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Geology. — "On the behaviour of fossil shells in water containing carbonic acid." By Dr. P. TESCH. (Communicated by Prof. S. HOOGEWERFF).

#### (Communicated in the meeting of September 26, 1908).

It is a well-known phenomenon that all strata which are more or less calcareous and are situated above the surface of the groundwater, when not consisting of wholly impenetrable clay, are exposed to a slow action of solution. The explanation of this extraction of lime is easily given by the dissolving action of the penetrating rainwater, by which the quantity of lime is gradually withdrawn from the higher parts of the deposit and in some cases is concentrated in the lower parts in marl-puppets (for instance in the löss), in other cases however is totally carried off (as a boulder-marl can be transformed in a clay without any lime). The rain-water contains already a good deal of oxygen and carbonic acid; the part that sinks away in the bottom still takes up the carbonic acid which is formed in the upper-crust by the putrefaction of the vegetable rests and thus it is enabled to exercise an oxidating action on the ironcontaining minerals and a dissolving action on the present lime.

Especially the fossiliferous glauconitic sands are totally changed by this alteration. In the first place the glauconite is dissected and the iron which for a great part exists already in the ferri-form, is separated as limonite and forms a binding for the grains of sand. The sand in the beginning of a dark or light green changes into a yellow or brown sand, which in some cases is bound so strongly that the name of a limonite sandstone may be given. Everywhere where glauconitic sands are situated above the surface of the groundwater and are not covered by protecting clay-beds, this phenomenon can be observed. In the southern parts of the Lower Rhine basin for instance the upper-oligocene sea-sands show everywhere where they have kept their original niveau, a yellow or brown colour by the disintegration and oxidation of the glauconite grains (heaved block of Myhl between Huckelhoven and Birgelen on the eastern bank of the Roer, the sandquarries of Gerresheim, Grafenberg and Rothenberg east of Dusseldorp etc.). In Belgium the "sables et grès ferrugineux de Diest", the "Crag jaune d' Anvers" etc. are so converted glauconitic sands.

In the second place however the water with carbonic acid acts as a solvent upon the lime shells of the fossils, which disappear totally or rest as printings and stones and are more difficult to

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determine, in consequence of which the direct remedy of fixing the age fails or at least becomes uncertain. Especially in Belgium the division of the upper-tertiary deposits has given rise to many contradictions during a long time because the incomplete and indistinct fauna opposed the question of the exact parallelism with similar strata in a high degree. Only by the extensive researches of E. VAN DEN BROECK and others in the Antwerpian pliocene, when those deposits were uncovered on a large scale by the establishment of harbours and docks, this alteration was recognized as a general secondary action which appears everywhere where the circumstances of penetrable cover and a situation above the level of the ground-water allow it. The limit between the decomposed glauconite sand (yellow crag) and the original sand (gray crag) is not at all to be considered as a geological limit but denotes only the level of the ground-water.

I have mentioned these well-known facts in order to arrive at another observation which was made by inquiring the altered deposits and for which an acceptable explanation was ready. It was fixed that the resistance of the different shells against the dissolving action was a different one and thus more and less resisting shells were to be distinguished. The still recognizable stones and printings belonging to the genera Terebratula, Ostrea, Pecten, etc. and these shells being known to consist of calcite, while the small gastropoda shells are composed of aragonite, it was concluded that *calcite is dissolved in water containing carbonic acid with much more difficulty than aragonite.* In the "Handbuch der Palaeontologie" of KARL A. VON ZITTEL (Volume II, page 12) for instance this is expressed as follows:

"Die Kalkspathschalen zeigen eine ziemlich beträchtliche, die Aragonitschalen eine sehr geringe Widerstandsfähigkeit gegen die auflösende Thätigkeit kohlensaurehaltiger Gewässer. In Ablagerungen, wo fast alle fossilen Muscheln oder Schneckengehause zerstört und nur durch Steinkerne angedeutet sind, findet man wohlerhaltene Schalen von OSTREA, PECTEN, PINNA, TRICHITES, u. a."

I do not know whether this fact ever has been examined by experiments upon the pure minerals. The failing of any communication concerning that subject in different mineralogical test-books suggests that this has not taken place and thus it may be useful to examine this different behaviour experimentally, so far as the difference of solubility has an importance for the practical geology <sup>1</sup>).

<sup>1</sup>) Some time after having finished this communication I got acquainted with an essay of H. W. Foore: Ueber die physicalisch-chemischen Beziehungen zwischen Aragonit und Calcit (Zeitschrift für physikalische Chemie, Band 33, pag. 740) to

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A. Solubility of calcite and aragonite in pure water.

In all following experiments were used: for calcite fragments of the calcite of Iceland and for aragonite crystals of BILIN in Bohemia.

By pulverizing and sieving a powder was obtained the grains of which were all smaller than 2 mm. and larger than 1 mm. in order to equalize the circumstances.

To compare the solubility of the two minerals in pure water, a quantity of 1 or 2 grams of this powder was exposed during a week to 200 cm<sup>3</sup>. of newly distilled water and afterwards the quantity was again weighed accurately.

I obtained the result that the same quantity of pure water in the same time dissolved:

from the calcite powder:

and from the aragonite powder:

On these numbers a remark is to be made, to which prof. Dr G. A. F. MOLENGRAAFF drew my attention. The grains of calcite will have the form of the cleavage rhomboeder and will moreover show small internal fissures. This has the consequence that the attackable surface offered by the calcite powder is much larger than that of the aragonite powder.

For this reason I experimented another time with the finest powder of the two minerals which had passed a silk sieve of 64 openings on the m.M.<sup>2</sup>. I acted during the same time with the same quantities.

The relations of solubility found in this essay agree satisfactorily with the results found by me by direct weighing.

which Prof. Dr. S. HOOGEWERTF drew my attention. According to the law that of two forms the least soluble is the most durable, the author finds in different ways that under the normal circumstances of pressure and temperature calcite is more durable than aragonite. Formerly it had already been shown by experiments of KOHLRAUSCH and ROSE that at the temperatures between 2° and 34° C. calcite is somewhat less dissoluble in water than aragonite. The author finds the same fact at the temperatures  $25^{\circ}$ ,  $50^{\circ}$  and  $59^{\circ}$  C. By means of the electric properties the difference in solubility in water containing carbonic acid is examined at the temperatures of  $8^{\circ}$ ,  $25^{\circ}$ ,  $41^{\circ}$  and  $48^{\circ}$  C. At  $49^{\circ}$  C. aragonite is still  $11^{\circ}_{0}$  more soluble than calcite, though the difference becomes smaller at rising temperature.

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The result was that was dissolved:

from the finest calcite powder: 4,- milligrams

and 4,1 ,

,,

from the finest aragonite powder: 5,4

and 5,7 ,,

The quantities of dissolved mineral are very small and so the inaccuracies of the weighing have a great influence. Though these numbers cannot have an absolute validity, I hold myself authorized to say, that an important difference in solubility does not exist. Spoken practically calcite and aragonite are both nearly insoluble in pure water. The number found for calcite agrees sufficiently with the knowledge that 10000 parts of pure water dissolve 0,2 or 0,25 parts of calcite.

B. Solubility of calcite and aragonite in water containing carbonic acid.

The solubility in water containing carbonic acid in the form of bicarbonate depends on the duration of the action and on the strength of the dissolving liquor or on the quantity of carbonic acid. I always prepared the liquor immediately before adding the mineral powder, by leading through 200 cM<sup>3</sup> of distilled water a slow current of pure carbonic acid during twenty minutes and by closing the glasses during the experiment. So the strength of the liquor may always have been the same.

I obtained the result that 200 cM<sup>3</sup> of water containing carbonic acid had dissolved after one week:

from the coarse calcite powder: 54,7 milligrams from the coarse aragonite powder: 61,8 milligrams

The same quantity of the liquor had dissolved after two weeks:

from the calcite powder: 76,5 milligrams

from the aragonite powder: 86,2 milligrams and after four weeks:

from the calcite powder: 108,4 milligrams

from the aragonite powder: 122,4 milligrams

For the same reason as is mentioned sub A, a second series of experiments was made with the finest powder of the two minerals.

 $200\ \mathrm{cm}^3.$  of water containing carbonic acid had dissolved after one week :

from the finest calcite powder: 267,8 milligrams

from the finest aragonite powder: 332,8 milligrams

From these numbers I conclude:

1. that indeed uragonite is dissolved a little faster by water con-

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taining carbonic acid than calcite. At the same time it is evident however that the difference of solubility is too small to serve for a practical remedy of determination.

2. that this little difference is not sufficient to explain the different behaviour of the fossil lime-shells, but that we must be taken into consideration still other causes: the long duration of the dissolving action, the continuous supply of new liquor, the absolute size of the shells and the relative size of the outer surface.

One finds in the common test-books the notice that 100 grams of water containing carbonic acid dissolve 0,1 or 0,12 grams of calcite which agrees sufficiently with the number mentioned above ').

When examining the mineralogical composition of some shells, the question rose what remedy is the most suitable to distinguish calcite from aragonite practically. The little difference in hardness is of no use to this purpose, as a small quantity of silex may neutralize this difference. A calcite shell for instance may equal locally the hardness of aragonite by mixed silex and a determination depending only on this property seems precarious. Nor is the specific weight to be used as a certain quantity of silex, phosphatic lime, magnesia carbonate and organic materials influences it. On the contrary the test with dilute cobaltcarbonate solution of W. MEIGEN is very useful (Central-blatt für Mineralogie, Geologie und Palaeontologie, Jahrgang 1901, Seite 577). With the aid of this test I examined a number of shells of the following genera, availing myself in some dubious cases of the optical properties.

Of calcite consisted : Ostrea (recent, pliocene and senon, Pecten (recent, pliocene and senon) Pectunculus (miocene) Arca (miocene) Nucula (miocene) Leda (miocene) Venus (miocene) Venus (miocene) Socardia (miocene) Littorina (recent) Buccinum (recent) Aporrhais (miocene) Ancillaria (miocene)

<sup>&</sup>lt;sup>1</sup>) Here it must still be added that all these experiments took place at the common chamber temperature  $(15^{\circ} \text{ or } 20^{\circ} \text{ C.})$  and that the glasses were shaken once a day in order to promote the action of the dissolving liquor,

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Of aragonite consisted: Cardium (recent and pliocene) Ensis (recent and pliocene) Donax (recent and pliocene) Tellina (recent and pliocene) Astarte (pliocene) Cardita (pliocene) Cytherea (recent) Venus (recent) Unio (recent) Mactra (recent and pliocene) Mya (recent) Corbula (recent and pliocene) Pholas (recent) Scalaria (recent) Natica (recent) Cypraea (recent) Turritella (miocene) Cancellaria (miocene) Cassidaria (miocene) Cerithium (recent) Murex (recent) Conus (recent and miocene) Trochus (recent) Turbo (recent) Bulla (recent) Strombus (recent) Ficula (recent) Terebra (recent, miocene) Niso (miocene) Dentalium (pliocene, miocene and oligocene) Ringicula (miocene)

On looking through the above list it is evident that a great deal of the examined Lamellibranchiata consists of aragonite though among the fossil species enough calcite shells occur. A specimen of the miocene Cytherea incrassata consists without any doubt of calcite and a specimen of the recent Cytherea meretrix consists with the same certainty of aragonite. Such was also the case with the miocene Venus multilamellosa and the recent Venus albina. Among the Gastropoda shells the majority consists of aragonite but four shells form an exception. For the fossil specimina of Aporrhais and Ancillaria perhaps it is permitted to think of a later inversion of aragonite into calcite but for the very new specimina of Buccinum undatum and Littorina littorea this explanation seems excluded. Possibly the form in which the lime carbonate is separated depends on external influences and a species which builds as a rule an aragonite shell may be able to separate calcite under abnormal circumstances (temperature, composition of the water). This appears to me the more probable as we can precipitate artificially calcite or aragonite according to the circumstances of temperature and composition of the solution. If this should be true the composition of the shell is no specific property.

# Geophysica. — "Earthcurrent-Registration at Batavia." (3<sup>d</sup> communication). By Dr. W. VAN BEMMELEN.

In the preceding communication about my earthcurrent registration in Java, I expected to be able before long to throw more light on the question of the abnormal intensity of the current between Batavia and Anjer (a place in the neighbouring residency of Bantam)

The kind co-operation of the Superintendent of Government Railways, who allowed me the use of the railway telegraph lines during night time, enabled me to realise my intention of measuring the currents flowing between Batavia and some other places situated in the residencies of Batavia and Bantam.

In order to obtain an exact control over the new results, I registered next to the currents flowing through these wires, those between Anjer and Batavia flowing through the direct telegraph line between these towns, i.e. by means of the line formerly used by me. Moreover the N—S component of the magnetic force was recorded.

By means of the railway telegraph-wires I obtained connection with the following places:

Laboean on the Westcoast of Java, 32 K.M. to the S.S.W. of Anjer. Serang 28 K.M. to the East of Anjer.

Rangkas Betoeng 40 K.M. to the East of Laboean.

Between Anjer, Serang, Rangkas Betoeng and Laboean there rises a volcanic chain, the volcano Karang (1780 M.) being the culminating summit.

Tangerang 21 K.M. to the West of Batavia.

Bekassi	20	,,	,,	,,	E.S.E.	,,	,,
Krawang	54	,,	.,	,,	E.S.E.	,,	,,