

tive rate of the reaction throughout the crystallization process.

Similar curves have been derived for other sulfides, selenides, tellurides, arsenides, and antimonides. The technique has been shown to be particularly adaptable to the study of isomorphous minerals. Two series [galena (PbS)—clausthalite (PbSe) and covellite (CuS)—klockmannite (CuSe)] now being investigated show gradational changes of the curves from one end of each series to the other.

Preliminary curves show initial temperatures for several simple metallic sulfides or selenides as follows: covellite (CuS), 115°C; clausthalite (PbSe), 160°C; klockmannite (CuSe), 225°C; Alabandite (MnS), 340°C; greenockite (CdS), 410°C; arsenopyrite (FeAsS), 475°C; and pyrite (FeS₂), 505°C. The temperatures indicated are preliminary estimates, since the accompanying x-ray studies for these and more complex compounds are still incomplete.

It appears from preliminary results that differential thermal pyrosynthesis offers a convenient and reasonably exact method for investigating the fundamental properties of a number of sulfides or related minerals during their formation. When used in conjunction with differential thermal analysis and x-ray analysis, a more complete survey of the temperature relations of these minerals may be conducted. Study to date shows that differential thermal analysis is particularly adaptable to studies of mineral sequences which involve cation substitution, whereas differential thermal pyrosynthesis now appears more applicable to sequences involving anion substitution.

Since the method is dynamic and present equipment is limited to the study of dry systems, the results obtained are relative, and the data derived must be applied to natural mineral formation with caution. Present knowledge of temperatures of formation of mineral deposits leaves much to be de-

sired, and the results of this technique, although only relative, may prove of considerable value in estimating such temperatures. The dynamic method readily demonstrates that the assumption frequently made that long periods are necessary for the formation of "sulfide type" minerals may be misleading (3).

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References and Notes

1. E. Jensen, *Am. J. Sci.* **240**, 695 (1942).
2. P. F. Kerr and J. L. Kulp, *Am. Mineralogist* **33**, 387 (1948).
3. This study was made possible through the assistance of the National Science Foundation. 18 November 1959

Effect of Lesions in the Septal Forebrain of the Rat on Sleeping Time under Barbiturate

Abstract. Rats with electrolytic lesions in the septal forebrain show increased sleeping times after injection with thiopental sodium or barbital, as compared with normal and other control rats and rats with lesions in the cerebral cortex or caudate nucleus.

As part of a program investigating the effects of drugs on the emotional behavior in animals, we have studied the effects of barbiturates on the behavior of rats with lesions in the septal area of the forebrain. Such lesions ordinarily produce marked emotionality or hyperirritability. An earlier study found that meprobamate dramatically offset this irritability (1). In fact, rats with septal lesions showed clear sedation in response to doses of the drug that had little or no effect on the behavior of the intact animal.

In subsequent investigations of this phenomenon barbiturates were employed, because more is known about their metabolic fate and pharmacological action. These experiments have included not only rats with septal lesions, but also rats with lesions in the caudate nucleus or in the cortex and underlying white matter. All lesions have been bilateral and have been placed stereotaxically in the brains of 60- to 70-day-old male albino rats at an anteroposterio location 2 mm anterior to the bregma, by the passage of a 3-ma direct current for 45 seconds at each needle placement. The septal and cortical lesions were placed 0.5 mm lateral to the mid-line on each side, the septal 6.5 mm and the cortical 2.5 mm below the surface of the skull. The lesions in the caudate nucleus were placed 3.0 mm lateral to the mid-line on each side at a depth of 6.5 mm.

Histological confirmation of the lesions has been completed for all animals. These data have shown that the operative technique produces standard lesions with fairly restricted variability at the loci intended. The septal lesions were found to consistently destroy that area lying beneath the corpus callosum in the rostromedial wall of the hemispheres, bounded laterally by the lateral ventricles and extending from the frontal cortex to the gray of the hippocampal commissure dorsally and from the olfactory tubercle to the preoptic area ventrally. Animals with caudate lesions showed localized destruction beginning in the head of the caudate and extending through the medial aspect of the caudate nucleus with no damage to the septal region. The animals with cortical lesions showed small isocortical lesions lying close to the mid-line above the corpus callosum and extending from the level of the head of the caudate nucleus to the columns of the fornix.

In addition to normal control rats, most of the experiments also have included sham-operated, deaf, and reduced-weight control groups. In the sham operation, the rat was anesthetized, its scalp was incised and retracted, and the skull was drilled at the appropriate point, with the dura spared. The deaf control rats were anesthetized, and their ear drums were punctured by the stereotaxic ear plugs, when the other animals were given lesions, to provide a control for possible effects of incidental damage to the auditory apparatus on sleeping time. The reduced-weight control rats had their food and water intake restricted for 4 days prior to the test to control for effects of postoperative weight loss usually found in rats with septal and caudate lesions.

In the experiments with thiopental sodium, the drug was injected into the femoral vein after the skin had been incised and the vein exposed to permit viewing of the site. After the injection, each animal was placed on its back and left undisturbed until it turned over. Sleeping time served as the behavioral indicator of drug effect, defined as the number of minutes elapsing between the termination of the injection and the time when the rat righted itself spontaneously.

Figure 1 presents data for a representative experiment in which 20 mg of thiopental sodium per kilogram was injected intravenously at either 21 or 22 days postoperatively. In this experiment the rats with septal lesions showed a mean sleeping time between two and three times the mean sleeping time of any other group. The difference in sleeping time between the group with septal lesions and the com-

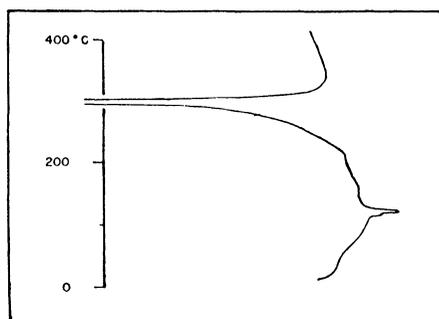


Fig. 2. Thermal record of the formation of galena by pyrosynthesis. The endothermic deflection to the right indicates the melting of sulfur, and the exothermic deflection to the left indicates the crystallization of galena.

bined group of those with other lesions was highly significant ($P=.017$), as was also the difference between the group with septal lesions and the controls as a group ($P=.004$). But the differences between the groups with

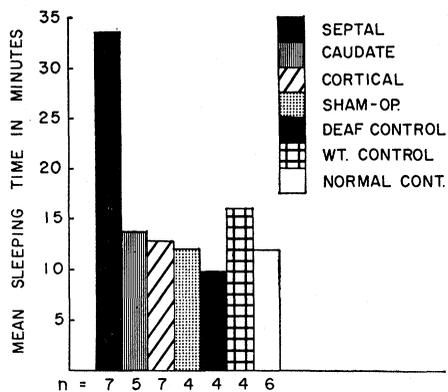


Fig. 1. Effect on sleeping time of rats of intravenous injection of 20 mg of thiopental sodium per kilogram, given 21 or 22 days postoperatively; room temperature, 37.2°C. The number of animals in each group is indicated below the vertical bars.

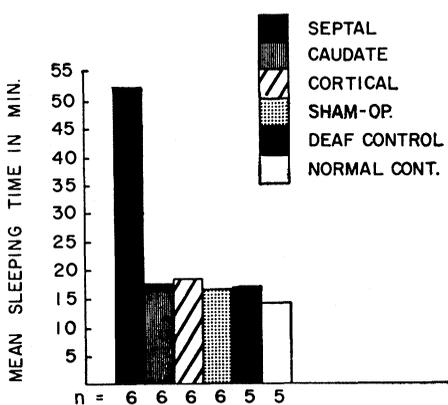
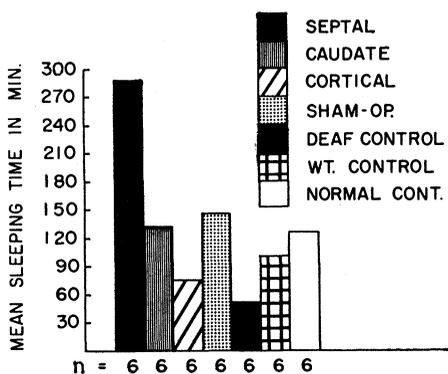


Fig. 2. (Top) Effect on sleeping time of rats of intraperitoneal injection of 160 mg of barbital sodium per kilogram, given 26 days postoperatively; room temperature, 25°C. (Bottom) Effect on sleeping time of rats of intravenous injection of 20 mg of thiopental sodium per kilogram, given 102 days postoperatively; room temperature, 28.2°C. The number of animals in each group is indicated below the vertical bars.

cortical or caudate lesions and the control groups did not even approach statistical significance.

Earlier experiments conducted at room temperature (25° to 29°C) had given essentially identical results, but it was found that the duration of barbital anesthesia was proportional to the fall in body temperature. Since septal lesions could possibly alter the temperature-regulating mechanisms of the rat and thus affect the duration of barbiturate action, the test room used in the experiment referred to in Fig. 1 was maintained at a temperature of 37.2°C to ensure the maintenance of normal body temperature by all rats during sleep. The rectal temperature of each rat was taken with a telethermometer attached to a thermistor sensing unit that had been placed in the rectum prior to injection. The rectal temperature of each animal was then recorded once per minute from the moment prior to injection of the drug to the time the animal awoke.

It was found under these conditions that the rectal temperature of rats with septal lesions did not differ from that of the groups with other lesions or that of control groups, and that normal rectal temperature was maintained without change during the entire sleeping time. Thus it is apparent that the effects of the septal lesion on barbiturate action are not secondary to effects on temperature-regulating mechanisms, since the potentiating effects of septal lesions are not abolished or even reduced by the maintenance of normal body temperature. We have also found that the rats with septal lesions can maintain normal rectal temperature for several hours under conditions of cold stress (0° to 5°C) and do not differ in this regard from normal rats or rats with other lesions.

In another experiment, rats with lesions produced and placed as described above, together with the control groups, were tested with barbital, a long-acting barbiturate that does not undergo chemical alteration in the body (2). Here, barbital sodium, at a dose of 160 mg of the acid per kilogram, was injected intraperitoneally 26 days postoperatively, with the test room at 25°C. Loss and recovery of the righting reflex, determined in accordance with a standard procedure in which all rats received equal stimulation and handling, was the indicator for induction and termination of sleep. Figure 2 presents the data for the barbital test. Again, the rats with septal lesions showed significantly longer sleeping times than either of the groups with other lesions or the control groups ($P<.02$), with no statistically significant differences appearing between the groups with the lesions in the cortex

and caudate nucleus and any of the control groups. To investigate the postoperative persistence of the effect of septal lesions of sleeping time after injection of barbiturates, all animals that had earlier received barbital now received a thiopental sodium test 102 days postoperatively, following the method described for the first experiment, with the room at 28.2°C. As the figures show, the data for the two drugs and for the two experiments agree substantially. That sleeping times under both thiopental sodium and barbital are increased by septal lesions suggests that the lesion does not produce this effect by altering drug metabolism.

All told, some 12 separate experiments have been performed with thiopental sodium, under these procedures but fresh groups of rats were used for each experiment. Uniformly, rats with septal lesions have shown elevated sleeping times in comparison with the groups with other lesions and with control groups as determined by histology. Taken together, the experiments have shown that this finding is not an artifact of postoperative debility and weight loss or derangement in temperature regulation. Further, the data available indicate that cortical lesions and lesions in the caudate nucleus do not increase sleeping time under thiopental sodium notably, if at all. Finally, in contrast with the transience of septal postoperative irritability, the effect of these lesions on drug response appears clearly at postoperative intervals up to 102 days.

The mechanisms responsible for this augmented response to drugs are as yet obscure. Because the septal area is known to have connections with the mesencephalic reticular formation (3) and because it has been reported that barbiturates have a selective action on the reticular formation (4), we are at present investigating the effects of lesions in other limbic and hypothalamic loci with known reticular formation connections on barbiturate action. Our further investigations of this problem also include studies on the effects of septal and other lesions on response to other centrally acting drugs, drug metabolism and distribution, and the possible contribution of hormonal function to the phenomena we have observed (5).

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References and Notes

1. H. F. Hunt, *Ann. N.Y. Acad. Sci.* **67**, 712 (1957).
2. E. W. Maynert and H. B. Van Dyke, *J. Pharmacol. Exptl. Therap.* **98**, 184 (1950).

- W. J. H. Nauta, *J. Comp. Neurol.* **104**, 247 (1956); *Brain* **81**, 319 (1958); — and H. G. J. M. Kuypers, *Reticular Formation of the Brain* (Little, Brown, Boston, 1958).
4. E. E. King, R. Naquet, H. W. Magoun, *J. Pharmacol. Exptl. Therap.* **119**, 48 (1957).
5. This research was supported by U.S. Public Health Service grant No. M-1918 and the Wallace C. and Clara A. Abbott Memorial Fund of the University of Chicago.

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Geochemistry of Graywackes and Shales

Abstract. Sixty-nine graywackes and 33 shales were analyzed spectrographically for 14 minor elements to illustrate the variation of composition within a graywacke bed, between beds in one section, between sections, and between formations. Analyses of several fractions of a graywacke indicate what each contributes chemically to the rock.

Some interesting features regarding the geochemistry of graywackes and shales are shown by 28 Normanskill-formation graywackes, 24 Quebec-group graywackes, 17 miscellaneous graywackes, and 33 shales analyzed spectrochemically for boron, barium, cobalt, copper, chromium, gallium, magnesium, manganese, nickel, scandium, strontium, titanium, vanadium, and zirconium (1) (see Table 1).

Turbidite graywackes result from deposition by turbidity flows which form when oversteepening of the continental shelf results in large-scale slumping of shelf or deltaic sediments. It might be expected that as these flows sweep down the gentle continental slope, the largest and heaviest mineral grains, which are often those showing relatively high concentrations of minor and trace elements, would be dropped first, and that the finer clay particles would be the last to settle. Therefore, a considerable difference in composition

between the bottom and the top of a bed might be expected.

The analyses show no statistically valid difference in composition between the top and bottom of a graywacke bed except for zirconium, which is always found in relatively high concentrations at the base. Such homogeneity results from the counterbalancing effect of elements contained in both the heavy mineral fraction and in the clay matrix. For example, the amount of boron present in a few grains of tourmaline at the base of a bed is counterbalanced by the smaller amount present in a large amount of clay near the top. Less zirconium is found in the clay matrix than in the heavy mineral fraction because of the absence of naturally occurring soluble zirconium compounds; thus, for zirconium, there is no counterbalancing effect.

There is little variation in average composition between graywacke formations, an indication that graywacke sediments are, in general, similar. Graywacke sediments are mechanical mixtures of most of the common rock types, derived from large areas of the continent and distributed to the ocean by the larger rivers.

Between stratigraphic sections in one formation and between beds in one section there are great differences which reflect the position of the section with respect to the shelf area and the position of the bed with respect to the source, since turbidity currents are inhomogeneous both laterally and vertically. The composition of a bed as a whole may change without any accompanying change in the compositional differences between the top and bottom, except for zirconium.

Normanskill graywackes contain seven major constituents—quartz, feldspar, clay matrix, carbonate cement, heavy minerals, clay rock fragments, and carbonate rock fragments. By

separating several fractions and analyzing them separately, the contribution of each fraction to the rock can be obtained. Feldspars add a considerable amount of barium but very little strontium. Carbonate cement contributes magnesium, manganese, strontium, and barium, the strontium arising from the redistribution of aragonite and radiolarian skeletal material by percolating intrastratal fluids. Heavy minerals are very rich in zirconium (over 10,000 parts per million) and contain much barium, cobalt, chromium, copper, nickel, scandium, titanium, vanadium, and silver but no detectable gold. The clay matrix adds considerable amounts of hydrolyzate elements such as boron, barium, cobalt, chromium, copper, gallium, nickel, titanium, and vanadium, but the levels of zirconium, manganese, magnesium, and strontium are very low.

A correlation of mineral composition, determined by detailed point-counting of thin sections, and chemical composition was attempted, but only gross correlations are visible—for example, graywackes rich in clay matrix tend to be richer in boron. The interplay of analytical and point-counting errors and the small range of mineral composition of the graywackes tend to obscure detailed correlations.

The effect of provenance is shown by the Normanskill formation (island-arc-derived) and the Quebec group (shield-derived) graywackes. Turbidites originating from the relatively more basic island arc environment show higher concentrations of the elements which are usually found in relatively high concentrations in basic rocks, while shield-derived graywackes are richer in elements such as zirconium, which are associated with acidic rocks.

No striking difference between the composition of graywackes and the average crustal rock is evident.

If each pair of elements is statistically treated to show the degree of correlation or interdependency of the concentration between the two, a great number of correlations are evident even at the 1-percent level of significance. This is largely the result of the presence of seven major constituents which form these graywackes. For example, graywackes rich in manganese tend to show high concentrations of strontium also, thus reflecting the quantity of cementing material in which these two elements are contained.

Analyses of 33 shales from formations of Ordovician, Devonian, and Cretaceous age show an increase in the boron content toward the present, suggesting that boron was added to the oceans by volcanism rather than by the condensation of volatile boron tri-chloride from a protoatmosphere.

Table 1. Results of spectrographic analysis of samples of graywackes and shales for 14 elements. All concentrations are given in parts per million except those for magnesium, which are given in percentages.

Sample	Concentration													
	B	Ba	Co	Cr	Cu	Ga	Mg	Mn	Ni	Sc	Sr	Ti	V	Zr
Quebec-group graywackes	70	220	15	88	9	10	.82	540	27	5	110	8500	43	810
Normanskill graywackes	35	380	22	140	33	14	1.2	600	43	8	260	5100	67	400
Kiskatom graywackes	120	530	28	250		6	1.9	850	77	11	120	11000	88	440
Rennselaer graywackes	32	750	14	130	14	9	1.5	750	25	8	190	6300	48	460
Miscellaneous graywackes (N = 9)	42	430	20	120	5	9	3.2	470	39	8	150	4500	52	260
Normanskill shale	130	360	32	87	37	20	2.4	400	58	15	150	7000	79	230
Miscellaneous shales (N = 33)	220	520	22	110	58	13	1.6	180	64	12	150	6000	150	340