographed over silica gel to obtain the hydrocarbon fractions which were weighed and set aside for isotopic analysis. The remaining portions of the saponified mixtures were acidified to pH 1 with HCl in order to precipitate acidic material which was assumed to be humic. This material was filtered and

also saved for isotopic analysis. Other acidic fractions were extracted from the filtrates with hexane and were esterified with BF₃ in methanol. Methyl esters were extracted from esterification mixtures with hexane and chromatographed on silica gel. Non-polar materials were eluted with hexane and methyl esters of fatty acids with benzene. The esters were dried and saved for isotopic analysis.

“Kerogen” was obtained from 100 g of extracted Sharon Springs shale by first treating with HCl:HF (1:1) for three days at 60°C. The resulting insoluble matter or “kerogen” was washed in saturated boric acid solution and collected by centrifugation.

In order to generate CO₂ for measurement of isotopic ratios, a portion of each chemical fraction was combusted in a closed vacuum line at 900°C in the presence of copper oxide and oxygen (Calder, 1969). Combustion gases were passed through a catalytic furnace to convert CO to CO₂. Mass spectrometric measurements were made in the laboratory of Dr. P. L. Parker at the University of Texas.

Carbon isotopic data is presented in δC^{13} units relative to National Bureau of Standards Isotope Reference Standard No. 20. δC^{13} is in units of parts per thousand and is defined as

$$\delta C^{13} = \frac{[(C^{13}/C^{12}) \text{ sample}]}{C^{13}/C^{12} \text{ std}} \times 1000$$

A negative number indicates the sample is depleted in C¹³ relative to the standard.

Table 1 shows that percent of total organic carbon and percent of extractable organic matter decreased with increasing age except for the Heebner shale, which deviated in other ways also. Correlation of quantity of organic matter with age may be meaningless because the content at time of deposition is unknown. Of more importance is the observation that the fraction of organic carbon which was extractable (A/B in Table 1) was not a function of age. Thus there appears no long-term trend of organic matter toward either smaller or larger molecules. It may be

¹ Department of Oceanography, Florida State University, Tallahassee, Florida 32306.

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TABLE 1.—Relative age and chemical fractionation of four shales.

	Sharon Springs Shale Member	Graneros Shale	Heumader Shale Member	Heebner Shale Member
Relative age	Increasing age →			
Weight extracted (g) ..	1016	1017	1611	1397
Total organic carbon in percent (B)	5.6	2.2	1.0	7.0
Weight of total extract (g)	4.84	2.21	1.49	7.51
Extractable organic matter in percent (A) ..	0.48	0.22	0.09	0.54
(A/B) × 100	8.6	10.0	9.0	7.7
Extracted fatty acids (mg)	44.8	11.9	2.9	63.9
Extracted hydrocarbon (mg) ..	61.1	61.5	21.1	311.5
Fatty acids of total extract in percent (Y) ..	0.9	0.5	0.2	0.9
Hydrocarbons of total extract in percent (X) ..	1.3	2.8	1.4	4.2
Ratio of % hydrocarbon to % fatty acid in extracts (X/Y)	1.5	5.6	7.0	4.7
Total organic carbon in "kerogen" (%)	15.0	---	---	---

significant that the two shales lowest in organic carbon (Graneros and Heumader) had the highest fraction of extractable organic matter. Formation of insoluble, high molecular weight compounds may have been hindered in these shales because of lower population density of organic molecules. This hindrance would have favored larger proportions of low molecular weight, extractable molecules.

Ratios of hydrocarbons to fatty acids increased with age except for the case of the Heebner shale. This increase is consistent with the process of production of hydrocarbons from fatty acids as proposed by Kvenvolden (1967) and also consistent with the process proposed by Hoering and Abelson (1963) in which molecules with functional groups enter the kerogen matrix and subsequently produce smaller molecules by cleavage of carbon-carbon bonds.

The δC^{13} data in Table 2 show significant differ-

ences among the shales. Dispersion of δC^{13} values among fractions of the Sharon Springs shale is 2.6⁰/00. Dispersion is 4.1⁰/00 for the Graneros Shale and 5.0⁰/00 for the Heumader shale. Wider dispersion of δC^{13} values with greater age may result from chemical processes involving cleavage of carbon-carbon bonds. Such processes would result in enrichment of C^{13} in high molecular weight fractions. The Heebner shale is peculiar in having a dispersion of δC^{13} values of only 1.2⁰/00. This narrow dispersion may indicate past exposure to higher temperatures which can cause greater randomization of carbon isotopes. High temperatures, however, should also have accelerated the production of hydrocarbons and the destruction of fatty acids, whereas the Heebner shale exhibits a ratio of hydrocarbon to fatty acid lower than either the Graneros or Heumader shales.

Hydrocarbon fractions show more uniform δC^{13} values than other fractions. The δC^{13} of the hydrocarbon fractions varies over a 2.4⁰/00 range, that of total organic carbon varies over a 6.2⁰/00 range, and those of other fractions vary over an intermediate range.

Very negative δC^{13} values exhibited by the Heebner shale may indicate either a high content of terrestrial organic matter (Sackett, 1964), or deposition during a time of cold climate (Rogers and Koons, 1969), or both. In any case the history of the Heebner shale must be significantly different from that of the other shales studied.

The following statements summarize these preliminary data:

1. Shales with low content of organic carbon (Graneros and Heumader) had (a) high percentages of extractable organic carbon, (b) greatest dispersion of δC^{13} among their organic fractions, (c) more than 5 times as much hydrocarbon as fatty acid, (d) the most positive δC^{13} for total organic carbon.
2. Shales with high content of organic carbon (Sharon Springs and Heebner) had (a) low percentages of extractable organic carbon, (b) smallest dispersion of δC^{13} among their organic fractions, (c) less than 5 times as much hydrocarbon as fatty acid, (d) the most negative δC^{13} for total organic carbon.
3. Significant trends were indicated in the Sharon Springs, Graneros and Heumader shales. These are the following: (a) larger ratio of hydrocarbons to fatty acids with greater age, (b) wider dispersion of δC^{13} values with greater age.
4. Results from studies of the Heebner shale fit none of the trends established by data on the other three shales.

TABLE 2.— δC^{13} relative to NBS 20.

	Sharon Springs Shale Member	Graneros Shale	Heumader Shale Member	Heebner Shale Member
Whole shale	-25.6	-23.4	-21.4	-27.6
Total extract	-25.9	-26.4	-23.6	-28.8
Fatty acids	-28.2	-26.3	-24.4	-28.5
Hydrocarbons	-27.2	-27.5	-26.4	-28.8
"Humic" acids	-26.8	-25.5	-22.7	-28.5
"Kerogen"	-26.1	-----	-----	-----

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ABSTRACTS

The following is a list of abstracts and titles of papers by Survey personnel presented orally and/or printed in publications other than those of the State Geological Survey of Kansas during the calendar year 1970. [Abstracts are reproduced exactly as printed in source or from copy supplied to editor.]

Angino, Ernest E.

GEOCHEMICAL PROSPECTING IN KANSAS

Public presentation, Meeting Kansas Geological Society, Lawrence, Kansas, October 24-25, 1969. *Guidebook, Thirtieth Field Conference, Kansas Geol. Soc., October (1969), p. 9-11.*

SELECTIVE ELEMENT RECOVERY FROM OIL FIELD BRINES

With the attention now being focused on the two problems of water pollution and usage and natural resource utilization, the recovery of compounds dissolved in subsurface brines takes on greater importance with each passing year. More than 325 billion gallons of oil field brines ($\sim 8 \times 10^9$ barrels) are brought to the surface yearly in the United States. Most of these brines are wasted and/or are returned to the subsurface without any attempt of stripping the contained salts. The volume of this brine is such as to warrant greater consideration of the economic feasibility of extracting much, if not all, of the dissolved components therein. In many instances the salts dissolved in oil field brines could be extracted profitably, if modern extraction techniques were used or refined. Simple extraction processes for soda ash, sodium carbonate, caustic soda, magnesium and calcium sulfate, trace elements and others are available. For example, sulfur can be recovered by using a barium resin to precipitate the sulfate as BaSO_4 , which can then be made to yield sulfur by a short four step conversion process. Magnesium can be precipitated in the hydroxide form and selected trace elements can be scavenged and concentrated by ferric iron precipitation.

Water Resources Res., v. 6, no. 5, 1970, p. 1501.

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——, Goebel, Edwin D., and Waugh, Truman C.

LEAD ISOTOPES AND METALLIC SULFIDES AS EXPLORATION GUIDES IN MID-CONTINENT PALEOZOIC ROCKS

Acetic Acid insoluble residues of Paleozoic cherty-carbonate rock cores commonly include several metallic sulfide minerals. Minerals identified are pyrite, chalcopyrite, marcasite, sphalerite, galena, and bornite. Pyrite and marcasite are present most often, followed by chalcopyrite, sphalerite, bornite, and galena—not necessarily in this order. Whole rock analyses of six cores from Woodson and Greenwood County, Kansas by semi-quantitative emission spectrography for Pb, Ni, Mn, Cr, V, Co, Cu, Zn, Mo, and Sn, indicated the presence of unusual concentration levels. Two highly mineralized cores had Ni concentrations of

300-1600 ppm with 11 of 28 samples greater than 1000 ppm. Cr levels (300-1250) also greatly exceeded background levels. Measured concentrations of Zn, Pb, Cu, Co, and Ag were comparable to or exceeded those of productive Jasperoid from several mining districts of the western United States.

In searching for "big" ore deposits of the Mississippi Valley type, Cannon and Pierce suggested that one search for J-type leads in which the $\text{Pb}^{206}/\text{Pb}^{207}$ ratio is near 1.40. Pb isotope analyses of galena samples from a wide area of the Mid-Continent are identified as J-type. Applying the concept of Cannon and Pierce, most samples examined yielded $\text{Pb}^{206}/\text{Pb}^{207}$ ratios in the range of 1.30-1.50. However, samples from the Big Jumbo, an abandoned pit mine in Pennsylvanian rocks in Linn County, Kansas, yielded a value of 1.41, which strongly suggests the need for further evaluation of this prospect.

Isotope ratios (206/204) of J-type Pb from surface and mine samples ranged from 21.6 to 22.5; in contrast ratios from subsurface core samples ranged from 22.5 to 27.1. Also $\text{Pb}^{206}/\text{Pb}^{207}$ ratios from the mine and surface samples ranged from 1.37-1.42; those from the second category were all greater than 1.49. Samples from succeeding older stratigraphic units yielded Pb that is generally more radiogenic. The significance of the seeming correlation between these two types of data is not clear, but the possibility of a meaningful relationship merits further investigation.

Third International Geochemical Symposium, Toronto, Canada, April 16-18, 1970.

——, Magnuson, Larry M., Waugh, Truman C., Galle, O. Karmie, and Bredfeldt, James E.

ARSENIC IN DETERGENTS: POSSIBLE DANGER AND POLLUTION HAZARD

Arsenic at a concentration of 10 to 70 parts per million has been detected in several common presoaks and household detergents. Arsenic values of 2 to 8 parts per billion have been measured in the Kansas River. These concentrations are close to the amount (10 parts per billion) recommended by the United States Public Health Service as a drinking-water standard.

Science, v. 168, 1970, p. 389.

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Attaway, David H.; and Parker, P. L., The University of Texas, Austin, Texas

STEROLS IN RECENT MARINE SEDIMENTS

Sterolic fractions have been isolated from Recent marine sediments representing two different environments. The fractions were characterized by infrared spectroscopy and thin-layer chromatography. The major sterols in the fractions were identified by gas chromatography and mass spectrometry. The demonstrated survival of these common plant and animal sterols for several thousand years suggests that these molecules will be useful geochemical indicators.

Science, v. 169, 1970, p. 674.

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—; Parker, P. L., and Mears, J. A., The University of Texas, Austin, Texas

NORMAL ALKANES OF FIVE COASTAL SPERMATOPHYTES

The alkanes of five marine grass-like plants which occur on the coast of Texas were characterized by infra-red spectroscopy and identified by gas-liquid chromatography. These fractions constitute approximately 0.01% of the dry weight of *Thalassia testudinum* Konig and Sims (turtle grass), *Halophila engelmanni* Aschers, *Diplanthera wrightii* Aschers, and *Syringodium filiforme* Kutzing which is also *Cymodocea manatorum* Aschers (manatee grass). Alkanes were seven times more abundant in *Ruppia maritima* L. (widgeon grass) than in the other four plants. The plants contained various mixtures of normal hydrocarbons with 15 to 31 carbon atoms. The chromatographic techniques could not detect normal hydrocarbons with more than 36 carbon atoms or less than eleven. The distributional patterns of the normal alkanes suggest the relative distinctiveness of each taxonomic group.

Contrib. Marine Science, v. 15, 1970, in press.

Davis, John C.

PETROLOGY OF CRETACEOUS MOWRY SHALE OF WYOMING

The Mowry Shale is a dark, siliceous, Lower Cretaceous shale found throughout Wyoming and in parts of adjacent states. The unit is composed of four facies: siliceous shale, nonsiliceous silty shale, sandstone, and cristobalite shale. Bentonite and porcelanite also are present.

Mineral constituents of the Mowry were determined by an X-ray diffraction technique combining internal and external standards. Mowry Shale contains an average of 50 percent quartz, 5 percent feldspar, and 2 percent organic carbon. The rest of the rock is composed of clay minerals, predominantly mixed layer, and minor zeolites. The lower part of the Mowry contains kaolinite and the upper Mowry is enriched in montmorillonite.

Feldspar is most abundant in a wedge-shaped zone extending from the west. Quartz is present in above-average amounts in an arcuate belt through the center of Wyoming. Organic carbon distribution roughly parallels that of quartz.

Mineral-distribution patterns in the Mowry Shale suggest that it is a transgressive clastic unit similar to other Cretaceous fine-grained deposits in the Rocky Mountains. Excess silica and organic carbon in the rock were derived from tests of Radiolaria and other planktonic organisms that proliferated in upper zones of a restricted terminus of the boreal seaway. Radiolarian bloom was promoted by a continual supply of silica to the seaway from the western margin. Deposition of Mowry Shale ceased when the boreal seaway became connected to the Gulf sea. Apparently, increased circulation destroyed environmental conditions necessary for radiolarian growth, and Mowry deposition was supplanted by normal marine deposition. *Am. Assoc. Petroleum Geologists Bull.*, v. 54, no. 3, 1970, p. 487.

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INFORMATION CONTAINED IN SEDIMENT-SIZE ANALYSES

Traditional measures of sediment size (mean, sorting, skewness, etc.) contain less information than the original weight-percent histogram from which they are computed. For purposes such as mapping, summary statistics are necessary, but little is known of the relative efficiency of traditional measures. By multivariate methods, the relative efficiency of sediment-size descriptors may be analyzed and sediment distribution patterns may be investigated, utilizing the histogram directly. The statistic most efficient for classification of sediments is one which is least variable within a sediment type and most variable between types. The statistic most useful from a practical standpoint is one that strikes a balance between ease of measurement and any resulting loss in efficiency. Principal components analysis of sediment-size data from Barataria Bay, Louisiana, suggests that the first principal component is as efficient as any traditional statistic, and can be approximated with no loss in efficiency by the sand percent in samples. Analyses of variance show that the sand percent is the most efficient as well as the most useful statistic for characterizing Barataria sediments. Only one sieve separation is necessary to obtain essentially the same information as obtained from more laborious traditional analytical techniques.

Intern. Assoc. Math. Geol. Jour., v. 2, no. 2, 1970, p. 105.

OPTICAL PROCESSING OF MICROPOROUS FABRICS

Characterization of a system consisting of solid elements and attendant pore structure is difficult using conventional techniques. Vectors describing size, shape, and orientation of each element must be determined. The problem can be simplified by considering only element projections on a plane through the solid and then directly measuring intercepts along parallel traverses. Unfortunately, most relevant information is lost in this approach.

All information contained within a plane through the porous system can be retained and treated by optical processing techniques. Using a laser optical bench, the Fourier transform of the image of the porous system can be created at the focal point of a simple lens. In the transform, elements of the image are resolved into their spatial and angular components; relative frequency is expressed as light intensity. With proper photographic techniques, the transform can be recorded and digitized. The result is equivalent to a two-dimensional histogram of all possible traverses at all possible angles across the image. Specific components of the transform may be isolated using appropriate pass-filters.

The technique is being evaluated as a method of analyzing the pore structure of petroleum reservoir rocks. Studies presently are being conducted to correlate engineering properties with details of the reservoir fabric. *Systematics Association special Volume No. 3: Data processing in biology and geology*, 1970, p. ?

—; and Preston, F. W., The University of Kansas, Lawrence, Kansas

LASER STUDY OF RESERVOIR PORE NETWORK BY OPTICAL PROCESSING—AN ATTEMPT TO AVOID THE COMPUTER

Public presentation, Meeting Kansas Geological Society,

Lawrence, Kansas, October 24-25, 1969. *Guidebook, Thirtieth Field Conference, Kansas Geol. Soc., October (1969)*, p. 8.

Galle, O. Karmie

THE DETERMINATION OF TRACE ELEMENTS IN BRINE BY ATOMIC ABSORPTION

A method for the determination of Cr, Mn, Fe, Co, Ni, Cu, and Zn in oil field brines is described. The elements are concentrated by passing a known volume of the brine through a column of Dowex A-1 chelating resin. The column is conditioned to a pH of 5 with ammonium acetate before the brine is passed through. At this pH, the trace metals are retained on the resin and the sodium and other alkali metals allowed to pass through. The metals are then eluted with HCl to a final volume of 25 ml and the concentration of the elements determined by atomic absorption. An alternate method which includes the determination of Ca, Mg, and Sr is also described.

The method is compared with the standard additions method and coefficients of variation calculated for both methods. The advantages and disadvantages of both methods are also discussed.

XXI Mid-America Symposium on Spectroscopy, Soc. Applied Spectroscopy, Chicago, Illinois, June 2-5, 1970, p. 66.

MAJOR CONSTITUENT ANALYSIS OF GEOLOGIC SAMPLES BY ATOMIC ABSORPTION

Some of the problems encountered in the major elemental analysis of geologic samples by atomic absorption are discussed. The literature is replete with many geochemical methods which utilize atomic absorption techniques for the determination of trace elements. However relatively few methods describing complete or total analyses (major and minor constituents) of geologic samples have been published. The ability to obtain a complete analysis in a minimum of time is one of the prime advantages of using atomic absorption instrumentation. The choice of this type of instrumentation places certain restrictions upon the size of sample to be used for analysis. The ability to achieve an analysis that is representative of an area under study, a rock ledge, or core can be hindered by using a sample size which is too small. Choice of sample size, sample solution methods, the size of aliquots, and dilution factors are discussed. The use of secondary resonance lines and various burner positions are explored. Possible sources of error in sampling techniques and sample preparation are also discussed.

Invited Paper, SW-SE Regional American Chemical Society Meeting, New Orleans, Louisiana, December 4, 1970.

Goebel, Edwin D.

EVALUATION OF FUTURE PETROLEUM PROVINCES IN KANSAS

Public presentation, Meeting Kansas Geological Society, Lawrence, Kansas, October 24-25, 1969. *Guidebook, Thirtieth Field Conference, Kansas Geol. Soc., October (1969)*, p. 20-21.

—; and **Chronic, John**, University of Colorado, Boulder, Colorado

NEW AGES BASED ON CONODONTS FOR SOME PRE-PENNSYLVANIAN ROCKS IN SOUTHERN FRONT RANGE, COLORADO

Acetic-acid insoluble residues from surface rocks near Beulah and Manitou Springs (Williams Canyon section), Colorado, contain conodonts which suggest that some units of the pre-Pennsylvanian Paleozoic sequence are older than previously reported. Microscopic euhedral quartz crystals have been reported previously from the upper beds of the Williams Canyon Limestone and the formation has been identified tentatively as Meramec and as Spargen Limestone equivalent. The overlying Hardscrabble Limestone (formerly Madison), has been equated with the St. Louis Limestone of the eastern Colorado subsurface.

At three places in the Williams Canyon section, beds barren of conodonts but containing authigenic euhedral quartz crystals, mark the upper boundary of an abundant fauna of robust early Ordovician conodonts, below, from a meager fauna of juvenile late Devonian-early Mississippian conodonts, above. At the Beulah section, only the younger fauna was recovered.

Diagnostic early Ordovician conodonts at Williams Canyon are *Oistodus*, *Drepanodus*, *Scolopodus*, and *Ulrichodina*. Most of these genera have been reported from the Manitou Limestone here. This is first report of the younger fauna, that includes *Polygnathus communis communis*, *Spathognathodus* sp. indet. and less well-preserved conodonts judged to be of less diagnostic value. *P. communis communis* ranges from late Devonian into early Osagian (Mississippian). On the basis of the presently known distribution of conodonts, the Hardscrabble Limestone can be no younger than early Osagian; the underlying Williams Canyon Limestone can be no younger than late Devonian. [Author's correction: On the basis of the presently known distribution of conodonts, the Hardscrabble Limestone and the underlying Williams Canyon Limestone can be no younger than early Osagian.]

Geol. Soc. America, Abstracts with Programs, v. 2, no. 6, 1970, p. 388-389.

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Grisafe, David A.; and Hummel, F. A., The Pennsylvania State University, University Park, Pennsylvania

PENTAVALENT ION SUBSTITUTES IN THE APATITE STRUCTURE PART A. CRYSTAL CHEMISTRY

The substitution of pentavalent arsenic, vanadium, chromium, manganese and antimony for phosphorus in apatites has been investigated. Arsenic, vanadium, and chromium completely replaced phosphorus in the calcium, strontium and barium fluor- and chlorapatites. X-Ray diffraction data showed that the calcium fluor-vanadate, -arsenate, and -chromate structures were distorted relative to the normal hexagonal apatite. Manganese completely replaced phosphorus in only the barium apatites while chromium and manganese could not be incorporated into lead apatites. Excluding these exceptions, continuous solid

solutions were formed between the phosphate and/or vanadate and the chromate or manganate analogues for given divalent and halide ions. The substitution of large amounts of antimony (> 20 mole %) for phosphorus was unsuccessful.

Jour. Solid State Chemistry, v. 2, 1970, p. 160.

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PENTAVALENT ION SUBSTITUTIONS IN THE APATITE STRUCTURE PART B. COLOR

Pentavalent chromium or manganese substituted into the pentavalent ion site always produced green and blue to green apatites, respectively. The positions of the absorp-

tion bands of the CrO_4^{3-} or MnO_4^{3-} oxyanions were not appreciably affected by changes in the composition of the apatite. Possible models based on the Ballhausen-Liehr molecular orbital scheme were used to interpret the reflectance spectra of apatites containing pentavalent vanadium, chromium, and manganese.

Jour. Solid State Chemistry, v. 2, 1970, p. 167.

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CRYSTAL CHEMISTRY AND COLOR IN APATITES CONTAINING COBALT, NICKEL, AND RARE-EARTH IONS

Simple substitutions of divalent cobalt and nickel and charge coupled substitutions of the alkali: RE^{3+} , $\text{RE}^{3+}:\text{Si}^{4+}$ and $\text{RE}^{3+}:\text{O}^{2-}$ ($\text{RE} = \text{La, Pr and Nd}$) types and defect varieties in the apatite structure have been explored. X-ray diffraction showed that the solubility limits of cobalt in the calcium fluor- and chlorapatite were 15 and 25 mole percent respectively but were less than 10 mole percent in the strontium analogues. The charge coupled substitutions produced apatites of a variety of stoichiometries. Lattice parameters were obtained for the defect silicate apatites $\square_2\text{Pr}_6(\text{SiO}_4)_6\square_2$, $\square\text{Sr}_3\text{Pr}_6(\text{SiO}_4)_6\square_2$, and $\square\text{Pb}_3\text{Pr}_6(\text{SiO}_4)_6\square_2$.

Cobalt, nickel, praseodymium and neodymium substitutions produce violet, pale yellow-green, light green and blue to blue-violet colored apatites respectively. Reflectance spectra for these apatites show that the positions of the absorption bands are not strongly affected by composition changes in the apatite. The cobalt and nickel spectra showed similarities to the spectra given by these ions in octahedral coordination.

Am. Mineralogist, v. 55, 1970, p. 1131.

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Hambleton, William W.

OVERVIEW OF THE SURVEY'S RESEARCH PROGRAMS

Public presentation, Meeting Kansas Geological Society, Lawrence, Kansas, October 24-25, 1969. *Guidebook, Thirtieth Field Conference, Kansas Geol. Soc., October (1969)*, p. 4-7.

TOWARD A CONCEPT FOR A NATIONAL GEOSCIENCE INFORMATION PROGRAM, A REPORT OF THE COMMITTEE ON GEOSCIENCE INFORMATION OF THE AMERICAN GEOLOGICAL INSTITUTE

The objective of the Committee on Geoscience Information is definition of an information program concerned

with generation, storage, and transfer of information in the geosciences. Of principal concern are bibliographic services and secondary publications, primary publications, a special resource inventory, vocabulary definitions and nomenclature, translation publications and services, meetings and informal communication, current research information, library resources and services, raw data processing, and user education. A national geoscience information system should be decentralized but provide centralized and comprehensive services and information integration, should be compatible and interactive, should have archival characteristics, deal with physical files such as samples, logs, maps and photographs, be strongly user-oriented so as to provide access, hard copy and manipulated transfer, and should be concerned with research, analysis, and the implementation and coordination of information transfer.

Geol. Soc. America, Abstracts with Programs, v. 2, no. 7, 1970, p. 565-566.

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Hardy, Ronald G.

THE INPUT-OUTPUT ECONOMIC MODEL AND ITS RELEVANCE TO THE PETROLEUM INDUSTRY

Public presentation, Meeting Kansas Geological Society, Lawrence, Kansas, October 24-25, 1969. *Guidebook, Thirtieth Field Conference, Kansas Geol. Soc., October (1969)*, p. 12-14.

Heckel, Philip H.

ORGANIC CARBONATE BUILDUPS IN EPEIRIC SEAS: SOME THEORETICAL ASPECTS

Organic carbonate buildups form where conditions are favorable for calcareous organisms to flourish and to secrete enough calcium carbonate to build up the substrate locally. Advantages from buildup include inducing better water-circulation patterns and providing firm substrate for organisms not suited to live elsewhere. Perhaps most importantly, buildup involves simply production of enough sediment for the substrate to remain continually in the optimum zone for proliferation of the organisms.

R. J. Dunham's distinction between "ecologic reefs" in which organisms provide rigid framework and bind sediment, and "geologic reefs" in which the restricted area of thickened carbonate is due to localized organic proliferation without necessity of framework or sediment binding, resolves much of the nomenclatural controversy concerning organic carbonate buildups. Perhaps distinction also can be made between geologic "reefs," which are elongate and differentiate facies on either side, and "mounds" which are merely bumps on the sea floor. Ecologic reefs can be either geologic reefs (barrier and fringing) or mounds (patch reefs); a bank is a geologic reef with no organic framework.

All calcareous organisms are capable of providing sediment to buildups. The more important modern contributors are algae, foraminifers, corals, and mollusks; in the Paleozoic they include pelmatozoans, bryozoans, and brachiopods. Organisms providing framework in large-scale ecologic reefs today are mainly hexacorals, but formerly have included rudistids, stromatoporoids, and perhaps tetra-

corals. Sediment binding on the same scale is provided mainly by red algae today and has involved blue-green algae, stromatoporoids, and *Problematica* in the past. Builders of small-scale "mounds" that also are ecologic reefs, include red algae, foraminifers, sponges, corals, bryozoans, brachiopods, polychaete worms, oysters, and sessile gastropods. In many of these mounds, the same organism served as frame and binder; in others, blue-green algae, red algae, *Problematica*, or bryozoans were binders. Some modern carbonate mounds are not organic in origin, but are merely hydrodynamic accumulations of sediment; perhaps some ancient carbonate mud mounds have a similar inorganic origin.

Formation of organic carbonate buildups results from any combination of environmental factors that causes localized organic proliferation. Favorable oxygenation, water circulation, and nutrient replenishment are necessary for all organic buildups; other factors may have different optima for different organisms, and exclusively invertebrate buildups can form at any depth. Buildups containing algae, however, are restricted to the photic zone, thus are more predictable as to initiation and maintenance. Algal buildups tend to start on better-lit topographic highs, and with bottom subsidence, grow upward where the algae remain in optimum photic conditions. Invertebrate buildups, however, form where other factors are optimal, which may or may not be on highs.

Initiation of a geologic reef involving algae requires simply a bottom slope upon which algae proliferate only above a certain depth. The interval on the slope within which subsidence is equally compensated by algal sedimentation eventually becomes steeper and forms a "reef front" as algal and associated sedimentation keeps the entire shallower side near the surface, whereas the deeper side on which algae are inhibited receives progressively less autochthonous sediment and eventually depends primarily on allochthonous material from any source.

Am. Assoc. Petroleum Geologists Bull., v. 54, 1970, p. 851-852.

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Hilpman, Paul L.

SOME PRACTICAL PROBLEMS IN ENVIRONMENTAL GEOLOGY

Public presentation, Meeting Kansas Geological Society, Lawrence, Kansas, October 24-25, 1969. *Guidebook, Thirtieth Field Conference, Kansas Geol. Soc., October (1969)*, p. 15-16.

URBAN GROWTH AND ENVIRONMENTAL GEOLOGY

No abstract given.
The Governor's Conference on Environmental Geology, Colorado Geological Survey Spec. Pub. No. 1, (1969), p. 16-19.

THE CHALLENGE OF THE URBAN ENVIRONMENT

No abstract given.
25th Annual Convention Proceedings, Kansas Assoc. Soil Conservation Districts, (1969), p. 2-28.

GEOLOGY AND SOLID WASTE DISPOSAL [GEOLOGIC DATA FOR SOLID WASTE DISPOSAL, HILTMAN, PAUL]*

The major source of contaminants in the earth's atmosphere, hydrosphere, and lithosphere is the waste created by modern man. As our expanding population is becoming concentrated in metropolitan centers and per capita waste production increases, man-introduced contaminants have become pollutants and locally pose the threat to human welfare.

Technology used to handle and dispose of solid waste in the U.S. lags well behind that to diminish air and water pollution, and geologists can make valuable contributions to this technology. We must define those geologic factors critical to successful operation of sanitary landfills. Furthermore, we must develop new and rapid inventory techniques that will produce the kinds of data needed for land-use planning. In several areas of the United States geologists are meeting this need.

**Geol. Soc. America, Abstracts with Programs, v. 2, no. 1, 1970, p. 25 [appears in Abstracts with Programs, v. 2, no. 7, 1970, p. 762].*

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THE ROLE OF THE GEOLOGIST IN ENVIRONMENTAL EDUCATION

Public presentation, Meeting National Association of Geology Teachers, Pittsburg, Kansas, March 21, 1970.

A GEOLOGIST'S LOOK AT THE ENVIRONMENTAL FLURRY

Public presentation, Carleton College, Northfield, Minnesota, April 14, 1970.

GEOLOGY IN THE '70's

Public presentation, University of Wisconsin, Madison, Wisconsin, April 16, 1970.

THE ROLE OF GEOLOGY IN THE ENVIRONMENTAL CRISIS

Public presentation, The University of Kansas, Lawrence, Kansas, April 20, 1970.

FACT AND FANCY IN OUR ENVIRONMENT

Public presentation, Pembroke Country Day School, Kansas City, Kansas, April 22, 1970.

TO BE OR NOT TO BE—THE ENVIRONMENTAL QUESTION

Public presentation, Meeting Heart of America Geology Club, University of Missouri at Kansas City, Kansas City, Missouri, May 11, 1970.

THE PETROLEUM INDUSTRY AND ENVIRONMENTAL CONCERN

Unchecked growth of the world's population, coupled with per capita increases in resource consumption and waste production has given rise to anxieties about the

future of mankind. The past decade has produced intensified concern for the integrity of earth's ecosystems. Although the petroleum industry has contributed much toward the physical comfort and industrial might of modern society, it has also unwittingly contributed to excessive waste and environmental deterioration through its somewhat limited perspective. By action and influence, the industry can do much to ameliorate these conditions through programs of remedial engineering and hydrocarbon conservation.

Efforts in remedial engineering should be comprehensive enough to not only eliminate pollution of our coastal waters and estuaries by leaking wells, pipelines and tankers, but also to arrest contamination of surface water and ground water systems.

Hydrocarbon conservation programs should ensure that fossil fuels (petroleum, natural gas, and coal) are conserved for uses that cannot be met by other resources. Furthermore, extraction processes employed in the future must be chosen on the basis of reserve-recovery ratios rather than the rapidity of investment returns.

Society of Petroleum Engineers, Am. Inst. Min. Met. Eng., 45th Annual Fall Meeting, Houston, Texas, October 4-7, 1970, p. 1-6 (preprint).

GEOLOGY TEACHERS AND ENVIRONMENTAL EDUCATION

Within geology, the decade of the 60's witnessed an ever-increasing interest in applied research, paralleling the emergence of a broad ecological conscience within society. With the initial stage of problem-recognition largely complete, attention must focus on application of procedures that reduce environmental degradation. Through environmental education, the new conservation movement has (1) substituted a multidisciplinary approach for specialized offerings and (2) implemented programs that not only give people an understanding of ecological relationships, but move them toward action preventing environmental problems. Geology teachers must recognize their responsibilities to all segments of society and not restrict their focus to the training of applied earth scientists. A great need exists for integrated environmental programs in teacher preparation for grades K through 12. In addition, curriculum offerings to the overall undergraduate student body must be given higher priorities than in the past. Finally, nonmatriculating professionals and the lay public pose a need for expanding evening classes, conferences, and summer workshops as part of a continuing education program. Above all, the geology teacher must establish a mid-ground between the specialist and the dilettante, thereby becoming a "generalist of substance" capable of working at discipline interfaces.

Geol. Soc. America, Abstracts with Programs, v. 2, no. 7, 1970, p. 577-578.

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Hornbaker, Allison L.

GEOLOGIC STRUCTURES AND INDUSTRIAL MINERAL DEPOSITS IN THE PLAINS STATES

Seminar presented to Research & Engineering Group, Pittsburgh-Corning Corp., Pittsburgh, Pennsylvania, February 20, 1970.

A CASE HISTORY—VOLCANIC ASH RISES AGAIN

Millions of tons of volcanic ash were widely distributed over central and western Kansas during late Tertiary time, reworked by wind and water and redeposited in depressions of varying shapes and sizes. Until the 1950's, volcanic ash was mined in Kansas for use primarily as an abrasive. More recently, large tonnages have been used as low cost filler and stabilizer in hot-mix deep-strength asphalt pavement on interstate and federal highway routes.

In 1964, the Kansas Geological Survey initiated a research and development program designed to convert low unit value minerals that have little or no market demand to high unit value materials with large market demand. Filter aids made from volcanic ash are a good example.

Early in 1970 a special project was undertaken to develop a new type of high quality, insulative, non-absorbent, warp-resistant, pre-finished building material made from expanded volcanic ash, the key ingredient, and suitable bonding materials. The new material is adaptable to the manufacture of interior and exterior doors, cabinet doors, wall panels, and other special-purpose products.

The Pearl-lite Company was incorporated to manufacture and market the newly formulated building material, the first product being pre-hung, pre-finished exterior and interior doors with hardware. As the plant expands, new product lines will be introduced.

Public presentation, Meeting Society of Mining Engineers, Am. Inst. Min. Met. Eng., St. Louis, Missouri, October 21-23, 1970.

Merriam, Daniel F.

COMPARISON OF BRITISH AND AMERICAN CARBONIFEROUS CYCLIC ROCK SEQUENCES

Classification is of interest to geologists as a convenient means of expressing ideas and concepts. Most classification schemes categorize a continuum into discrete classes or states based on some prominent character of the objects being classified. Unknowns then are identified as to their position within the classification scheme. Until recently most geologic classification schemes have been qualitative. With advent of the computer, applications of many quantitative statistical techniques have become practical. These techniques offer the advantages of repeatability and objectivity. This report gives results of the applications of several techniques for classifying Carboniferous cyclic rock sequences. Twenty sections were measured in detail in Great Britain and the United States. Particular importance was placed on noting transition from one lithology to another. Seven lithologic types were distinguished: (a) sandstone, (b) siltstone, (c) nonfossiliferous shale, (d) seatearth or underclay, (e) coal, (f) fossiliferous shale, and (g) limestone. It was noted also which part of the sequence was marine and which nonmarine. From the original data, the number of changes per 100 ft were calculated as well as an entropy index indicating the "orderliness" of the sequence and a matching index obtained by comparing the similarity in sequences of lithology between pairs of sections. The matching index is based on qualitative characters and in this regard belongs to a type of sequential analysis of scaleless nonnumeric data. The matching coefficients were clustered and displayed as dendrograms. A cluster analysis also was performed using

nine variables (number of changes per 100 ft, entropy index, percentage thickness of sandstone, siltstone, non-fossiliferous shale, seatearth and coal, fossiliferous shale, and limestone, and percentage of nonmarine units) and the results displayed as dendrograms. In addition principal components analysis utilized the nine variables to determine if groups were present in the data. The first three principal components were interpreted geologically and a three-dimensional model constructed. Three loosely grouped clusters could be recognized in this display: (1) cyclic sequences associated with deltaic complexes, (2) sequences characteristic of deposition farther offshore, and (3) those composed mainly of marine sequences formed in an offshore open-marine environment.

Intern. Assoc. Math. Geol. Jour., v. 2, no. 3, 1970, p. 241.

COMPUTER APPLICATIONS IN STRATIGRAPHIC PROBLEM SOLVING

Quantitative techniques have been used in stratigraphic correlation to (1) assist in zonation of nondescript or complex sections, (2) to smooth "noisy" data and search for fundamental trends, (3) to compare lithologic sections of approximately the same composition and sequence to find similarities in sedimentation patterns and sequence of depositional environments, (4) to correlate fossil assemblages to approximate a relative time sequence within certain confidence limits, and (5) to compute "absolute" ages, for example from radiometric decay, and determine their significance. Correlations have been effected on a local, regional, and worldwide basis using single or multiple characters. Techniques presently in use are similarity coefficients, cluster analysis, principal components analysis, factor analysis, time-series analysis, crosscorrelation, cross-association, and analysis of variance. Examples of different quantitative applications to stratigraphic problem solving are reviewed.

9th Intern. Sym. on Techniques for Decision Making in the Mineral Industry, Montreal, 1970, in press.

—; and Robinson, J. E., Union Oil Company of Canada

TREND ANALYSIS IN GEOLOGIC AND GEOPHYSICAL EXPLORATION

No abstract given.

Mathematical Methods in Geology and Geophysics: Hornicka Pribram ve vede a technice (Pribram, Czechoslovakia), 1970, 41 p.

Spitz, Owen T.

USE OF PRODUCTION DATA TO PREDICT FUTURE CRUDE OIL PRODUCTION AND ULTIMATE RESERVES

This thesis describes an investigation of the use of growth curves as a prediction tool to forecast future crude oil production. The effects of solution techniques, data weighting and production cycles on the determination of curve constants for two growth curves, the logistic curve and the Gompertz curve are studied.

The logistic curve is shown to be a consistent and conservative estimator of future production. Production cycles are shown to be the major source of inconsistencies in predictions by the logistic curve, but data weighting can reduce much of the variation caused by production cycles.

The Gompertz curve is shown to be very sensitive to solution methods, data weighting and production cycles. Ultimate production as determined by the Gompertz curve is, for all methods of solution, considerably higher than any value predicted by recognized authorities by any means.

It is concluded that either the Gompertz or the logistic curve may be used to represent the observed data. As a prediction tool, the logistic curve is judged to be superior to the Gompertz curve.

Predictions of annual crude oil production for 1970-1979 are given for Kansas, Illinois, Oklahoma and total U.S. production using the curve form thought to be most appropriate for these data.

Unpub. M.S. thesis, Dept. Chem. and Petrol. Engr., Univ. Kansas, 1970.

Tien, Pei-Lin, and Bauleke, Maynard P.

A METHOD FOR PREPARING PELLETED CLAY SAMPLES OF SEMI-MICRO QUANTITY FOR DIFFERENTIAL THERMAL ANALYSIS

A semi-micro quantity (10-15 mg) sample of clay is pressed into a 3 mm diameter pellet for differential thermal analysis (DTA) in a STONE-TRACOR ring microsample holder. The pellet is transferred to the sample holder dish with a vacuum tweezers. Platinum sample dishes are also handled by vacuum tweezers to avoid denting the dishes or damaging the thermocouple wires. The DTA curves obtained by the pellet method are highly reproducible. The resolution and sensitivity of reaction peaks are equivalent to or better than those produced by a large sample (200 mg) packed into a nickel block holder.

Clay and Clay Minerals, v. 18, no. 3, 1970, p. 179-181.

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Watson, Jerry A., Texas Instruments Inc., Dallas, Texas; and Angino, Ernest E.

IRON-RICH LAYERS IN SEDIMENTS FROM THE GULF OF MEXICO

Thin yellow layers (0.5 to 2 cm) examined in seven cores in the west and central portions of the Gulf of Mexico are enriched in iron, manganese, cobalt, and nickel with respect to the surrounding sediments. The average enrichment is 66, 33, 51, and 28 percent, respectively. The highest correlation coefficients between single pairs of elements yield Co:Ni ($r = 0.53$), Fe:Ni (0.64), Fe:Co (0.62), and Mn:Co (0.50).

The yellow, iron-rich sediments commonly occur in the Pleistocene-Holocene transition zone and in the upper Pleistocene sediments. The iron-rich zones are considered to be the result of a reduced sediment accumulation rate. Carbon-14 dates support this argument. The close association with iron-stained foraminiferal tests in the sediments

suggests post-depositional scavenging. The yellow layers are most prevalent on the lower continental slope, continental rise, and Sigsbee abyssal plain.

Jour. Sed. Petrology, v. 39, no. 4, (1969), p. 1412.

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Waugh, Truman C.

ARSENIC IN OUR WASHDAY PRODUCTS

Qualitative analysis on the total solids of Kansas River water led to a study of a few washday products. Several reappearing lines in the qualitative spectra of these washday products were from arsenic. Semi-quantitative analysis was tried using a D. C. arc method with a Jarrell-Ash 1.5 meter Wadsworth spectrograph.

XXI Mid-America Symposium on Spectroscopy, Soc. Applied Spectroscopy, Chicago, Illinois, June 2-5, 1970, p. 38.

Wilson, Frank W.

HIGHWAY PROBLEMS AND THE GEOLOGY OF KANSAS

No abstract given.

Proceedings of the 21st Annual Highway Geology Symposium, University of Kansas, Lawrence, Kansas, April 23-24, 1970, in press.

KANSAS—A GEOLOGIC PROFILE

No abstract given.

KANSAS! 3rd Issue, Kansas Department of Economic Development, 1970, p. 2-8.