

## BULLETIN OF THE GEOLOGICAL SOCIETY OF AMERICA

VOL. 31, PP. 419-424

NOVEMBER 30, 1920

CHEMICAL RESEARCHES ON SEDIMENTS <sup>1</sup>

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*(Read before the Society December 31, 1919)*

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## GENERAL CONSIDERATIONS

The chemical problems growing out of studies of sedimentary rocks must, even more than other problems, be viewed from many angles. Each such problem is likely to lead to several highly specialized studies in restricted chemical fields. The mere statement of any one of these special problems will often require an extended study of its general chemical, geological, and biological setting. Because of the special nature of these chemical problems, no general outline for their study needs presentation here, but it may be worth while to present some viewpoints from which the problems may be seen.

From the standpoint of physical chemistry many of the problems of sedimentary rocks are especially difficult, because the solutions concerned may be very dilute and very complex; the solid phases are often ill-defined physically, or are stable at temperatures so little above the ordinary that heat to speed up reactions can not be effectively applied; or unstable forms may appear and persist indefinitely.

An important chemical consideration respecting the consolidation or recrystallization of sedimentary rocks is the effect of differential stress. Adjacent grains are partially separated by films of liquid. These films are so thin in places that they are able to transmit stresses from grain to

<sup>1</sup> Manuscript received by the Secretary of the Society March 3, 1920.

This paper is one of a series composing a symposium on sedimentation.

grain; on the other hand, they do not greatly impede the migration of ions. Material which is thus and otherwise forced into solution by unequal stresses can be readily deposited on parts of the grains which are less stressed or in open pores. Cementation, accompanied by diminution of pore space, results, and smaller grains tend to disappear.

Diffusion of the constituents of one crystal into another crystal which is in intimate contact with it has been proposed from time to time as a factor in petrogenesis, but I have seen no adequate discussion of the mechanism. Diffusion could hardly be expected unless the diffusing material can have a definite place in the crystal structure into which or through which it diffuses. Thus, dolomite and siderite might interdiffuse to form mix-crystals of intermediate composition. Diffusion should be slower in hard than in soft minerals and should increase with rising temperature.

A crystal which is forming or growing in a complex solution concentrates and holds at its surface certain of the constituents of the solution. The smaller the crystal the greater this tendency. Commonly in cases of very slightly soluble substances the nuclei of incipient crystals become covered to such an extent with this (adsorbed) material that definite crystals do not grow, but the nuclei and adsorbed material become aggregated into "amorphous" or fibrous minerals. More or less of the surrounding solution is usually enmeshed in the aggregates and is later partly replaced by other matter. The elucidation of the genetic relationships of materials of this character, such as chert, bauxite, glauconite, hydrated oxides of iron and manganese, garnierite, phosphate rocks, etcetera, will require much cooperative study.

In some cases slightly soluble substances may form nuclei which do not at once become sufficiently aggregated as to be held by such filters as are ordinarily used in water analysis. Such material may be transported to considerable distances and finally be precipitated quite otherwise than if it had been in true solution. Silica especially should be considered from this viewpoint.

The formation of nuclei does not take place until a certain supersaturation, varying greatly under different conditions, has been reached. Such supersaturation may be so great that the solution becomes saturated with respect to a second crystalline substance, and the second substance may appear and continue to crystallize to the exclusion of the first, which is the more stable. The crystal structure which is to result from the growth of the nuclei as compared with the structure of the ions and the complex atomic groups of the solution must help to determine whether

stable or unstable phases appear.<sup>2</sup> Both may be forming at the same time, but the relative rates of growth may be overwhelmingly in favor of the less stable form. As soon as active growth of the deposit has ceased the supersaturation which allowed the growth of the unstable form may be reduced so as to permit the more stable form to continue its slow growth at the expense of the less stable form. The factors controlling the rates of formation of substances (besides the well known temperature effect) are little known. Numerous reactions involving liquids and gases are known to be greatly speeded up by the presence of certain substances, called catalysts, which furnish no material to the substances which are formed. Almost nothing is known about that action of catalysts which finally results in increasing the rate of growth of crystals from solutions.

### SOME ILLUSTRATIVE PROBLEMS

#### *DOLOMITE*

Knowledge of the chemistry of dolomite goes scarcely farther than inferences from the relations of this mineral as revealed from geological studies. It is apparent that in some localities calcium carbonate reacts with sea-water to produce dolomite; furthermore, the sea is, and probably has been, the only adequate source of magnesia for the great dolomite formations. Many of the dolomites do not bear evidence of being replacements of limestones. Thus arises the question whether or not they formed as primary deposits through direct precipitation, either chemical precipitation or precipitation through the intervention of minute dolomite-producing organisms of unknown characteristics. Is dolomite and not calcium carbonate the stable phase in presence of sea-water under the various conditions of temperature of the oceans? Would a slightly higher ratio of magnesia to lime in sea-water cause either a chemical precipitation of dolomite or a rapid alteration of calcium carbonate to dolomite? Or is dolomite one of those substances which at ordinary temperatures forms very slowly, in solutions in which it is stable, unless a catalyst is present? Is the general similarity but greater complexity of the crystal structure of dolomite as compared with calcite a dominating cause of the slow reaction of calcite to form dolomite?

Inasmuch as rates of reaction are about doubled by increases of tem-

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<sup>2</sup> The terms "stable" and "unstable" are used here in the ordinary sense, which disregards the effects of the adsorbed layer of foreign material on the surface of the nuclei. In reality this layer is not in general a permanent thing, for it is subject to the jostlings of the swiftly moving ions of the solution, which are tending thus to break it down and allow additions to be made to the nuclei.

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perature of 10° centigrade, and as dolomite has been formed artificially at somewhat elevated temperatures, it seems not an unpromising laboratory task to attempt—possibly by extrapolation of a series of quantitative results at elevated temperatures—to answer some of the geologists' questions concerning dolomite. The fact that both dolomite and the common forms of calcium carbonate usually crystallize well adds much to the hope of getting definite results.

*OCEANIC RED CLAY*

The oceanic red clay has been considered to be nearly the end product of the chemical action of sea-water on materials sinking through great depths of the ocean and resting on the bottom. The sources and means of distribution of parent materials have been discussed, the clays have been analyzed chemically by different methods with different objects in view, they have been studied microscopically—chiefly from the viewpoint of the biologist—and certain well founded conclusions have been reached; yet it seems probable that when critical studies of the structures of the complex granules of the clay have been made by means of the petrographic microscope, after suitable chemical treatments, more silica of organic origin and less decomposed pumice will be found than has hitherto been supposed. The solubility relations of the elements most sparingly present in sea-water and comparatively abundant in the red clay need much study, and the chemical effects of the working over of constituents of the mud in the alimentary tracts of animals should not be neglected.

*THE PRIMARY ROCK PHOSPHATES*

Geological relationships indicate that the extensive bedded phosphate rocks were formed on sea floors either by direct deposition or by replacement of oolitic or other limestones. Microscopical studies seem not to have settled the question of replacement for any particular deposit; but the more general chemical problems involved need not take this question into consideration.

At present no formation of phosphate comparable in purity with older deposits is known to be taking place. In fact, no source of phosphorus adequate for such deposits under any probable method of concentration is evident from the most recent water analyses, with the possible exception of water bodies in inclosed basins such as Lake Van, Armenia, which covers many thousand square miles and may, like certain well known lakes containing highly saline sulphate and carbonate waters, be relatively rich in phosphorus. In ocean water phosphoric oxide is remark-

ably low, but lime, the other essential constituent of phosphate rock, is abundant. If the phosphorus in a 1,000-foot column of sea-water were precipitated as tricalcium phosphate a layer less than half a millimeter thick would be produced. The lime in a similar column would give, if sufficient  $P_2O_5$  were available, a layer about 30 centimeters thick. Practically all of this lime could be precipitated rapidly from sea-water as phosphate if the sea-water were mingled with such highly phosphatic waters as were previously mentioned. If the phosphatic waters contained high sulphate, mixtures of calcium phosphate and calcium sulphate would be expected.

Many other problems involving chemical factors, some of them of long-standing interest, might be reviewed, but they would only further illustrate how necessary it is that the problems of sedimentary rocks be attacked from many directions.



# Geological Society of America Bulletin

## Chemical researches in the investigation of sediments

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*Geological Society of America Bulletin* 1920;31, no. 4;419-424  
doi: 10.1130/GSAB-31-419

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### Notes

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