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Barytes and Celestite in the sedimentary rocks of Sweden.

By

Assar Hadding.

With an Appendix by **Sven Palmqvist.**

Communicated, February 9, 1938.

Barytes and celestite are occassionally found in free crystals or crystal aggregates in the sedimentary series of strata in Sweden. As these deposits are little known and the occurrence of the minerals is of some mineralogical and petrographical interest, I have collected some of my observations of their forms and typical modes of occurrence in the following account.

Barytes.

Barytes has been observed in the sedimentary rocks of Sweden partly as larger or smaller, freely developed, simple crystals, partly as concretionary nodules and lenses. To my knowledge the different forms as a rule do not occur together. The smaller crystals are found in clayey sediments, the larger in limestones. Hitherto barytes has not been shown to be present in sandstones in Sweden, neither as cement nor as crystals. The Swedish limestones also seem as a rule to be devoid of barytes. But relatively large free crystals occur in beds of impure limestone embedded in Upper Ordovician shale and marl.

In connection with an account of the sedimentary deposits of barytes it deserves to be noted that the mineral preferably occurs, in Sweden as elsewhere, in dykes and in breccias together with fluorite, blende, manganese ore and in several places together with iron ores.

The sedimentary barytes in Sweden shows three somewhat different types: —

1) small crystals in alum shale;
2) concretionary nodules in alum shale;
3) larger crystals in clayey limestone.

Small Crystalls of Barytes in the Upper Cambrian Alum Shale.

Small fusiform crystals of barytes forming a characteristic ingredient in certain zones have long been known. The tapering at both ends is always pronounced but no distinct faces are to be seen. The edges and faces are corroded and rounded. The crystals are 3—8 mm long and about 1 mm wide. Their form reminds us of grains of oats (Fig. 1).

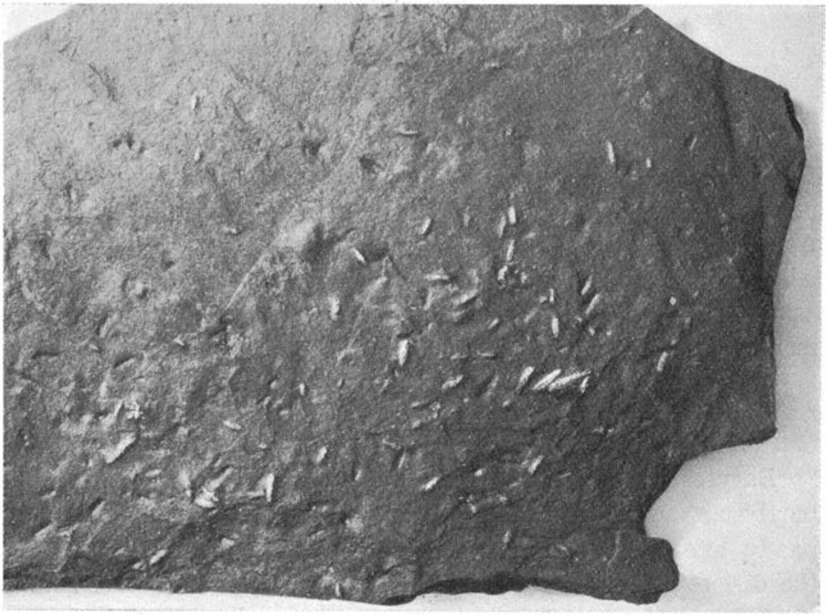

Fig. 1. Crystals of barytes with pyrite crust. Upper Cambrian alum shale. Röstånga, Scania. — Nat. size. (Pl. 719.)

As a rule an orientation of the crystals after their faces is impossible but there is no difficulty to perform it after their cleavage, which is always perfect, even in grains rich in inclusions. The crystals have as usual their greatest extension along the brachy-axis.

The inclusions consist of bitumen and marcasite or pyrite. They are zonally arranged parallel to the brachydome (011) or to the faces formed by corrosion (Fig 2). The pyrite and the more frequent marcasite occur in the form of small dispersed crystals or crystal aggregates, most abundantly in the peripheral parts of the barytes. The bituminous matter has a fairly uniform distribution in several zones, even in the core of the crystals.

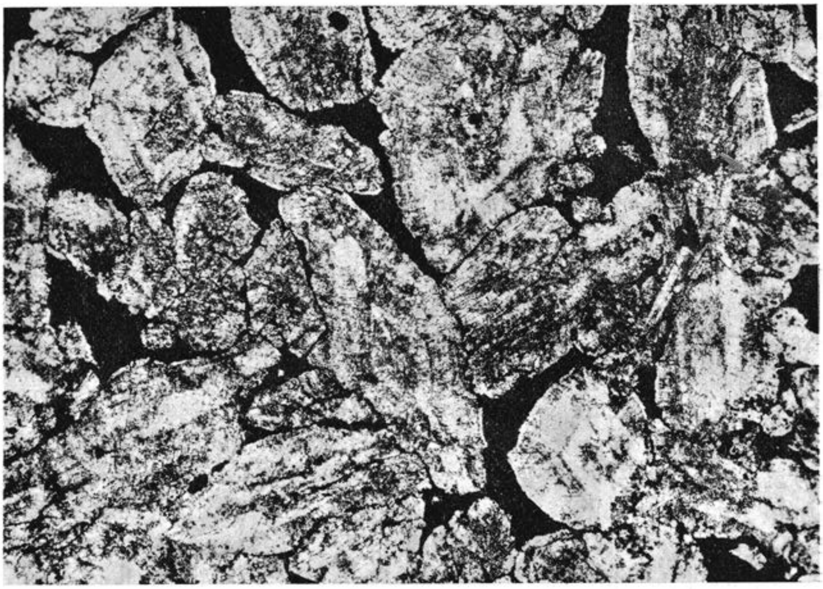

Fig. 2. Crystals of barytes with zonal arrangement of inclusions. Upper Cambrian alum shale. Röstånga, Scania. — 17 ×. (Pl. 720. Pr. 3037.)

Besides these inclusions there are other, undetermined ones which appear, under the microscope, to consist of liquid or gas in cavities of regulary parallelepipedic or irregular form.

The barytes cyrstals are very often coated with small marcasite (or pyrite) crystals.[1] The occurrence of marcasite (pyrite) together with barytes has caused certain investigators to regard the latter as a pseudomorph formed on the former. The marcasite cannot be the older of the two minerals; occurring as a fine-crystalline

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[1] Here also pyrite may be present instead of marcasite but the latter mineral is much more frequent. The sulphide is always called pyrite in older literature.

coating on the barytes crystals it must be formed after, or in connection with, the corrosion of these crystals. The small marcasite grains enclosed in barytes are probably also formed during a break in the growth of the barytes crystal. After the formation of marcasite the barytes may have been partly, or completely, removed by leaching, sometimes also replaced by other material. STOLLEY (1909, 353) showed that the form of the small pyrite-coated bodies cannot be referred to the crystal forms of pyrite but must originate from some other mineral. He also thought it evident that this was not gypsum, a mineral which is sometimes said to be found inside the pyrite coating; the gypsum he regarded as a secondary formation. It was quite plain to him that the primary crystal must be orthorhombic, and he discussed what minerals might be formed first. He did not mention barytes but referred to celestite, though he considered the primary crystal most probably to be Gaylussite or Pirssonite.

A few years later KAREN CALLISEN (1914) subjected the pyrite-coated formations to a renewed investigation and showed that the primary crystal, which was often preserved, consisted of barytes. The honour of giving the first real characterization of the crystals is, however, due to J. C. MOBERG and H. MÖLLER, who as early as 1898 showed the presence of barytes and also touched upon the probability that the spools had primarily consisted of barytes.

Concerning the interpretation made by these and other authors I refer to the following short history.

We don’t know for certain when barytes was first observed in the alum shale of Sweden but as early as 1826 HISINGER (p. 216) published an analysis of barytes from the alum shale at Andrarum in Scania. It was not, however, the small, free crystals that he analysed but a concretionary aggregate of the type known already at that time under the name of *hepatite* (see further p. 9).

It was, I think, G. FORCHHAMMER who first called attention to the small fusiform bodies which are now known as barytes crystals. FORCHHAMMER himself has not published anything about his observations or his opinion on this object, but in a paper by H. R.

Göppert (1859, p. 446) we find the following statement: — »Spindelförmige, $^1/_2$—1 Zoll lange und etwa 1—3 Linien breite, aus Schwefelkies bestehende Gebilde aus den untersilurischen Alaunschiefern Bornholms teilt mir auch Forchhammer mit, vielleicht organischen Ursprunges».

F. Johnstrup (1889, p. 21) also thought an organic formation probable. He wrote: — »Im obersten Niveau (*Peltura*-Schicht mit *Sphaerophthalmus, Ctenopyge* und *Eurycare*) enhält der Alaunschiefer in erstaunlicher Menge eine in Schwefelkies umgewandelte, fast immer hohle, spindelförmige Versteinerung (12 mm lang, in der Mitte 4 mm dick) von rhombischem Querschnitt. Die stumpfen Kanten sind mit einen scharfen Kiel versehen, und die Form ist im ganzen so constant, dass diese Körper unzweifelhaft einen organischen Ursprung haben müssen.»

A few years later, however, the nature of the fusiform bodies was made clear when J. C. Moberg and H. Möller (1898, 211) wrote as follows: — »The Dictyograptus strata in the brook of Sandby are covered by alum shale quite replete with small, somewhat fusieform bodies, with a rhombic transverse section, attaining the approximate size of a grain of oats and consisting of crystalline heavy spar. Similar bodies, though preserved in pyrite and often hollow,[1] were found in the Dictyograptus shale at Limensgade on Bornholm and in the upper part of the Peltura stratum at Vasagård. Johnstrup seemed inclined to consider them to be of organic origin.»

Certainly W. Deecke (1899, 40) was not aware of the work of Moberg and Möller when he wrote: — »Alle Schichtenflächen — — sind — — im obersten Niveau (mit *Peltura* und *Ctenopyge*) wie gespickt mit 1 cm langen spindelförmigen Eisenkiespseudomorphosen nach Gyps.» Nor seems the work of Moberg and Möller to have been known to E. Stolley when in 1909 he published his

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[1] That the original kernel in this case also may have consisted of heavy spar is evident for inst. from Hofmann's description of the ore veins at Pribram. He says: »ebenso kann häufig beobachtet werden, dass die ganze Barytmasse fortgeführt und nur die Hüllen das ehemalige Vorhandensein des Schwerspathes anzeigen» (Ein neues Whiterit-Vorkommen von Pribram. Sitzungsber. d. k. Böhm. Ges. d. Wiss. Math.-naturw. Classe. 1895. XV.). Pyrite is also specially mentioned there among the minerals enclosing heavy spar.

quite extensive investigation on the same formations, which he interpreted as pseudo-Gaylussite and pseudo-Pirssonite. As MOBERG & MÖLLER and DEECKE, STOLLEY also clearly saw that the formations are inorganic, and that pyrite was secondarily formed round an older crystal. STOLLEY shows that the gypsum or calcite sometimes found inside the pyrite crust must be a pseudomorph. In his opinion the primary crystal would have been an aqueous carbonate, Gaylussite or Pirssonite. Very probably, however, the simple crystals with perfect cleavage, which STOLLEY observed in some of the pyrite-covered grains, were barytes and not gypsum.

When A. H. WESTERGÅRD in 1909 (p. 73) mentions the small fusiform bodies from alum shale in Scania he agrees most with STOLLEY's interpretation of them. As WESTERGÅRD worked at that time in the institute of MOBERG it is a natural conlusion that MOBERG had then abandoned his opinion from 1898: if not, this ought at least to have been mentioned by WESTERGÅRD. It is also evident from MOBERG's statement in 1906 (p. 33) on the fusiform bodies in the Dictyonema shale at S. Sandby that he himself was in doubt as to the correctness of his earlier observation. He only says that they are »no doubt partly formed of pyrite but mostly of a sparry mineral (not calcite)».[1]

The question of the nature of the crystals was at last made perfectly clear by KAREN CALLISEN's elaborate and extensive investigation (1914). Only a few lines of CALLISEN's description will be quoted here: — »The crystals differ somewhat externally. While those known from the alum shale of Bornholm are always enclosed in a crust of pyrite and correspond closely to the description published by JOHNSRUP, the spindles in the Dictyograptus shale at Sandby have always a black coating outside the layer of pyrite. In the shale at Jerrestad the are smaller throughout, and the pyrite does not form such a distinct crust but is more dispersed in the crystals. When the crystal is broken, the three cleavage planes of heavy spar are distinctly seen and on that account there has been no difficulty to provide satisfactory sections for measurement

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[1] In his lectures on the geology of Sweden in the autumn term of 1908 Moberg characterized the fusiform bodies as twin crystals of calcite or heavy spar, and in the spring term of 1909 when the work of Stolley had been published, he expressed the opinion that a number of different minerals had probably succeeded each other within the pyrite-crust.

of the angles. This showed that the crystals are extended in length along the »*a*» axis, and that the perfect lengthwise cleavage of the crystals is parallel to (001). Of the external crystal faces the brachydome is as a rule rather conspicuous but, owing to the pyrite layer, it gives no reflection — —.» »The shale from Laesaa sometimes contained crystals of a broader and more flattened form among the fusiform ones. — — — The external crystal faces naturally gave no reflction in the goniometer, but the brachydome and the strongly developed basal pinakoid were very conspicuous.» »All the crystals show a great conformity in form as well as in optical properties. They have straight extinction in thin sections parallel to (001), and their cleavage parallel to (110) is perfect.»

In her work quoted above KAREN CALLISEN gives a rather exhaustive description of the varying appearancy of the barytes crystals (with a résumé in German). I may therefore content myself with referring to this and to the short reports and photos I have published above. An investigation of the rock and the series in which it is found is, however, necessary for the interpretation of the occurrence and the orgin of the mineral.

The series of strata: The small fusiform barytes crystals are found in the Upper Cambrian and the Lower Ordovician, viz. in the Olenid and the Dictyonema shale. They are exceedingly abundant in certain strata of the Dictyonema shale at S. Sandby, 10 kilometres E of Lund, in the corresponding shale at Flagabro in SE Scania, and at Limensgade on Bornholm. As a rule the crystals lie free from each other, but not infrequently they are more amply accumulated in certain parts of a bedding plane. Sometimes they are gathered in larger quantities on a small spot or packed together into relatively solid lumps. These may resemble concretions externally, but their structure is nevertheless different. All the small crystals are embedded in the clayey matter; they are free in relation to each other and show, all of them, the same development as when lying dispersed in the shale. In other parts of the Dictyonema shale there are real barytes concretions, which will be further discussed in the following (p. 9 seq.). As a rule the rock shows only slight variation in the different parts of the series. The shale is soft and often cleaves readily.

Barytes crystals have also been observed in the corresponding series of strata at Röstånga, Andrarum and several other places. Most exposed and best investigated are the strata at Andrarum.

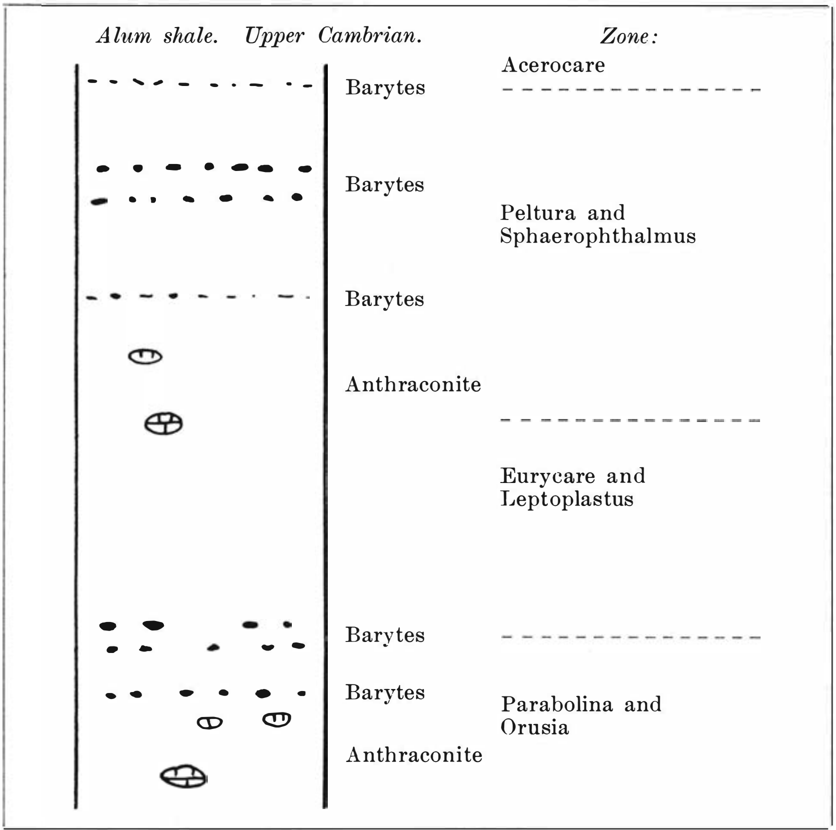

Fig. 3. Barytic strata in the Upper Cambrian of Andrarum, Scania. Thickness of the series about 13 m.

As shown in the section fig. 3 drawn after Westergård's (1922) measurements, barytes occurs in several different levels, mostly in the form of concretions. The rock in which they lie embedded shows very sligth variation, mostly in structure. It consist of soft, bituminous shale (alum shale) with dispersed nodules of stinkstone. The fauna of these strata is almost wholly composed of small trilobites and in a lesser degree of brachiopods.

Both barytes and calcite (the stink-stone nodules) crystallized at an early stage after the deposition of mud (cf. HADDING 1913, p. 25). The marcasite and pyrite present in alum shale, mostly in the form of concretions but also in small crystals, is formed somewhat later. As mentioned above the iron sulfide is, when occurring together with barytes crystals, distinctly younger than these. The order in which crystallization and dissolution took place was in many cases as follows: —

1) Crystallization of barytes.
2) Partial dissolution of barytes.
3) Crystallization of iron sulfide.
4) Continued dissolution of barytes.
5) Crystallization of calcite.

It should be noticed that the calcite occurring as a pseudomorph after barytes was not formed under the same conditions as the calcite in the stink-stone nodules. They are also met with in different zones. It should further be noticed that iron sulfide, like calcite (the stink-stones), mainly has an independent occurrence, i. e. in strata which do not contain concretions or crystals of barytes. There can hardly have been any circulation in vertikal direction. The strict confinement of the minerals to certain levels as well as the character of the strata argue against it.

The peculiar sequence in crystallization, dissolution and formation of pseudomorphs must of course be a result of certain definite geochemical conditions. I requested Dr SVEN PALMQVIST to make an investigation of the solubility conditions of barytes, and he has kindly placed an account of his results at my disposal. I annex it to this paper.

Concretions of Barytes in Alum Shale.

Concretions of barytes, known in the Swedish literature as *hepatite,* occur in the Upper Cambrian and the Lower Ordovician, that is in the same series of alum shales as that mentioned above in connection with the small, free crystals of barytes. The concretions are more dispersed than the crystals. I cannot enter into a discussion on the cause of this, as I have found no variations in the rocks that might help us to solve the problem. If the circulation in a stratum has been good, there ought to be more chances for the formation and growth of a concretion than for the formation of a number of small, isolated crystals of the same material. As a rule hepatite aggregates do not occur in the same stratum as the crystals, and a difference in the mud may therefore have played a rôle in such cases. But small crystals and concretions are also known to occur in the same level, although, to my knowledge, not mixed with each other. A curious intermediate form are the externally concretion-like clusters of small crystals mentioned above.

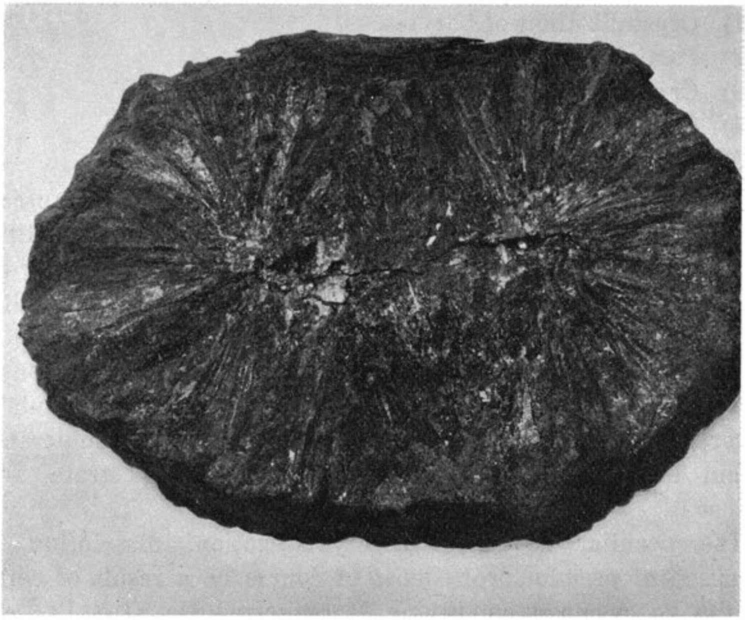

Fig. 4. Hepatite. Concretionary barytes radiating from two centra. Dictyonema shale. Flagabro, Scania. — Nat. size. (Pl. 1024.)

The barytes concretions vary considerably in size and form. The smaller ones, from a walnut to a tennis-ball in size, are almost spherical and have a relatively smooth surface. The larger ones, from 10 to 20 cm in diameter, are always flat and irregular in form (Figs. 4—6).

The structure generally is radial columnar, sometimes with two centres (Fig. 4). The »columns» show distinct cleavage planes. They generally do not exceed 2—3 mm in breadth, but sometimes they are considerably broader.

In the concretions as in the crystals barytes is rich in inclusions, particularly bitumen. The concretions also contain small crystals of marcasite or pyrite, especially on the surface of the nodules. Calcite is sometimes present in fissures and cavities.

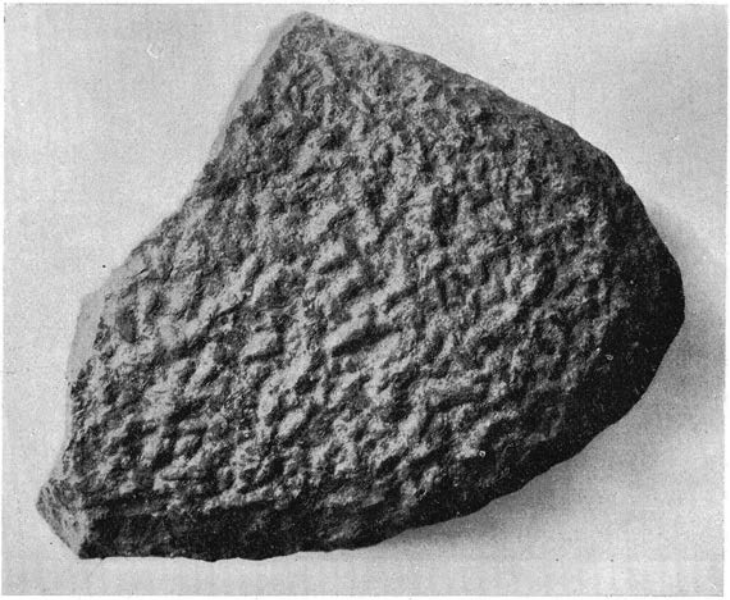

Fig. 5. Hepatite. Concretionary barytes with granulare structure. Upper Cambrian alum shale. Andrarum, Scania. — Nat. size. (Pl. 716.)

A partial analysis of a hepatite nodule from Röstånga gave the following results: —

$BaSO_4$	83.1
$SrSO_4$	—
CaO	1.3

Of impurities bitumen, iron sulphide and ferric hydroxide are abundantly present.

Localities for hepatite nodules: — Andrarum, Flagabro, Röstånga.

From the Upper Cambrian alum shale in Kinnekulle **Holm** (1901, 21) mentions highly bituminous strata of barytes. The beds are coarse-crystalline, blackish brown in colour and resemble bedded stink-stone. Even without closer examination, however, their considerably higher specific gravity distinguishes them from the latter. As a rule the layers are not very thick, but at Hönsäter a 70 cm thick bed has been observed. As I have not had the opportunity of studying these beds, I cannot express any opinion of their formation and their relation to the hepatite nodules. The occurrence in the same level and the formation in similar environments seem to me, however, to show that there cannot be any essential difference in the character of these barytes.

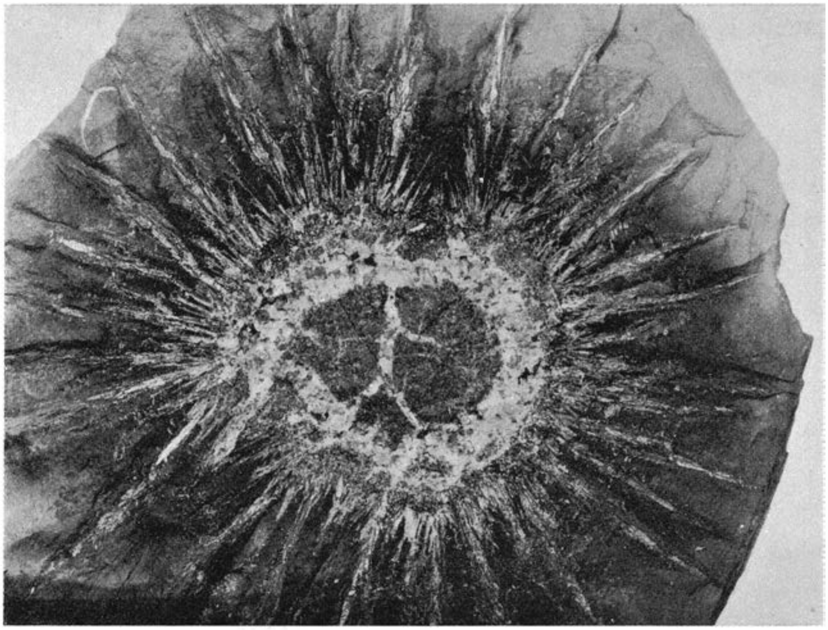

Fig. 6. Radiating barytes. Lower Ordovician alum shale. Flagabro, Scania. — $^3/_4$ nat. size. (Pl. 1022.)

Large Barytes Crystals in Ordovician Limestone.

In a relatively hard, marlstone-like, Ordovician limestone at Jerrestad large crystals of barytes are fairly abundant. Like the earlier described small crystals in the alum shale they have a prismatic form extended along the brachy-axis and tapering at both ends. The faces are often distinctly developed, uneven but only slightly corroded. The most common forms are the brachydome (011) and the pyramid (133), but others also occur together with these (see Figs. 7 and 8). The cleavages parallel to (001) and (110) are always distinct and particularly important for the orientation, as the crystals can never be separated from the rock in such undamaged condition as to be measurable in a reflection goniometer.

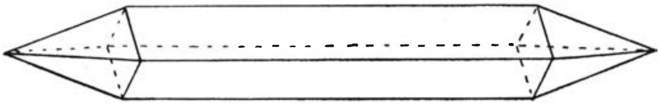

Fig. 7. Barytes. Jerrestad, Scania. Type I. (010) and (133).

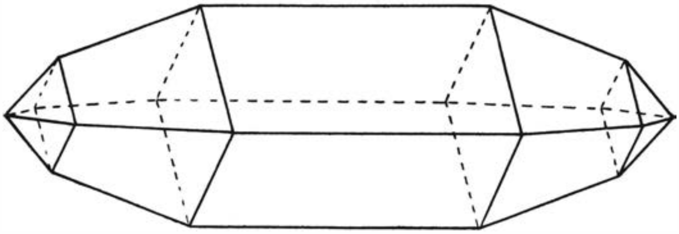

Fig. 8. Barytes. Jerrestad, Scania. Type II. (010), (133) and (111).

The limestone is studded in all directions by the crystals. No orientation in a certain plane can be traced (Fig. 9). As a rule the crystals are quite free and irregularly spread in the rock, but sometimes we find them in clusters or coarse, radial columnar aggregates (Fig. 10). They can be more than 10 cm long. The barytes crystals are often completely removed by weathering. The cavity is often exceedingly well preserved (Fig. 9), and a cast of it gives a form with as sharp edges and as plane surfaces as the original crystal. The calcium carbonate of the surrounding limestone has completely escaped the dissolution to which the barytes has fallen a victim. Considering the general opinion of the solubility of calcite and barytes, the observed circumstance must be of a certain interest. It is further discussed in the annexed paper by Palmqvist.

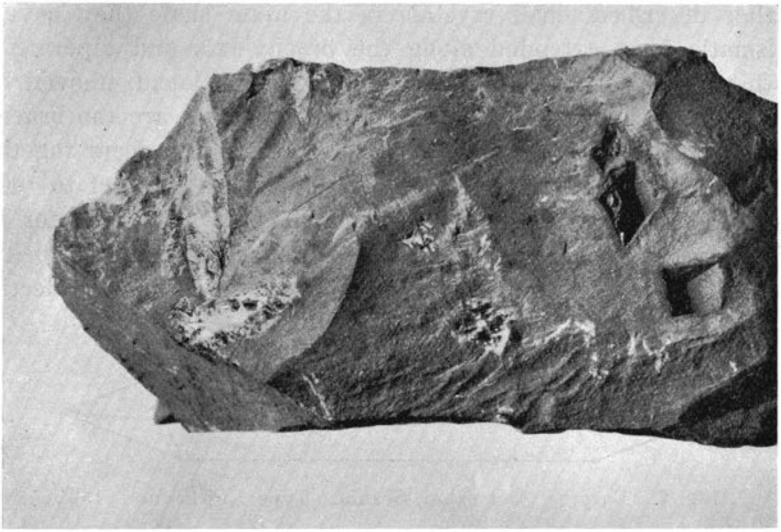

Fig. 9. Barytes, crystals and cavities. Ordovician limestone. Jerrestad, Scania. — Nat. size. (Pl. 717.)

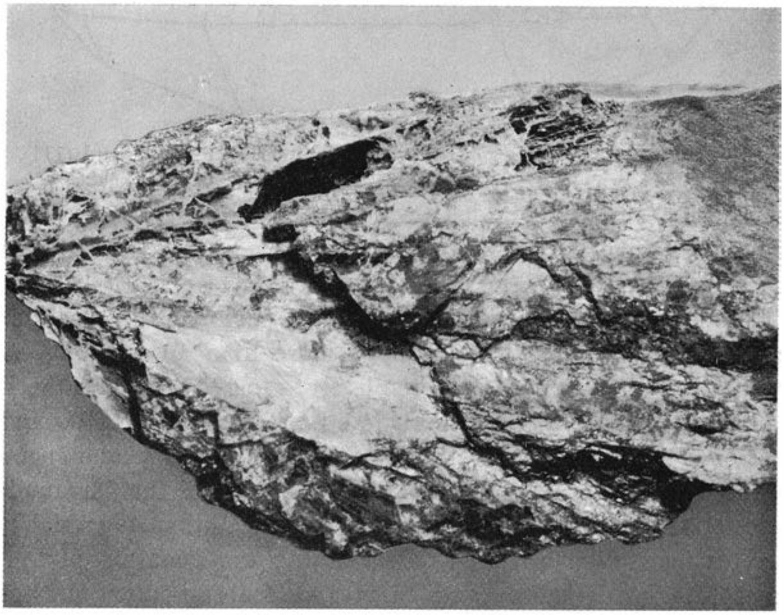

Fig. 10. Radiating barytes. Ordovician limestone. Jerrestad, Scania. — Nat. size. (Pl. 973.)

Here and there calcite occurs as filling in the cavities after barytes, sometimes in thin lamellae and sometimes in fine-grained aggregates. Pyrite has not been obseved.

The barytes crystals are rather impure. An analysis of apparently fresh material showed $BaSO_4 = 78.2$ per cent. Among the impurities noticed were iron, manganese and calcium. A determination showed $CaO = 4.7$ per cent. The sample contained a fairly abundant quantity of carbon dioxide, and an exchange of $BaSO_4$ for $CaCO_3$ has probably taken place already in the crystal.

As it was of a certain interest also to know the chemical composition of the barytes-bearing limestone, I had it analysed.

Barytes-bearing limestone, Jerrestad (Analyst Sven Palmqvist): —

SiO_2	18.75	Na_2O	0.31
Al_2O_3	3.10	K_2O	1.49
Fe_2O_3	2.26	$H_2O +$	0.87
FeO		$H_2O -$	0.25
MnO	0.96	CO_2	30.91
MgO	2.22	TiO_2	0.57
CaO	36.45	P_2O_5	0.09
BaO	0.84	SO_3	0.44
			99.51

As shown by the analysis the rock contains a noticeable quantity of $BaSO_4$, though less than 1 per cent BaO.

The limestone is compact, extremely fine-crystalline, and the bed shows no stratification or banding. It lies anclosed in a gray shale. Fossils are practically absent, only algal marks are to be seen. The limestone belongs to the Trinucleus stage. Its relation to the surrounding fossiliferous strata is evident from the adjoining section, fig. 11.

Besides the barytes crystals described above others of a somewhat different form have occasionally been found. Special attention should be called to the occurrence of more isometric crystals with (011) and (102) as dominant forms.

Barytes crystals of a similar sharacter as those mentioned above, though as a rule much smaller, are also found in shale belonging to the Lower Silurian. To a very large extent the crystals are completely disintegrated by weathering. The formations in the Dalmanites shale at Tommarp in Scania, mentioned by Troedsson (1918, 21 and 22) as aragonite also belong to this

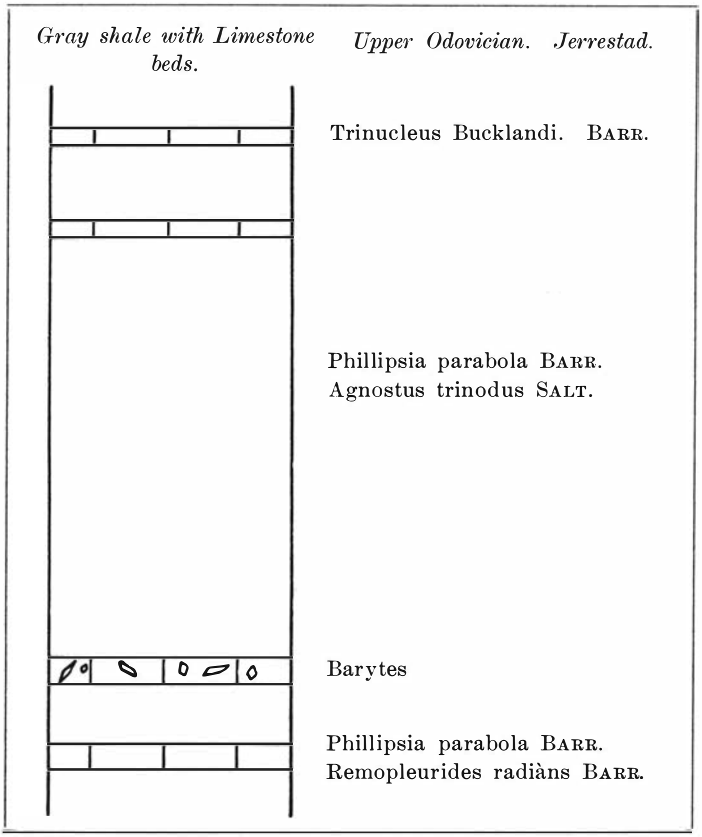

Fig. 11. Barytic limestone in the Upper Ordovician section of Jerrestad. Thickness of the section 2.5 m.

type. In the cavities strongly corroded remains of barytes and besides that single better preserved crystals were found. The determination was controlled by means of an optical examination of splinters from a number of crystals.

Formation and Alteration of Barytes.

Concerning the formation of barytes in the Swedish sediments mentioned here the following facts may be established: —

1) Barytes was not formed by secondary influence. Hydrothermal, pneumatolytic and other similar processes must be entirely

left out of account, as no traces whatever of such processes have been visible. The occurrence is practically simultaneous over large areas, a fact which induces us to look for regionally acting forces and conditions as barytes-forming.

2) Barytes was formed after deposition of the sediments in which it lies enclosed. The occurrence of the hepatite nodules and the position of the crystals in the strata provide the proofs of this. The age relation is particularly distinct in the Ordovician limestone with the long crystals that lie strewn in all directions, at right or oblique angles as well as parallel to the bedding planes. Sometimes a secondary enrichment of the crystals formed has been effected by the washing away of surrounding mud. In such cases the crystals are found lying in large quantities on a bedding plane.

3) The material for the formation of barytes was confined to certain mud-beds, and no transport from one stratum to another can be shown. The conditions for crystallization were strictly limited as to time. The variation in the environmental conditions caused the variation in form in different zones.

4) Pyroclastic material or mineral formation caused by volcanic exhalations has not been established in the barytes-bearing series of strata. These differ petrographically from the surrounding strata only by their percentage of barytes. Fossils are absent or only sparingly present in the barytes-bearing layers, even if the series is for the rest fossiliferous.

Concerning the disintegration and the replacement of barytes by other mineral the following facts may be established: —

a) Sometimes the barytes was dissolved (corroded) before the surrounding sediments were consolidated. Disintegration and precipitation (growth) may have alternated. The small crystals in the alum shale with a coating of bitumen and iron sulfide on corroded surfaces often show several such layers in the crystals. This rhythmic alternation of crystallization and corrosion has only been observed in bituminous shales poor in calcium carbonate.

b) In some cases the surrounding sedimentary mass was consolidated before the disintegration of barytes began. Then the sharpedged cavities after the crystals are not deformed. This form is best developed in limestone.

c) Marcasite, pyrite and calcite occur as new minerals in the form of the barytes. Where they occur together the iron sulfides are always the oldest. Pyrite is only found on corroded surfaces. It appears to have been formed in direct connection with the disintegration of barytes.

d) Calcite was formed by a crystallization quite independent of the disintegration and removal of barytes. This is specially evident from the fact that fissures in the barytes originating from the induration of surrounding mudstone, may have been filled with calcite without traces of corrosion being seen in the barytes. At a later dissolution of barytes the lamellae of calcite were left quite untouched. Under the conditions then prevailing barytes was far more easily dissolved than calcite.

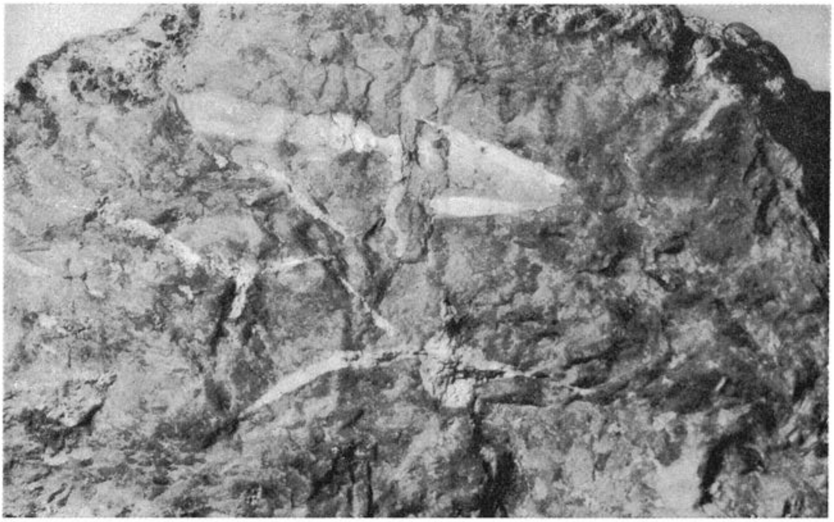

Fig. 12. Celestite crystals in a siliceous sponge. Senonian chalk. Kvarnby, Scania. — Nat. size. (Pl. 713.)

e) A secondary formation of calcite in the cavities after barytes crystals is not common but has been observed. A secondary formation of barytes crystals by the crystallization of the disintegrated and removed material has not been observed anywhere in the series of strata.

Concerning the problems of the formation and disintegration of barytes I refer for the rest to the annexed paper by Sven Palmqvist.

Celestite.

Contrary to barytes, celestite is a relatively well-known mineral in sedimentary rocks. From Sweden, however, it is not mentioned before, and the finds I shall give an account of here are inconsiderable. Barytes seems to have a much wider and more general distribution than celestite in the Swedish sediments.

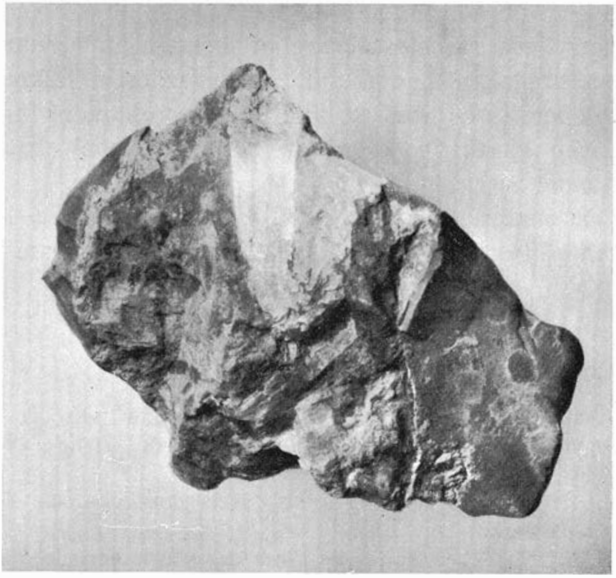

Fig. 13. Celestite crystal in flint. Erratic block. Scania. — Nat. size. (Pl. 714.)

Celestite was found in the chalk at Kvarnby in Scania. The mineral occurs as a concretionary, radial kernel in siliceous sponges. A partial analysis showed: —

$SrSO_4$	70.1 %
$BaSO_4$	1.0 %
CaO	5.1 %

The mineral is impure not only from calcite but also from silica.

The crystals are white, somewhat dull from the impurities, but with distinct and very brilliant cleavage planes (fig. 12).

Celestite was also found in an erratic block of grey flint, deriving from the Danian beds. In this case the mineral consists of a white, granular mass enclosing a few transparent, heaven-blue crystals about 5 cm in length. The cleavages are perfect, the external form, however, irregular. A partial analysis showed the following composition: —

$SrSO_4$	93.4 %
$BaSO_4$	1.0 %
CaO	2.8 %

The said finds of celestite are of interest on account of the mode of occurrence of the mineral. Earlier celestite is known from the chalk deposits of Denmark, and the concretions of the mineral found in the chalk in Möen are of the some character as those mentioned here.

A richer material is, however, required to investigate the occurrense and to understand the origin of this strontium sulphate.

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APPENDIX.

On the Solubility Relations of Barium Sulphate.

By

Sven Palmqvist.

In order to understand the factors that may contribute to the peculiar leaching of coarse-crystalline heavy-spar from limestone int. al. at Jerrestad, ascertained by HADDING, it is necessary to investigate the different factors possibly influencing the solubility product of the barium sulphate and on that account its solubility.

To explain the mechanism of formation of heavy-spar VON ENGELHARDT (1) has collected a number of data concerning the solubility of barium sulphate under various conditions. He supposes that by reason of the extremely low average percentage of barium in the earth's crust — in the eruptive rocks 0.048 per cent and in the sediments 0.043 per cent BaO — the barium ions must be relatively easily transported. Otherwise it is difficult to understand why great secondary enrichments of heavy-spar are obtained under certain conditions.

He stresses a few factors that may be imagined to increase the solubility of the barium sulphate and points out the solubility-increasing influence of the chloride ion. Attention is further drawn to the fact that the solubility of barium sulphate in pure distilled water is in itself sufficiently high (acc. to F. KOHLRAUCH and F. ROSE (2) 2.30 mg per litre water) to allow a considerable transport of barium ions in pure water-solutions. From the values cited by him the conclusion can be drawn that the barium ions may in addition be transported together with sulphate ions, provided a sufficient amount of chloride ions is present. The concentrations to be considered in this connection lie between 1 and 100 mg per litre solution. It is further evident from von Engelhardt's excedingly interesting account that, in order to explain the occurrence of the heavy-spar strata in »bunter» and in calcareous and dolomitic strata, he supposes a transport of the barium ion together wiht sulphate inos in solutions rich in chloride ions or by the leaching of the barium compounds. A neutralization of an eventual excess of free acid in the limestone as well as a precipitation of barium sulphate may then be imagined. (As to a few other solubility-increasing factors v. von Engelhardt l. c.)

Professor Hadding has kindly given me an opportunity to examine a few heavy-spar-rich limestones from Jerrestad. An analysis of the baryte crystals and one of the groundmass is found on p. 15. Already the macroscopic analysis of the stage showed, as Hadding had stated, a number of large baryte crystals. These have been avoided as far as possible in the preparation of the sample for analysis of the groundmass.

The quantity of barium present in the groundmass was determined acc. to common methods as $BaSO_4$ after the slightly calcined incineration remainder had been leached with water and reincinerated. The analysis shows the value found, 1.28 per cent $BaSO_4$. For control sulphate sulphur was also determined in the same sample in the form of $BaSO_4$. All the sulphate sulphur present in the sample was then proved to be combined with barium as sulphate, the analysis in this case giving 1.25 per cent $BaSO_4$.

An interesting fact in this limestone from a geochemical point of view is, acc. to the above-mentioned statement by Hadding, that all the macroscopically visible crystals of heavy-spar had dissolved out in the secondarily altered (weathered) parts. A partial analysis of the altered part showd a carbon dioxide percentage of 22.06 and a barium sulphate percentage of 0.78. Regarding the solubility of heavy-spar an enrichment of it might, contrary to the actual fact, be presumed in the weathered part, specially in consideration of the apparent relatively high solubility of the calcium carbonate.

In the following I shall not discuss the origin of this great enrichment of barium. This problem requires a more intimate knowledge of the chemistry of the surrounding rocks, especially of their percentage of barium, and no such material exists as yet. I shall, instead, dwell solely upon the dissolving-out process itself and investigate what factors may be imagined to have so powerfully influenced the solution of heavy-spar.

We know that, if the geological conditions are not specially favourable (ocurrence af salt deposits, etc.), the average percentage of chlorine in the lithosphere (igneous and sedimentary rocks) is as low as 0.045, and that there is very little likelihood of the water-solutions, that partake in the weathering processes, containing essential quantities of chloride ions and being therefore specially suited to act as a dissolvent on barium sulphate. Of course, this holds good only under the presumption that the water has not previously passed through any salt deposits.

The geological occurrence of the limestone in question here excludes such a possibility. In other words, some other reason for the separation of the crystals of heavy-spar from the limestone by solution than a high percentage of chloride ions in the weathering solution must be sought for. It is also impossible to suppose that heavy-spar was dissolved out together with calcium carbonate by direct solution by water free from electrolytes, as in that case, the solubility of the barium sulphate (as stated above) being considerably lower than that of the calcium carbonate, a larger per cent of calcium carbonate than of barium sulphate would be leached. The analyses however show that

$$\frac{\text{the percentage of } CaCO_3 \text{ in the unaltered part}}{\text{the percentage of } CaCO_3 \text{ in the altered part}} = 1.4,$$

and that

$$\frac{\text{the percentage of } BaSO_4 \text{ in the unaltered part}}{\text{the percentage of } BaSO_4 \text{ in the altered part}} = 1.7.$$

This must be owing to the fact that the mechanism of solution has acted in a different way, as, contrary to what could be predicted, the least water-soluble part was most dissolved out.

Therefore other reasons for the high solubility of heavy-spar in relation to calc-spar must be looked for. Suppose that solid barium sulphate is shaken with a solution of a carbonate, for inst. K_2CO_3. Part of the barium sulphate will then be converted into barium carbonate, part of which will be precipitated so that the ground phase will be composed of a mixture of solid barium sulphate and barium carbonate. Then the following equilibria hold good in the solution: —

$$Ba^{++} . CO_3^{--} = L_{BaCO_3}$$
$$Ba^{++} . SO_4^{--} = L_{BaSO_4}.$$

It is evident from these expressions for the solubility products of the two salts that the equilibrium arising in the solution on shaking will be dependent on the relation between the concentrations of the carbonate and sulphate ions. As the value of $L_{BaCO_3} = 1.9 \times 10^{-9}$ and of $L_{BaSO_4} = 1.0 \times 10^{-10}$ we find that the value of this ratio is approximately equal to 20. This means that if we treat solid barium sulphate with a water-solution containing carbonate ions in such a quantity that the carbonate ion concentration is more than 20 times as high as the sulphate ion concentration then all the barium sulphate may be converted into carbonate. As a definite equilibrium is also prevalent now between the concentrations of the carbonate and the bicarbonate ions it follows that natural water-solutions containing bicarbonate ions also contain a carbonate ion concentration dependent on the external conditions. Now let us imagine the conditions in limestone subject to weathering: the weathering solutions will there be saturated with regard to calcium bicarbonate as well as carbonate, i. e. the solution will be especially rich in that kind of ions that make a conversion of barium sulphate (heavy-spar) into barium carbonate possible. Owing to the great difference in solubility of barium sulphate and calcium carbonate, the solution will also contain a considerable excess of bicarbonate and carbonate ions in relation to the concentration of sulphate ions. The barium carbonate thus formed may then be dissolved as bicarbonate in the same manner as calcium carbonate, and be carried away together with equivalent amounts of calcium sulphate. Consequently the solubility of these two salts in water containing carbon dioxide is of conclusive importance for the solution. This is shown in the following table. (SCHLÖSING (3).) It is evident from the table that there is a great difference in solubility between barium carbonate and calcium carbonate in water containing carbon dioxide, and that barium carbonate has the higher solubility of the two. This may be a concurrent

TABLE 1.

$PCO_2 . 10^4$ in atm.	*Ba* millieq./l.	$BaCO_3$ mg/l.	*Ca* millieq./l.	$CaCO_3$ mg/l.
5.04	1.204	118.9	1.492	74.6
8.08	1.465	144.6	1.700	85.0
33.3	2.362	233.1	2.744	137.2
138.7	3.923	387.2	4.462	223.1
282	5.094	582.8	5.930	296.5
499	6.237	615.6	—	—
501	—	—	7.200	360.0

cause to the fact that barium sulphate is more rapidly dissolved out from limestone than the carbonate of calcium itself.

If, however, we take into consideration that, regarding barium sulphate, the weathering solution contains large quantities of other salts, among which the calcium salts in this case dominate, we must also examine to what extent this may influence the solubility of the barium sulphate or barium carbonate. If we take barium sulphate as an example of a binary sparingly soluble salt, we find that its solubility product is defined by the equation: —

$$1. \quad c\mathrm{Ba}^{++} . c\mathrm{SO}_4^{--} = \mathrm{L'}_{\mathrm{BaSO_4}}$$

The concentrations of ions are then expressed in analytical concentrations. That the value of this solubility product varied not only with the temperature, but also with other factors, f. inst. the concentration of other ions, is due to the fact that for some reason or other part of these ions have assumed an inactive form, so that only a small proportion of the anlytical concentration takes an active part in the equilibrium of the solution. This fractional part is called the active concentration or the activity, and is here represented by a. Thus the value of the thermodynamic solubility product is obtained by the equation: —

$$2. \quad a\mathrm{Ba}^{++} . a\mathrm{SO}_4^{--} = \mathrm{L}_{\mathrm{BaSO_4}}$$

(Cf. H. WATTENBERG (4)). At a dilution ad infinitum $a\mathrm{Ba}^{++} = c\mathrm{Ba}^{++}$, $a\mathrm{SO}_4^{--} = c\mathrm{SO}_4^{--}$ and consequently the equations 1. and 2. are also equal. The ratio $\frac{a\mathrm{Ba}^{++}}{c\mathrm{Ba}^{++}}$ = the activity coefficient. In the following it is represented by f_x. In other words, if the law of mass action is to hold true, the analytical concentration of the barium ion must be multiplited by f_{Ba}. Consequently we obtain

$$3.\quad f_{\mathrm{Ba}} \,.\, c\mathrm{Ba}^{++} \,.\, f_{\mathrm{SO}_4--} \,.\, c\mathrm{So}_4^{---} = \mathrm{L}_{\mathrm{BaSO}_4}$$

but

$$4.\quad c\mathrm{Ba}^{++} \,.\, c\mathrm{SO}_4^{---} = \mathrm{L}'_{\mathrm{BaSO}_4}$$

and then

$$\mathrm{L}'_{\mathrm{BaSO}_4} = \frac{\mathrm{L}_{\mathrm{BaSO}_4}}{f_{\mathrm{Ba}} \cdot f_{\mathrm{SO}_4}}$$

As the value of f_x always lies between 0 and 1, this means that the thermodynamic constant is lower than the apparent one. The value of the activity coefficient varies with the ionic concentration in the solution.

The elctrostatic significance of f_x is evident from the following formula (v. E. Eggert (5) p. 380): —

$$5.\quad ln\ f_x = -0.816 \,.\, z^2 \frac{\sqrt{\Gamma}}{1 + 0.232 \,.\, 10^8 \,.\, a \,.\, \sqrt{\Gamma}}$$

where a = the ionic radius,
z = the charge of the ion in question and
Γ = the ionic concentration, defined as the total of the products of the concentration of neutral salts present in the solution and the square of the charge. We call this sum $c_i \,.\, z_i^2$.

The formula shows that an increase of the ionic concentration of the neutral salts causes a decrease of the f_x value. This involves an increase of for inst. the value of $\mathrm{L}'_{\mathrm{BaSO}_4}$, i. e. an increase in the solubility of barium sulphate.

Accordingly the presence of chloride ions will also increase the solubility of barium sulphate, a fact considered to be of great geological significance.

Formula 5, applicable to the value of the activity coefficient, shows us that the charge of the ions plays an importane rôle, as it always enters with the square value. That means, a divalent ion has a proportionally much greater solubility-increasing power than a univalent one, because in that case the values of z_i^2 are 4 resp. 1. This means that in equal concentrations in a solution the ionic concentration will be 4 times as high in the former case as in the latter.

A weathering solution that passes or has passed through a limestone is rich in int. al. calcium ions. The solubility-increasing influence exercised by this kind of ions on barium sulphate must therefore, even if the calcium ion concentration is small and chloride ions are present, be the dominating factor on account of its higher valency, as the calcium ion concentration is normally higher than the chloride ion concentration in a weathering solution. Not until the chloride ion concentration becomes four times as great as the calcium ion concentration is their influence equivalent.

It is obvious that to explain the sometimes abnormally great solubility of barium sulphate, it is not necessary to presume the occurrence of any kind of ions unusual in a normal weathering solution. Even a usual weathering solution may possess the requisite qualities for an easy solution of certain, difficulty soluble substances.

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Errata.

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