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SASSOLITE FROM THE KRAMER BORATE DISTRICT, CALIFORNIA*

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Abstract

Sassolite (H_3BO_3), previously unreported from the Kramer Borate District, California, was found near the base of the borate-bearing shales underlying the ore body. Probertite, ulexite, colemanite, borax, and kernite, all found within the borate body, produce alkaline borate solutions (pH values of 8.3 to 9.2) when dissolved in water. Thus the presence of sassolite, which forms in an acidic environment, is distinctly anomalous.

Sodium, borate, and sulfate form the major portions of the water-soluble materials in the sassolite-bearing rocks; calcium and iron form lesser concentrations. Efflorescences of copiapite, mirabilite, sassolite, ulexite, borax and a little calcite and halite confirm the presence of their constituents in the wall rocks. The phase relationships between Na_2SO_4-$Na_2B_4O_7$-H_3BO_3-H_2O thus approximate the limiting conditions under which the sassolite probably formed. It is concluded that after lithification, sulfuric acid was formed by oxidation of iron sulfides by groundwater; this reacted with earlier formed borates to form acidic borate solutions, and from these sassolite was deposited at some temperature below about 35°.

The optical properties and x-ray patterns of sassolite and copiapite are given; an analysis of the copiapite shows it to contain iron, sulfate, and minor copper and phosphate.

Introduction

Sassolite, not previously reported from the Kramer Borate District, was found by two of the writers in the mine of the California Borate Company. Sassolite is normally the product of an acidic environment. In rocks characterized by borates that form strongly alkaline solutions, the presence of this acidic mineral is striking. The purpose of this paper is to describe the occurrence and properties of the mineral and to speculate briefly on its origin.

Sassolite has been reported previously in California from efflorescences around Siegler Springs in Lake County and Tuscan Springs in Tehama County (Bailey, 1902), from The Geysers, Sonoma Co. (R. L. Smith, this issue, page 1204), and from Death Valley (Allen and Kramer, 1957). It has also been found in spring deposits at Steamboat Springs, Nevada, and Yellowstone National Park (R. L. Smith, this issue). Several Italian, and Tibetan localities, some of which have been worked commercially for sassolite, are noted by Palache, Berman, and Frondel (1944).

Geology

Kramer Borate District

The Kramer ore body, located in southern California (Fig. 1), is the

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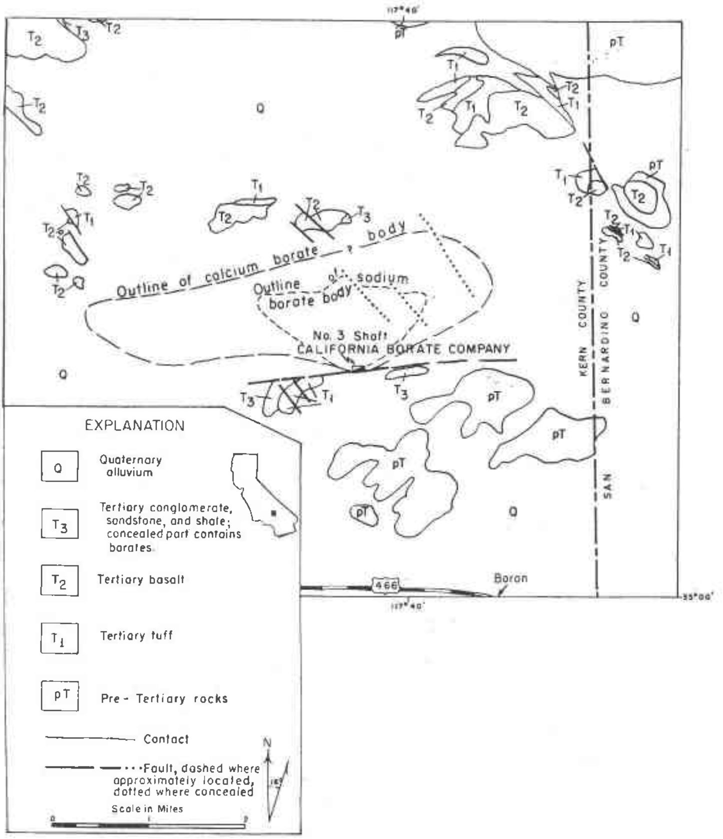

FIG. 1. Index map showing the location of the Kramer Borate District and the No. 3 Shaft of the California Borate Company. Geology and outline of the borate bodies after Gale (1946).

largest known deposit of sodium borates in the world. As described by Gale (1946), the sodium borate ore body, consisting chiefly of borax and kernite, occurs as a lenticular bed up to 250 feet thick which lies at depths varying from 300 to 1000 feet below the surface of the alluvial basin. The ore is surrounded by shales containing smaller percentages of calcium and sodium-calcium borates. The northern two-thirds of the borate body is underlain by basalt; the southern one-third is underlain by arkosic sandstone and conglomerate. Sandstone and conglomerate overlie the borate body at all places.

The matrix rock of the Kramer ore body is chiefly shale or clay, some of which appears to be beidellite (Schaller, 1930). Chemical analyses of the clay indicate an unusual concentration of lithium (Anon., 1956). Some beds of clay have notable concentrations of carbonaceous material.* Quartz, feldspar, and mica form the bulk of the coarser detritus; some beds contain fine-grained pyroclastics.

Schaller (1930) and Gale (1946) report the following borate minerals: borax and kernite form the bulk of the ore minerals; in the shale surrounding the ore body, probertite, ulexite, colemanite, and howlite are found. Lesserite and inderite have been described (Frondel, Morgan, and Waugh, 1956; Frondel and Morgan, 1956). Searlesite is locally abundant (R. C. Erd, written communication). The non-borate minerals listed by Schaller and Gale are pyrite(?), stibnite, realgar, chert, and calcite (or aragonite). Gerstleyite was described by Frondel and Morgan (1956). Unidentified iron sulfides and beds of analcime crystal sand are also found (R. C. Erd, written communication).

Sassolite locality

The chief sassolite locality occurs in the part of the D-level of the California Borate Company mine (the "Western Borax mine" of Gale's (1946) report) shown in Fig. 2a. This part of the mine is about 25 feet from the southernmost edge of the ore body, and stratigraphically in the northeast-dipping rocks underlying the ore. Traveling toward the north in this drift is equivalent to passing up through the section which underlies the ore. Figure 2b shows the approximate extent of the borate minerals. The solid lines indicate the ranges of the largest mineral concentrations, the dashed lines indicate the range of visible but smaller concentrations.

The largest concentrations of sassolite are in units 6 and 8 where the mineral is concentrated in rocks underlain by a trough of fault gouge. It is closely associated with probertite, searlesite, analcime, and a little gypsum. Here, the sassolite abundance increases back into the wall for a depth of at least six inches. Sassolite is also found in small amounts north and south of the main exposures in units 6 and 8, and throughout the rest of the mine where the rocks underlying the ore are penetrated.†

Sassolite very possibly existed prior to the opening of the mine. The chief mineral localities are along a mine drift that was enlarged several feet within the last few years. Other occurrences, along the underlying E-level, were noted only a few days after the workings were developed. Although the rocks throughout the mine are brecciated, there is no evi-

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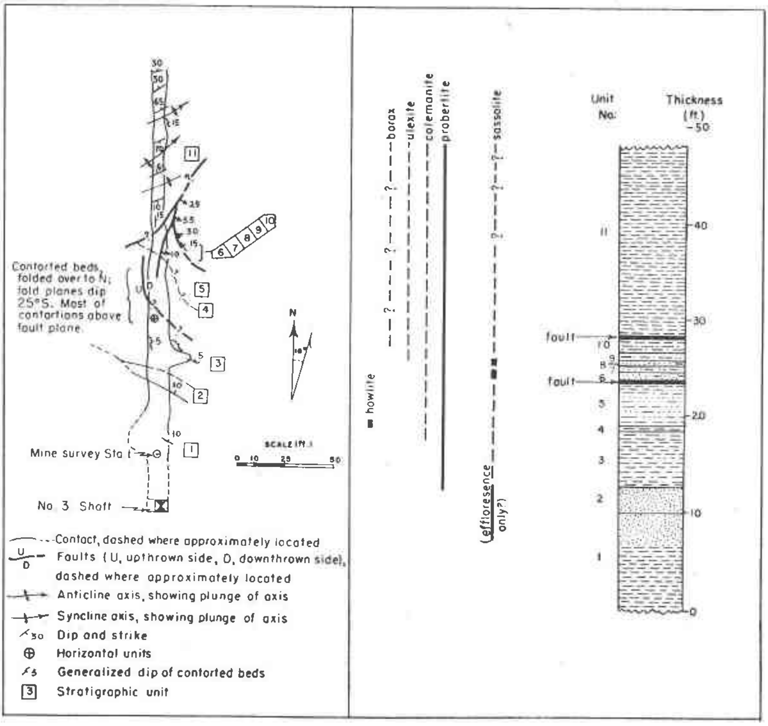
* A partial analysis (by H. Almond) of one such bed, at the base of unit 3 shown in figure 2b, shows the following percentages: $P_2O_5=0.06$, inorganic $CO_2=1.3$, organic C $=8.9$, total S as $SO_4=0.66$, As $=0.008$, Ge $=0.005$.

† Sassolite was subsequently found as an efflorescence at the exposed contact of shale and basalt in the Pacific Coast Borax Company mine during a visit by one of the writers.



a. b.

FIG. 2a. Geologic map of a portion of the D-level of the California Borate Company mine, Kramer Borate District, California. Stratigraphic unit numbers refer to those shown in Fig. 2b. Mapped October, 1956.

FIG. 2b. Stratigraphic units exposed in the portion of the mine shown in Fig. 2a north of Mine Survey Station 1; also shown are the approximate stratigraphic ranges of the borate minerals present, the solid and dashed lines indicating major and minor amounts respectively. The lithologic symbols for sandstone, siltstone, and shale are those commonly used.

dence at most sassolite localities, or in thin sections, for the introduction of solutions since the workings were made.

The probertite probably formed later than the host rock (Schaller, 1930, p. 139) which consists of clastics, searlesite, analcime, and iron sulfides. The sassolite, in turn, was formed later than the probertite as it forms coatings on the surfaces of the probertite clusters. Consequently, these sassolite crystals, if also formed at depth, are unique. All other known deposits of sassolite were formed at or near the surface.

In moist parts of the mine, especially the upper part of unit 1 and unit 2, efflorescences occur on the mine walls and along cracks and joints within the rocks. The mineralogy of these is significant because they consist of the water-soluble materials in the wall rocks, and some of them are not detectable in the dry parts of the mine. The following efflorescent minerals have been found: mirabilite, copiapite, sassolite, ulexite, borax, and a little calcite and halite (R. C. Erd, written communication). The exact relationships between these minerals has not been determined, but apparently the first three tend to coexist to the exclusion of the others. The presence of copiapite and mirabilite shows that water-soluble sulfates exist within the rocks, although a little gypsum is the only sulfate mineral detected in the dry parts of the mine.

MINERAL DESCRIPTIONS

Sassolite

The sassolite crystals occur most abundantly as small flexible flakes which fill numerous fractures within the shale beds. Most of the crystals are 0.5 mm. or less in diameter, but some are as large as 5 mm. Several are about 5 microns thick. In the most abundant patches, sassolite flakes appear to cover as much as 75 percent of the hand specimen area; more commonly, however, they form only enough of the surface area to furnish a pearly "sparkle." In thin section, the mineral is seen to form the entire filling of lenticular veins that cut through the host rock. Individual veins range in size up to 0.3 mm. thick and 20 mm. long and commonly taper gradually to a featheredge.

Individually, the crystals are very thin colorless wafers, commonly with several edges conforming to a pseudohexagonal pattern. In reflected light, many flakes show interference colors ("Newton's rings"), mostly red or green. There is generally no preferred orientation of the individual crystals in hand specimen or thin section. The crystals show a fair to good pseudohexagonal parting.

Crystals lying on the basal plate or cleavage are nearly isotropic, β and α being nearly identical. The indices of refraction, determined in sodium light, are $\gamma' = 1.454 \pm 0.003$, $\alpha = 1.337 \pm 0.005$. The α index was measured in a mixture of acetone and water saturated with H_3BO_3, the mixture having a known refractive index. The apparent optic angle $(-2E)$ is very small and slightly variable. Dispersion is not apparent. Some crystals are faintly zoned(?) parallel to the pseudohexagonal faces. Polysynthetic twinning is found in most crystals; the twin law was not determined. An x-ray pattern of one sample gave the results shown in Table 1.

Copiapite and mirabilite

Neither copiapite nor mirabilite has been previously reported from the Kramer Borate District. Both occur as efflorescences and, for this reason,

TABLE 1. *X*-RAY POWDER DATA FOR BORIC ACID (C.P.), SASSOLITE, AND COPIAPITE

Fe/Mn radiation λ=1.9373 Å

Boric acid[1] (C.P.)		Sassolite[2] (Kramer Borate District)		Copiapite[3] (Kramer Borate District)	
d Å	I	*d* Å	I	*d* Å	I
6.06	1	6.1	2	10.49	10
5.90	<1	5.9	1	8.90	<1?
4.80	<1	4.8	<1	8.01	1
4.60?	<1	4.60	<1	7.18	<1
4.21	1	4.27	<1	6.87	3
4.06	<1	4.05	<1	6.40	1
3.51	1	3.52	2	5.96	2
3.19	10	3.19	10	5.47	1
3.03	<1	3.04	<1	5.32?	1
2.96	<1	2.97	1	5.12	2
2.92	<1	2.92	1	4.92	2
2.84	<1	2.85	1	4.80	1
2.72	<1	2.73	<1	4.58	2
2.65	1	2.65	2	4.39	1
2.56	<1	2.57	1	4.15	3
2.50	<1	2.50	1	3.87	<1
2.30	<1	2.29	<1	3.75	1
2.25	<1	2.27	<1	3.66	3
2.23	<1	2.23	1	3.59	<1
2.17	<1	2.17	<1	3.43	4
2.10	<1	2.10	1	3.24	1
2.07	<1	2.07	<1	3.16	1
2.04	<1	2.05	<1	3.06	4
—		1.992	<1	3.01	<1
1.695	<1	1.697	<1	2.92	1
1.674	<1	1.674	<1	2.82	1
1.648	<1	1.654	<1	2.72	4
—		1.636	<1	2.64	1
1.593	1	1.598	1	2.57	2
				2.54	<1
				2.47	2
				2.41	3
				2.29	1
				2.18	<1
				2.09	1
				2.05	2
				1.992	2
				1.923	2
				1.873	1
				1.815	1
				1.786	3
				1.762	<1
				1.662	1
				1.621	<1
				1.600	1
				1.580	2
				1.510	2
				1.466	<1
				1.452	<1
				1.225	<1
				1.144	<1

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[1] Sample ground for 1½ hours, scanned on diffractometer at rate of 1°/min., over the range 5° to 80°.

[2] Sample picked and ground slightly, mounted on glass fiber. Lines from glass have been omitted.

[3] Sample crushed but not ground. (On previous attempts, sample was ground and the pattern consisted of lines at 4.11 Å (10), 3.71 Å (5), 2.49 A (1), and a broad dark zone between 8–12 Å).

have only secondary importance in this paper. For the benefit of future workers, however, the habits and data for these minerals are given below.

The best copiapite efflorescences form as yellow balls, 0.1 to 0.5 mm. across. The most dense blooms cover the surface of the rock. Microscopically, the efflorescent material is a very fine-grained aggregate of crystals which have a faint yellow color. The optical properties are as follows (R. C. Erd, written communication):

$$\text{Opt.}(+)\qquad \begin{aligned} \alpha' &= 1.512 \pm 0.002 \\ \beta &= 1.534 \pm 0.002 \\ \gamma &= 1.576 \pm 0.002 \end{aligned}$$

The mineral is pleochroic with Y = colorless, Z = greenish yellow; 2V is about 70°. It is present as lath-shaped individuals flattened into "books" along $\{010\}$ and giving rise to radiating aggregates. Two distinct cleavages are visible. Extinction, parallel to one of them, gives an anomalous blue color. An *x*-ray pattern for this sample of copiapite is given in Table 1.

An analysis of 10 mg. of the same sample gives the following (H. Almond, analyst):

$Fe = 27.0$ percent
$Cu = 0.5\text{-}0.6$ percent
$P_2O_5 = 0.15$ percent
$SO_4 = 46$ percent
$H_2O = 26$ percent (by difference)

Tests for Mg and Ca were negative.

Mirabilite is found in small patches as a white "fuzz" where moisture has seeped through the mine walls. Individual fibers are commonly 5 to 10 mm. long. When collected and brought to the surface, the fibers collapsed and the mineral rapidly altered to thenardite.

ORIGIN OF SASSOLITE

On the basis of the field relationships, we conclude that the sassolite formed by the reaction of ground water on the earlier-formed sodium and calcium borates, iron sufides, and their host rocks. To further test this conclusion, two additional lines of evidence are considered: 1) the phase relationships between the associated minerals, and 2) the composition of the water-soluble portion of the sassolite-bearing rocks. It is reasoned that analyses of the water-soluble extract from these rocks should report the same constituents that were present in the sassolite-forming solutions, although the relative amounts of the constituents may be different. This premise may be wrong for solutions that deposit many minerals, but with a very soluble material (sassolite) as one of the precipitates, only a small number of still more soluble compounds could have passed through the rock without leaving a trace. All equally or less soluble

TABLE 2. PARTIAL COMPOSITION OF WATER SOLUBLE EXTRACT. ANALYSIS BY H. ALMOND

	Sample			
	Unit 8a	Unit 8b	Unit 6	Unit 2
BO_3	3.5 (6)	9.3 (16)	5.0 (8)	0.15 (0.3)
SO_4	2.4 (2)	2.3 (2)	2.9 (3)	1.0 (1)
Na	0.89 (4)	2.8 (12)	2.4 (10)	0.24 (1)
Ca	0.18 (0.4)	0.84 (2)	0.44 (1)	0.09 (0.2)
Fe	—	nil	nil	0.0025
pH	8.5	7.12	6.85	6.49

Values are in weight percents; parenthetical values are moles$\times 10^2$.

The sample numbers refer to those defined by Fig. 2b.

Unit 8a was digested with cold water; all others were digested with boiling water.

Qualitative tests on the solutions for chloride, carbonate, bicarbonate, phosphate, and nitrate were negative.

All pH values are of a slurry of ground-up sample and distilled water allowed to stand for 1.5 hours.

compounds will be represented in the analysis. Those only partly dissolved by the excess-water extraction will tend to exceed their original relative concentrations.

Table 2 shows the composition of the water-soluble portions of the sassolite-bearing rocks. Disregarding the calcium content, the system Na_2SO_4-$Na_2B_4O_7$-H_3BO_3-H_2O can be used to approximate the mineral and chemical environment found here. The relationships within this system are shown in Fig. 3. The pH values for these mixtures have been observed experimentally for the points bordering the sassolite field and are added to the diagrams. This figure shows three things of interest: 1) With increasing temperature, the sassolite field diminishes in size, and, if extrapolated linearly, ceases to exist above 35° C. 2) The stable associated sodium borate is $Na_2B_{10}O_{16} \cdot 10H_2O$, a form not known to occur naturally; this borate may exist in the vicinity of the sassolite deposists.* 3) All of

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* Since this manuscript was written, this mineral has been found and named sborgite. C. cipriani, Un nuovo minerale fra i produtti boriferi di Larderello: *Atti accad. nazl. Lincei, Rend. classe sci. fis., mat. e nat.* **22,** 519–525, (1957).

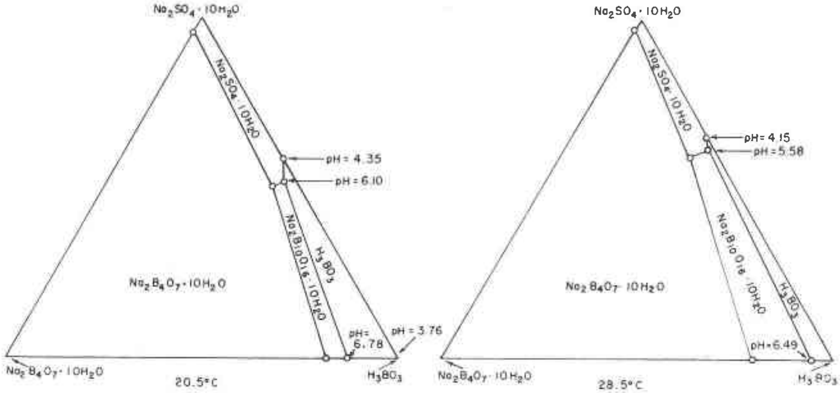

FIG. 3. The system Na_2SO_4-$Na_2B_4O_7$-H_3BO_3-H_2O at 20.5° C. and 28.5° C. The solid phases are borax ($Na_2B_4O_7 \cdot 10H_2O$), mirabilite ($Na_2SO_4 \cdot 10H_2O$), sassolite (H_3BO_3), and the synthetic sodium pentaborate. Analytical data recalculated from Teeple (1929, system XXI), pH values by H. Almond.

the solutions of this system which will precipitate sassolite are acidic.

In this borate body, circulating water is normally alkaline. Table 3 lists the pH values of solutions in contact with samples of the sodium, sodium-calcium, and calcium borates known to exist in the Kramer ore body. Solutions of kernite or tincalconite would resemble borax: howlite is not present in significant amounts. Sassolite cannot be deposited from solutions such as these.

Consequently, the problem of the origin of the sassolite is one of finding a source of acidifying solutions. The presence of the sulfates, gypsum, copiapite, and mirabilite, indicate sulfuric acid solutions in particular.

TABLE 3. THE pH OF SLURRIES OF CRUSHED BORATE MINERALS AND WATER

Sample	pH		
	1	2	3
ulexite	8.88	8.88	8.98
probertite	8.31	8.41	8.69
colemanite	8.94	8.93	9.10
borax (0.1N)	9.2		

1. The pH after standing 1.5 hours at 19° C.
2. The pH after standing 4.5 hours at 21.5° C.
3. The pH after standing 7 hours at 60° C.

The figure for borax is taken from the Handbook of Chemistry and Physics, 30th edition; other pH values by H. Almond.

The most probable explanation is as follows: Neutral ground water penetrated the lower part of the borate section, oxidized the unidentified iron sulfides found throughout the section, and produced sulfuric acid; this, in turn, reacted with the pre-existing borates and formed sassolite.

Reactions of sulfuric acid with the available borates might be as follows:

$$3H_2SO_4+\overset{\text{(probertite)}}{2CaNaB_5O_9\cdot 5H_2O}+14H_2O=$$

$$\overset{\text{(gypsum)}}{2CaSO_4\cdot 2H_2O}+\overset{\text{(mirabilite)}}{Na_2SO_4\cdot 10H_2O}+\overset{\text{(sassolite)}}{10H_3BO_3}$$

$$H_2SO_4+\overset{\text{(borax)}}{Na_2B_4O_7\cdot 10H_2O}+5H_2O=\overset{\text{(mirabilite)}}{Na_2SO_4\cdot 10H_2O}+\overset{\text{(sassolite)}}{4H_3BO_3}$$

$$2H_2SO_4+\overset{\text{(colemanite)}}{Ca_2B_6O_{11}\cdot 5H_2O}+4H_2O=\overset{\text{(gypsum)}}{2CaSO_4\cdot 2H_2O}+\overset{\text{(sassolite)}}{6H_3BO_3}$$

Reactions with ulexite, tincalconite, or kernite would differ only in the balance of water molecules. If calcite, aragonite, or the easily leached constituents of biotite were added to the reactions, additional sulfates would appear in the products. As written, each reaction produces sassolite and sodium or calcium sulfate, with three or more moles of sassolite being produced for each mole of the sulfate. Some corroboration of these reactions is found in the analyses for units 6 and 8 listed in Table 2 which have a BO_3 to SO_4 mole ratio of the correct order of magnitude. Furthermore, sassolite is abundant enough to be visible to the naked eye on the mine walls, whereas the coproducts, except for a little gypsum, are found only where they are concentrated as an efflorescence.

One problem remains: the manner in which water permeated the shale and clay. At present, groundwater penetrates only to the base of unit 3, whereas sassolite, which resulted from the oxidizing reactions of such water, is present in traces throughout the entire section shown in Fig. 2b. This excessive penetration may have resulted from greater hydrostatic pressures while buried at greater depth, from penetration before the sediments had reached their ultimate compaction, or from some unsuspected mechanism. More detailed work on the entire mining district is needed to supply this answer.

ACKNOWLEDGMENTS

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