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*Palaeophysiology: the organic origin of some minerals
occurring in sedimentary rocks.*

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DURING the last few years I have applied myself to the study of some minerals occurring in the sedimentary rocks of a definite geological horizon. The success of my investigations was greatly favoured by the fact that the mineralogical material was collected during the course of the systematic geological exploration of the phosphate deposits of Russia, which during the past eight years has been under my immediate supervision.¹

The explorations just mentioned were begun in the north-eastern part of European Russia, and several occurrences of barite were found in the first year during the field study of the phosphate deposits in the government of Kostroma. These barite deposits are associated with the Upper Jurassic strata, namely with the Oxfordian-Sequanian horizon. Such a definiteness in their stratigraphical position especially attracted

¹ 'Report on the geological investigations of the phosphate deposits' (Russ.), edited by Prof. J. Samojloff, 1909-1915, vols. i-vii.

my attention, and it was with much interest that I began to study the available material. During the second year of our geological investigations several other occurrences of barite deposits were met with, and all of them were found to belong to the same geological horizon. On the other hand, the most minute examination of the mineralogical material derived from other horizons failed to detect the presence of barium sulphate in any one of them.

The material so collected enabled me to describe¹ the barite deposits of the following nine localities: (1) Usole village on the Unzha river (left affluent of the Volga), (2) Dmitrieva village on the Unzha river, (3) Obrosimova village on the Nelsha river (left affluent of the Neya), (4) Fedikova village on the Neya river (right affluent of the Unzha), (5) Pogost village on the Neya river, (6) Tykolovo village on the Neya river, (7) Ogginetz village on the Gelvat river (left affluent of the Volga), (8) Dolgovo village, near Navoloki village, west of Kineshma, (9) Pushkino village, S.W. of Kostroma.

At these localities the barite is included in clay beds, and appears either in the form of very characteristic nodules, or else as a filling of the interstices and the cracks for the most part in marly septaria and sometimes in phosphatic concretions. In the article bearing on this subject I have given a detailed mineralogical account of all the barite deposits developed in the localities indicated above. These deposits are scattered over a large area, extending over 120 kilometres in a latitudinal direction and 100 kilometres in a meridional direction, and comprising parts of the districts of Kologriv, Makariev, Kineshma, and Kostroma in the Kostroma government.

Of course there are no reasons to believe that the occurrence of barite deposits in this part of the Kostroma government is confined to the places just mentioned; on the contrary, if we bear in mind that the samples of heavy-spar were being collected more or less accidentally, and that in the course of our field investigations our attention was directed to a wholly different problem, we must concede that it is obviously safer to infer that we have here a vast region where barite deposits are developed. Further, for this region the discovery of heavy-spar in a stratum gave evidence as to the age of this stratum, serving to some degree as a distinctive indicator or 'fossil'.

Covering, as time went on, a larger area, our investigations of the

¹ J. V. Samoilov, 'The deposits of heavy-spar in the east part of the government of Kostroma' (Russ.), Bull. Acad. Sci. Petrograd, 1910, vol. iv (2), pp. 857-880.

phosphate deposits extended south-eastward into the territory of the Kazan government. And here, too, near the Ozernoe Abyzovo village in the Yadrinsk district (at the boundary with the Kurmysh district of the Simbirsk government), heavy-spar was met with in the large marly nodules embedded in the clays of the Sequanian horizon.¹ In the Tetiushi district, 120 kilometres farther S.E. in the Baikovka village, there have been again encountered spherical marly concretions, associated with a similar heavy-spar, which has not yet been described in detail. These newly-encountered occurrences of barite are situated at a considerable distance, about 250 kilometres, from the area of development of the Oxfordian-Sequanian heavy-spar of Kostroma. Nevertheless they present the same characteristics and belong to the same geological age as those of Kostroma.

All these observations recall the old data concerning the discovery of barite on the banks of the Sura and Piana rivers, where too the Sequanian clay beds are developed ('Schwerspathbälle am Ufer der Sura und Piana').² The region of these two rivers is situated at a comparatively short distance from the area occupied by the barite deposits of Kostroma, and it seemed highly probable that these 'Schwerspathbälle' were enclosed in the same horizon. And two years ago in the course of our phosphate field-work heavy-spar enclosed in Sequanian marls was discovered at several localities, namely near the Sobatschy Ostrov village, in a ravine cutting the right bank of the Malaja Medjanka river, and near the Radova village on the left side of Sura river. Further, barite has been discovered in the same locality near the Ratova village in phosphatic nodules embedded in grey, marly clays of a rather later age—namely of that of the Kimeridgian. Associated with strata of this last horizon, heavy-spar was encountered also at the Mineshino village, in a ravine opening into the valley of Piana river, and near the Riapino village situated on the left bank of the Sura and Menja rivers.

Thus the age of the sediments enclosing barite deposits must be somewhat extended (Oxfordian-Kimeridgian). It may be noted here that in the above-mentioned regions of the Kazan and Kostroma governments deposits of the Kimeridgian horizon do not attain such development as in the Kurmysh district of the Simbirsk government.

¹ J. V. Samoilov, 'On the distribution of the Oxfordian-Sequanian barites in the eastern part of European Russia' (Russ.), Bull. Acad. Sci. Petrograd, 1912. vol. vi (2), pp. 939-944.

² J. G. Georgi, 'Geographisch-physikalische und naturhistorische Beschreibung des Russischen Reiches,' Königsberg, 1798, Theil iii, p. 142.

Some years ago in a work treating with the subject of the crystallography of barite I described¹ crystals obtained from the deposits of this mineral lying in a remote region of north-eastern Russia, namely from the region of the Izhma river and of its tributary the Ukhta, in the basin of the Pechora river. This barite is very like some of that of the Kostroma government; it is enclosed in nodules embedded in dark Jurassic clays. At that time the exact geological age of these dark clays did not interest me, but if now we endeavour to answer this question we could with a great degree of probability, according to our present knowledge of the Jurassic beds in this remote region, assign these barite deposits like those already examined to the clay beds of Oxfordian-Kimeridgian age.

There are thus barite deposits distributed over a comparatively large area and belonging to a quite definite geological age.

The petrographical character of the Upper Jurassic and Lower Cretaceous beds covering this region is now well known (with the exception of the region of the basin of the Pechora river), as a result of the geological investigations mentioned above. This petrographical character cannot afford any explanation as to the presence of barite deposits in this series. It is difficult, therefore, to admit here the supposition of the secondary origin of the barite, though it is common to resort to such an explanation in cases of a similar mode of occurrence of various minerals.

Under these circumstances I have ventured to suggest that these barite deposits are of primary origin, having been deposited together with the materials which gave rise to the enclosing sedimentary rocks.²

The Oxfordian-Kimeridgian clays, which include the heavy-spar, are of marine origin, and the question naturally must arise whether barite deposits are met with in the contemporaneous sediments of the sea-floor. Our knowledge in this respect is very scanty, but we have nevertheless the interesting data of Jones,³ concerning the discovery of heavy-spar nodules on the sea-floor from dredgings at a depth of 675 fathoms near Colombo. This abyssal barite in its external appearance, composition,

¹ J. Samoilov, 'Materials towards the crystallography of barite' (Russ.), Bull. Natur. Moscou, 1902, vol. xvi, p. 228.

² Recently K. André (Neues Jahrb. Min., 1914, Beil.-Bd. xxxvii, p. 348) and A. Bergeat (Zeits. prakt. Geol., 1914, vol. xxii, p. 287) mention the primary mode of origin of celestite and barite deposits.

³ E. Jones, 'Examination of nodular stones obtained by trawling off Colombo,' Records Geol. Survey India, 1888, vol. xxi, p. 35.

and to some extent in its microscopical structure presents characters strikingly similar to those of the Russian occurrences mentioned above. In fact the descriptions given by Jones would apply equally well to the nodules from, for example, Tykolovo and Pogost in the Kostroma government.

It can be admitted, therefore, that barium sulphate was deposited on the floor of the Oxfordian-Kimeridgian ocean in the north-eastern part of Russia.

I do not intend to dwell just now on the details of the question concerning the proportion of barium in ocean waters and in marine sediments. Data bearing on this subject can be found in the works of Forchhammer,¹ of Sir J. Murray and A. F. Renard² (barium contained in a sample of diatom-ooze and traces of barium in the globigerina-ooze), of F. W. Clarke³ (analysis of terrigenous deposits—blue and green muds, and red clays). It may only be noted here that in the contemporaneous epoch, as in the previous geological times, the barite nodules are not to be found universally over the sea-floor, and that their distribution is evidently controlled by certain conditions peculiar to the different regions. I would venture to raise the question whether these conditions are not to be searched for in the peculiarities of the fauna and flora of the region, and whether there might not exist organisms which would contain barium in the substance of their shells or of their bodies. Were this the case, it could be assumed that the accumulation of the remains of such organisms on the bottom of the sea would have had as a result the enrichment in barium of the corresponding marine deposits. The subsequent diagenetic processes would tend to concentrate into separate nodules the stable compound of barium, namely the sulphate.

Turning to the literature we find, however, a remarkable scarcity of data regarding this subject. All we know is limited to some, not numerous, indications as to the presence of barium in the ash of marine plants and animals, of which a *résumé* is given by Quinton.⁴ At the same time it must be borne in mind that in general our knowledge of the chemical composition of the skeletons of marine organisms is being

¹ G. Forchhammer, Phil. Trans. R. Soc. London, 1865, vol. clv, p. 218.

² J. Murray and A. F. Renard, Report on deep-sea deposits (Challenger Expedition), 1891, pp. 437 and 446.

³ F. W. Clarke, Proc. R. Soc. Edinburgh, 1907, vol. xxvii, pp. 167 and 269; also Journal of Geology, 1907, vol. xv, p. 788.

⁴ R. Quinton, 'L'eau de mer milieu organique,' Paris, 1904, p. 810.

very slowly increased,¹ and that we often meet in zoological works with the complaint about the almost total absence of precise chemical analyses of the skeletal parts of organisms.

The hypothesis which at first suggested itself to me assumed the existence of organisms capable of taking up and concentrating barium; but at that time no such organisms were as yet known to me. For this reason I had to content myself only with the analogy, the principal ground for which I had in the fact of the presence, according to O. Bütschli,² of sulphate of strontium in the skeletal substance of one group of Radiolaria, namely that of the Acantharia. It will be clear, therefore, with what a keen interest I read the recent works of F. E. Schulze³ and A. Chepotiev⁴ concerning a particular group of Rhizopods—namely that of the Xenophyophora. This group was established by Schulze, who worked out a portion of the zoological material collected by the German 'Valdivia' expedition, the Dutch 'Siboga' expedition, and the American 'Albatross' expedition; moreover, all the material of the 'Challenger' expedition was at his disposal.

In the bodies of these Xenophyophora there are some peculiar formations, which Schulze called 'Granellen'. These he describes as small, lustrous, quite colourless and transparent, rounded, oblong or fusiform bodies, with a high refractive index and low birefringence. The size of the 'Granellen' varies between 1–6 μ . They are represented by Schulze in his Plate II, figs. 2, 4, 11, &c. The chemical analysis proved that they are composed of barium sulphate (BaSO_4). In order to verify this fact, Schulze handed the 'Granellen' for investigation to the professor of physiological chemistry, Thierfelder, who confirmed the accuracy of the first analysis. According to Thierfelder,⁵ they consist of barium sulphate with a very small quantity of calcium sulphate. One can agree with Schulze that this fact constitutes an 'auffällige und überraschende Tatsache'.

¹ Quite recently there have been published the articles of F. W. Clarke and W. C. Wheeler, containing analyses of Brachiopod shells and of Alcyonaria. Proc. Nat. Acad. Sci. Washington, 1915, vol. i, pp. 262 and 552.

² O. Bütschli, Zoologischer Anzeiger, 1906, vol. xxx, p. 784.

³ F. E. Schulze, Wissenschaft. Ergebnisse d. deutsch. Tiefsee-Expedition auf d. Dampfer 'Valdivia', 1905, vol. xi, Lief. 1, p. 14.

⁴ A. Chepotiev, 'Explorations of low organisms' (Russ.), Petrograd, 1910, pp. 2, 7.

⁵ H. Thierfelder, Sitzungsber. Gesellsch. Naturforsch. Freunde, Berlin, 1905, No. 1, p. 4.

As to the distribution of the *Xenophyophora*, Schulze¹ in one of his papers gives a detailed list of all the localities where these interesting animals have hitherto been met with. He enumerates thirty-three such localities; three of them in the Atlantic Ocean, six in the Indian Ocean, and twenty-four in the Pacific. Only five of these localities are situated in subtropical regions, and the remainder in the tropics. The depth at which *Xenophyophora* have been found is very great, the average depth of their occurrence being about 4,000 metres. Only in one place of the Pacific have these animals been met with at a depth of 981 metres.

Chepotiev also gives some interesting data, which extend considerably the region where these animals are met with. This author has found representatives of the group of *Xenophyophora* amongst the coral-reefs bordering the northern end of Ceylon, on the shore of the Palk's Strait, where he found them at very low ebb, at a depth of only 1-5 metres. Chepotiev has observed 'Granellen' of a greater size (from 1 to 25 μ in length), appearing in the form of more regular crystals of the same shape as the 'Granellen' of the abyssal *Xenophyophora* (see Chepotiev, Plate II, figs. 13 and 14). This occurrence of *Xenophyophora* off the coast of Ceylon becomes especially interesting in connexion with the fact that the only heavy-spar nodules hitherto obtained from the sea-bottom by dredging come, as already mentioned, from the vicinity of Colombo.

Thus, owing to the observations just cited, the problem regarding the presence of barium sulphate in the bodies of some marine organisms can be recognized as solved. It will, of course, fall to the task of specialists to grasp the full physiological meaning of the fact under consideration. I need here only point out its mineralogical importance, which is especially great in connexion with the question of the primitive origin of minerals. To the list of the types of barite deposits already known must now be added a new type—namely that formed by the accumulation of the remains of marine organisms belonging to the group of *Xenophyophora*.²

With the study of minerals included in sedimentary rocks it is of particular importance from the present point of view to give an exact geological description of the strata containing the minerals under consideration ('stratigraphical' mineralogy), and to solve, as far as possible,

¹ F. E. Schulze, *Sitzungsber. Gesellsch. Naturforsch. Freunde, Berlin*, 1906, No. 8, p. 205.

² J. V. Samoilov, 'On sulphate of barium in animal bodies' (Russ.), *Bull. Acad. Sci. Petrograd*, 1911, vol. v (1), p. 475.

the question regarding the genetic relations of these minerals, i. e. whether they are of primary or of secondary origin.

Owing to my great interest in these questions I have recently taken up the study of another mineral closely related to barite—namely that of the celestite deposits of Turkestan. Thanks to the kind attention of several geologists engaged in the geological mapping of this region, I have at my disposal specimens of celestite derived from the deposits of this mineral discovered in the following ten different localities: (1) the vicinity of Suzak village, situated on the left side of the Kugart-su river (right tributary of the Kara-Darya river), 45 kilometres eastward from the town of Andizhan; (2) a place lying at 170 kilometres to the westward from the first locality, namely Kamuish-bashi, Kokand district; (3) Sel-Rokho, at a distance of nearly 35 kilometres westward from the last-mentioned locality, Kokand district; (4) at a distance of 250 kilometres to the S.S.E., in the basin of the Obi-niou river (right tributary of the Pyangy river), Garmak village, Kuljab district, in eastern Bucharia; (5) at a distance of 200 kilometres from the town of Shirabad; (6) Kukcha hill, lying at a distance of 60 kilometres to the N.E. of the town Petro-Alexandrovsk; (7) nearly 350 kilometres to the E.N.E., the island of Nicholas I on the Sea of Aral; (8) Chagabulak; (9) Udyuk, situated at a distance of nearly 80 kilometres westward from Tyube-Kuduk; (10) the mountain Ungozya at a distance of 4 kilometres from the Saruitash gulf. The three last-named localities are situated on the Mangushlak peninsula.

These celestite deposits are distributed over a vast area, extending from eastern Fergana to the coast of the Caspian Sea, and from the southern part of eastern Bucharia to the shores of the Sea of Aral. From the detailed description,¹ which I have already given in the Russian language, of these deposits, it can be realized how very accidental has been their discovery. No special efforts have been made to find the mineral, the explorers being engaged on a wholly different problem, and only occasionally happening to take up a specimen of a mineral unfamiliar to them. Consequently it may with confidence be inferred that the question regarding the local development of the celestite deposits in Turkestan is not in the least degree exhausted by the above-quoted enumeration of the places of its occurrence. It might be affirmed, on the contrary, in a region like Turkestan,

¹ J. Samoilov, 'On the genesis of some minerals occurring in sedimentary rocks.—Celestite of Turkestan,' *Materials towards the exploration of the geological structure of the Russian Empire* (Russ.), Moscow, 1914, p. 219.

standing as yet on the threshold of geological investigation and presenting in its greatest part a desert, that these accidental discoveries of celestite point undoubtedly to a vast distribution of strontium sulphate. Unfortunately, all of the celestite deposits of Turkestan are as yet not characterized from the geological point of view with the desired completeness. In some cases the age of the celestite-containing strata cannot be made out with sufficient exactitude; in other cases there are no reliable data for solving the question as to the primary or secondary origin of the mineral. We must, therefore, content ourselves with the general statement that almost the whole of the celestite deposits of Turkestan belong to the Upper Cretaceous formation.

Turning now to the sources of strontium which gave rise to the numerous celestite deposits of Turkestan, I venture to put forward the suggestion that the immediate source may be looked for in the accumulation of this metal by organisms. Some data relative to the presence of strontium in the skeletal parts (the shells) of animals of various kinds may be found in the literature (see, for example, O. Vogel¹). The valuable paper of Bütschli on the presence of strontium sulphate in the skeletons of the *Acantharia* has already been quoted above. It might be conjectured that there were, among the living forms of the Cretaceous sea, organisms containing a relatively large amount of strontium, and that the relative abundance of this alkaline-earthly metal in the Cretaceous sediments may be attributed to the existence of such organisms.

I conjecture a similar mode of origin in reference not only to the barium and strontium sulphates, but likewise to a number of other minerals occurring in sedimentary rocks. As is commonly known, the ocean waters contain a great many chemical elements in solution, but the proportion of many of these elements in sea-water is extremely small. A concentration of them to such an extent as to give rise to solid deposits would be therefore impossible under ordinary conditions, and a special apparatus is required, which would be able to accumulate such finely diffused matter. According to my opinion, such an apparatus is provided in the form of vegetable and animal organisms, which have the capacity of taking up the material indispensable for their existence even when this material is in a state of extreme dissemination. In such cases we have to deal therefore not with a simple chemical, but with a chemico-biological process.

¹ O. Vogel, *Zeits. Anorganische Chemie*, 1894, vol. v, p. 42.

Studying chiefly the morphological features of the fossil organisms palaeontology affords a clear understanding of those great changes to which the morphological structure of the organisms are subject. In the most recent times this science has made a step farther, and is now studying the problems of palaeobiology.¹ In this connexion we may consider whether physiological processes have revealed some changes as time went on. I mean, not the character of the physiological processes, but their intensity, and especially the materials with which these processes had to deal. An example will serve better for the elucidation of my meaning.

The blood of the animal organisms has always had to accomplish its essential, strictly determined function, and we know what a share in the fulfilment of this function is to be attributed to the iron contained in the blood of contemporaneous animals; but the same importance could conceivably be acquired by some other metal, for instance by copper. At present we have a not very extensive list of animals in the blood of which iron has been supplanted by copper; this list comprises those animals (e.g. amongst the Crustacea and Mollusca) the blood of which contains haemocyanin. And I think that it might reasonably be suggested that the quantitative relation between the animals containing as a constitutive part of their blood haemoglobin, on the one hand, and those containing haemocyanin, on the other, has not always been the same as it is in the present period of the earth's history. Have there not been periods in the earth's history when amongst the animals then existing those containing haemocyanin in their blood predominated?

As is commonly known, the chemical analysis of the ash of different kinds of plants sometimes reveals elements, the presence of which is quite unexpected and the proportion of which is exceedingly small. But has the relative amount of the various elements constituting the ash of plants always been the same, and have there not been past geological periods when plants of quite a different ash-composition prevailed?

We are entering here quite a new and unknown region, for the designation of which I should suggest the term of 'palaeophysiology' as the most suitable. For the solution of the questions involved there is, of course, no direct method, because the use of the evidence supplied by the fossil remains themselves is not available in the study of such problems. And yet the elucidation of these questions might afford a better understanding

¹ O. Abel, 'Grundzüge der Palaeobiologie der Wirbeltiere,' Stuttgart, 1912.

of the genesis of some mineral deposits, the origin of which has remained hitherto very obscure.¹

Let us now direct our attention to the particular case suggested by haemocyanin. The origin of the copper deposits of the Permian formation has given and still gives rise to much controversy. This metal occurs in the Permian sediments either as disseminated minerals or as deposits of economically valuable copper ore. But it must be remarked that the general geological features of the regions where copper-bearing beds occur are far from being similar. There is only one thing remaining constant in all these copper-containing sediments, that is, their belonging to the Permian age. And it is in this direction that the key to the genesis of these deposits must be searched for. If we admit that animals with haemocyanin in their blood prevailed during the Permian period, the question regarding the origin of the copper deposits will receive a new aspect. The presence of copper in the Permian sediments will appear quite natural and even necessary: it will only point to the development of a similar Permian fauna. The enrichment of some of the Permian sediments in copper will stand in connexion with the abundance of the fauna in the corresponding region during the Permian period. The presence of a rich fauna in the more extensive copper deposits of the Permian age has already been frequently observed; but hitherto it has been believed that the rôle of this fauna was confined to its reducing action on solutions of copper salts. I attach much more importance to this fauna, and I regard it as the source itself which gave rise to the copper deposits. I believe that the vital action of organisms caused the accumulation of copper secreted from the ocean waters.

On every occasion when there can be established the special association of a mineral with some definite geological horizon, it is necessary, according to my opinion, to examine closely the question whether the formation of this mineral could not possibly have been connected with the action of organisms.

The deficiency of our knowledge with regard to the chemical composition of contemporaneous animals is very much hindering the progress of the investigation of this problem. Indeed, it has not been supposed until quite recently that there were animals the skeletons of which consist

¹ Based on the evidence of the chemical components of vegetable and animal protoplasm, A. B. Macallum adduces interesting considerations regarding the composition of the sea-water in past geological periods (Trans. Canadian Institute, Toronto, 1904, vol. vii, Part 3, No. 15, p. 535).

of sulphate of strontium. Not less unexpectedly came the discovery of the group of marine animals *Xenophyophora*, the bodies of which contain grains of sulphate of barium. A paper has recently been published¹ which establishes the presence of vanadium in the blood of certain animals, namely the *Ascidia* (or *Phallusia*), in which it performs the same function as iron. A recent paper by A. E. Boycott,² 'On the occurrence of manganese in land and fresh water mollusca,' refers to earlier work by H. C. Bradley³ on the same subject.⁴

It would scarcely be reasonable to suppose that all the facts concerning this problem are restricted to those so recently and so unexpectedly discovered, and that we are not standing before some new and not less remarkable discovery. But even remaining within the limits of the facts already established, we must concede that a thorough mineralogical elucidation of the nature of this accumulation of strontium, barium, copper, and vanadium through the agency of vital processes should be considered seriously. And when we admit that the various organisms characterized by these unusual properties, although less numerous in the contemporaneous epoch, might have been more abundant and appear as a common and widespread group at some remote period of the earth's history, it will be clear then what importance must be attached to the detailed elucidation of all these questions for the proper understanding of the genesis of various minerals occurring in sedimentary rocks.

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¹ M. Henze, *Zeits. physiolog. Chemie*, 1911, vol. lxxii, p. 494.

² A. E. Boycott, *Naturalist*, London, 1917, pp. 11-18, 69-78.

³ H. C. Bradley, *Journ. Biological Chemistry*, 1907, vol. iii, p. 151; 1910, vol. vii, p. 287.

⁴ There are, thus, in the blood of different kinds of animals the following metals: iron, manganese, copper, and vanadium. But what have all these metals in common? They stand near to each other in their atomic weight in the following order: V = 51, Cr = 52, Mn = 55, Fe = 56, Co = 59, Ni = 59, Cu = 63. Perhaps, as the result of further investigations, there will be discovered organisms whose blood contains metals occupying the intervals in the range just adduced, namely chromium, cobalt, and nickel.