Die geraden Kreiskegel besitzen also bei festem M kleinstes F und ebenso bei festem F grösstes M. Ausserdem weisen sie bei festem F im Intervall $\arcsin(1/3) \leqq \psi \leqq \pi/2$ auch noch kleinstes Volumen V auf[7]. Diese doppelte Extremaleigenschaft wird gestatten, im Hauptproblem der konvexen Rotationskörper einen Fortschritt zu erzielen[8].

H. Bieri

Bern, 24. Mai 1957.

Summary

The proof of the problem which was studied in a former work, was now brought to an end: that among all convex rotatory bodies of the constant lengths l the cones possess the smallest surfaces if M is given.

[7] H. Bieri, Exper. *6*, 223 (1950).

[8] Hierüber wird an anderer Stelle berichtet werden.

The Problem of Solubilization and Precipitation and the Calcium and Phosphorus Cycle in Cavern Formation*

The process of solubilization of insoluble matter such as $Ca_3(PO_4)_2$ and $CaCO_3$ in nature and the transport of the solubilized materials is one of the fundamental problems in biology[1]. The redeposition or precipitation[2] which is concerned with the mechanism of formation of insoluble phosphates is, in a way, the opposite of solubilization. This process is basic for calcification in bone and teeth. The formation of stalagmites and stalactites in caves is another aspect of the same problem and a knowledge of the composition of the deposits should give insight into this mechanism.

We could find no data on stalactite or stalagmite analyses in the literature, including Clarke's *Data on Geochemistry*[3] which appears to be the most comprehensive reference source.

Stalactites and stalagmites are crystalline calcium carbonate. They are formed by waters which have become saturated with calcium bicarbonate by percolating through and partially dissolving the overlaying limestone. Where there are phosphatic formations the waters must carry the solubilized phosphates also, which then would be deposited on the roof or sides of the caverns or grow from the floor. Temperature probably does not affect the processes at this stage to any considerable extent, as nature has made caves natural air conditioners.

Calcium phosphate occurs in nature mostly as tribasic phosphate, especially as apatite, but also as dibasic phosphate e.g., brushite $CaHPO_4 \cdot 2H_2O$ and monetite $CaHPO_4$. Besides apatites, phosphates also occur as deposits of bats guano in caves. Furthermore the shells of giant crustaceans contain about 5 times as much P_2O_5 as those of present-day lobsters[4].

Our analytical results support the following assumptions. By various processes (e.g.[5]) apatite undergoes alterations and is slowly dissolved by percolating waters. A part of the dissolved phosphates is carried away with the waters and later on absorbed in living organisms, a part is retained by the soil and taken up by plants, another part is reprecipitated after the CO_2 has escaped or is deposited in the form of carbonates.

The mechanism for the solubilization process is:

$$(1) \quad Ca_3(PO_4)_2 \cdot Ca(OH)_2 + CO_2 = Ca_3(PO_4)_2 + CaCO_3 + H_2O$$

$$(2) \quad Ca_3(PO_4)_2 + CaCO_3 + 3CO_2 + 3\,H_2O \dashrightarrow 2\,CaHPO_4 + 2\,Ca(HCO_3)_2.$$

The final effect is one of transition into more soluble phosphates. Gulick[6] points out that life originated under conditions in which phosphorus was only partially oxidized and that these phosphites and hypophosphites were much more soluble than the completely oxidized forms.

The following mechanism leads to redeposition: If the solution contains an excess of H ions the formation of $PO_4^{\equiv}$ is repressed, in this case the tertiary salt does not separate, since it is soluble in weak acids, even in carbonic acid. (According to Baudisch[7] CO_2 under pressure is an extremely strong acid.) $Ca_3(PO_4)_2$ will be formed from concentrated solutions of $Ca(H_2PO_4)_2$ but not from dilute ones. With a certain excess of phosphoric acid it is possible to obtain $CaHPO_4$ as a solid phase without subsequent conversion into the primary or tertiary salt. As soon as some of the CO_2 escapes or has been deposited as $CaCO_3$ or other carbonates, the precipitation of calcium phosphate can start.

Experimental part.—As outlined in Table II: 14 specimens of different sources were analyzed for their phosphorus and calcium content. Qualitative tests for magnesium and iron were also made.

To avoid extraneous outside accumulations a center piece was cut out in the case of large specimens, whereas the small pieces were used as such. They were crushed and pulverized. Of these powders 0·2 to 0·3 g were used for each digestion. Two determinations of each were made. All acids used in the evaporation procedure were tested for phosphorus. There was no molybdenum blue reaction. All of these end solutions were tested for silicates by means of micrososmic salt $NaNH_4HPO_4$ beads. No SiO_2 was present. The phosphate content was determined quantitatively by the molybdenum blue reaction. We had found 2 methods for determination of phosphorus in presence of Si[8]. The method of Levine was adapted for the determinations as following. Of the powdered specimens 0·2 to 0·3 g were dissolved in 5 ml of 6 N HCl to avoid loss by splashing, in case there remained an undissolved rest the same was dissolved in additional 2 ml concentrated HCl. The weighing tube was rinsed 3 times with 1 ml of 6 N HCl. The HCl solutions were collected in a platinum dish and evaporated to dryness on a steam bath. Thereafter 1 ml concentrated HCl and 1 ml HF were added and evaporated to dryness. This was repeated once. Then it was evaporated with 5 ml concentrated HCl to dryness and thereafter with 2 ml concentrated HCl and 5 ml H_2O. The solution was transferred to an Erlenmeyer flask and 2 ml HBr and 0·5 ml concentrated

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[1] I. Mandl, A. Grauer, and C. Neuberg, Biochim. biophys. Acta *8*, 654 (1952); *10*, 540 (1953). – I. Mandl and C. Neuberg, Adv. Enzymol. *17*, 135 (1956).

[2] I. S. Forrest, A. Grauer, M. Kreidl, and C. Neuberg, Enzymologia *17*, 97 (1954).

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[7] O. Baudisch, Ber. dtsch. chem. Ges. *71*, 993 (1938).

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Table I

Stalactite	% Calcium		% Phosphorus		Fe	Mg
Gilley	39·28	38·61	4·105	4·115	neg.	+
Patterson	43·20	43·28	6·392	6·532	+	neg.
Speedwell	40·50	39·98	4·663	4·639	neg.	+
Eagle Rock	40·02	40·68	4·382	4·503	neg.	neg.
Lynn Hollow	40·38	39·88	2·868	2·934	neg.	+
Roberts	39·36	38·98	3·155	3·214	neg.	+
Laurium	39·05	38·77	9·88	9·78	neg.	trace
Angleur	35·59	35·88	0·721	0·729	+	+
Huactuca	39·81	40·01	9·95	9·90	neg.	+
Dubuque	38·79	38·65	9·22	9·15	neg.	+
Shenandoah	43·03	42·82	10·74	10·65	neg.	+
Bisbee	39·24	38·83	0·674	0·675	neg.	+
Carlsbad	25·39	25·08	0·724	0·706	neg.	+
Kentucky	38·58	38·40	0·797	0·791	trace	+

H_2SO_4 were added and it was heated until fumes evolved. After cooling, the solutions were transferred to 100 ml volumetric flasks and the volume was adjusted. The phosphorus determinations were made with a Lumetron Colorimeter, 660 Filter, otherwise as described in the paper of Levine *et al.*[9]. A reagent blank was run with each series. Table I gives the average of determinations of each specimen.

As CaF_2 is highly insoluble calcium was determined separately, 0·2 to 0·3 g each of the different samples were dissolved as above. The HCl solutions were collected in a porcelain dish and evaporated to dryness, the evaporation with 5 ml of concentrated HCl was repeated twice, after which the solution was transferred to a volumetric flask and made up to 100 ml. The calcium was precipitated as oxalate and titrated with 0·01 *N* $KMnO_4$ as described in F. P. Treadwell and W. T. Hall, *Analytical Chemistry*.

Of each specimen 2 separate samples were used and duplicate analyses were made, the averages of 2 determinations of each are in Table I.

Results and discussion.—The physical appearance of the specimens is described in Table II. Table I shows the values obtained for Ca and P, as well as tests for Mg and Fe.

Table II

The Specimens.

(1) Stalactite Gilley Cave, Lee Co. Va.: Cone shaped parts with a sandy colored layer at the outside, the inside is white. The material is hard and brittle.

(2) Stalactite Patterson Cave, Whyte Co. Va.: There is a layer of rust colored sandy matter on the cone shaped and cylindric white formations of about 2 cm lengths which are of vitrous appearance. The material is hard.

(3) Stalactite Speedwell, Whyte Co. Va.: It represents a banded formation. There are sandcolored layers with narrow bands which are whitishgray. The specimen is hard.

(4) Stalactite Eagle Rock, Quarry Cave, Va.: A planchet, which is of white color with vitrous and pearly layers, at the outside there is a sandy colored sedimentation. The specimen is hard.

(5) Stalactite Lynn Hollow, Va.: Paw and cone shaped formations with pisolitic appendages, banded with bands of different width, the layers are whitish and sand colored with small ocher colored lines between the bands, at the outside sand colored, the structure is very clear at the cleavage sections. The specimen is of medium hardness.

(6) Stalactite Roberts Cave, Smyth Co. Va.: A whitish flat slab, which is sand colored in its outer layer, with veined cleavage sections, of medium hardness.

(7) Stalactite Laurium, Greece: Cone shaped formation consisting of oolitic formations (resembling fish roe) of white color, with a light sandy colored outer layer, of pumice like consistence. The specimen is brittle.

(8) Stalactite Angleur, Belgium. A plate with small conelike formations, banded, white with brownish layers, the outside layer is thin and sandcolored. The structure is very clear at the cleavage sections. The specimen is hard.

(9) Stalactite, Huactuca Mts. Sonora, Mexico. Cylindric, conelike pisolitic formations on a plate, white, banded, with pearly and vitrous layers and a thin sand colored outside layer. The specimen is hard.

(10) Stalactite, Dubuque, Iowa. Small cone shaped and pisolitic formations, pearly white, with a light greyish thin outside layer, at the base there is a thin sandcolored layer. The specimen is hard.

(11) Stalactite, Grottos of the Shenandoah, Va. Cone shaped formations with narrow offshoots, arranged in concentric layers, the center is light ocher colored; there are alternating pearly white and light ocher colored layers and a thin greyish coating at the outside. The specimen is hard.

(12) Stalactite Bisbee, Arizona. Cylindric piece, whitish of medium hardness.

(13) Formative material (fractions of stalactites and stalagmites) from the Big Room of the Carlsbad Caverns, Carlsbad, New Mexico. White cylinders and cones with a light greyish coating at the outside. The material is hard.

(14) Cave Onyx from the Howes Valley, Western Hardin Co., Kentucky. Cone shaped formations, light yellowish and light ocher colored layers, vitreous appearance, the specimen is medium hard.

P values vary from 0·6–0·8% for Angleur, Bisbee, Carlsbad and Kentucky, whereas values for other specimens are as high as 9·2–10·7%. At the same time Ca values with the exception of the formative material from the Carlsbad Cavern (25·08%) are all around 40%. We must assume that the higher P content is due to phosphatic formations whereas specimens with less than 1% seem to derive their P from solubilization, migration and redeposition in cave formations in accordance with the late Prof. Neuberg's hypothesis. This study was made to test this assumption as planned by Prof. Neuberg, who unfortunately was not longer able to carry out the experiments or to interpret the results.

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[9] H. Levine, J. J. Rowe, and F. S. Grimaldi, Analyt. Chem. *27*, 258 (1955).

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C. Neuberg† and Amélie Grauer

New York Medical College, New York, May 28, 1957.

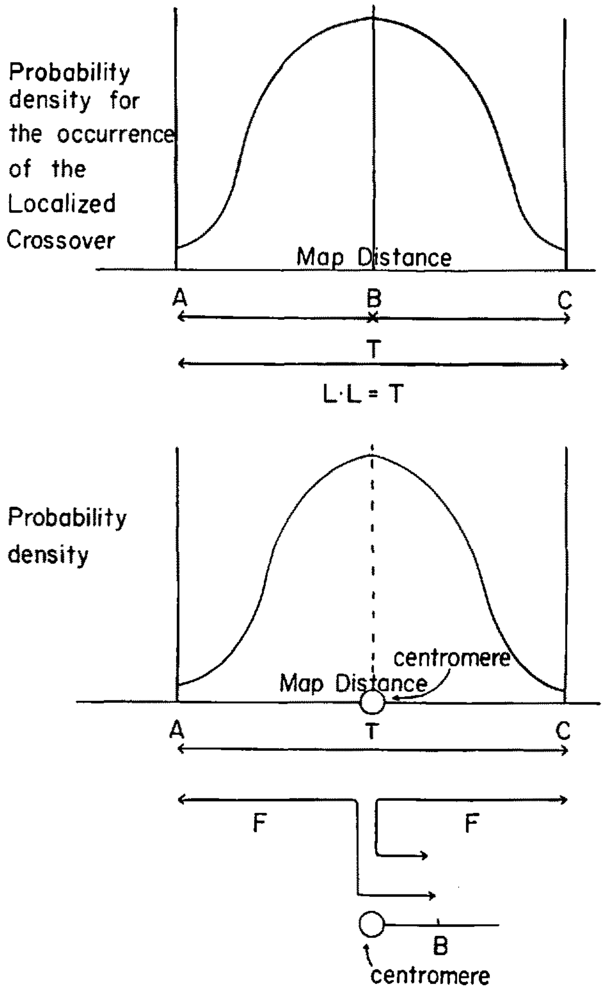
Zusammenfassung

Die Reaktionsmechanismen des Kalziumphosphat-Kreislaufs bei der Auflösung, Wanderung und Wiederabscheidung in Stalaktiten werden erörtert und eine Modifikation der kolorimetrischen Molybdänblaureaktion für kleine Mengen P in Gegenwart von Si beschrieben.

The Localized Crossover and a New Hypothesis of Chromosomal Interference*

Tetrad analysis of *Neurospora* and yeast indicate that a crossover in one region appears to facilitate crossing-over in an adjacent region, in direct opposition to the widely accepted view (originating from single strand analysis of *Drosophila* by Muller[1] and Sturtevant[2]) that a crossover occurring in a given region tends to minimize the probability that another will occur in the immediate vicinity. On the demonstration of locally specific chromatid interference in *Neurospora*[3] it was proposed that the low coincidence values in *Drosophila* could be explained by an excess of 4-strand double exchanges[4]. A simpler explanation is now available by the demonstration of localized crossingover in *Saccharomyces*.

The first report[5] of the localized crossover suggested that its occurrence was restricted to a relatively narrow region and no evidence was found at that time to indicate that the localized crossover was not confined to one specific place. Recent evidence indicate that the 'localized' crossover may extend over a region involving several identifiable *loci*[6]. This observation is critical since



(*a*) A diagram representing two regions over which a localized crossover is distributed. When it occurs between *A* and *B*, it does not occur between *B* and *C*, thus producing the fallacious appearance of mutually interfering pairs of exchanges. The marker pairs *A* and *B* and *B* and *C* will exhibit *L*-distributions (although the frequency of tetratype tetrads will not be less than 50%) whereas the distal pair of markers, *A* and *C* will exhibit the *T*-distribution characteristic of a localized exchange. Thus the relation between tetrad distributions for the triplet *A*–*B*–*C* is $L \cdot L = T$.— (*b*) The relation $F \cdot F = T$ would be produced where the centromeres of these two chromosomes segregate at random at the first division.

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[5] E. E. Shult, C. C. Lindegren, and G. Lindegren, Genetica (in press).

[6] Localized crossovers produce *T*-distributions[7] (tetrad distributions with a frequency of tetratype tetrads in significant excess of $^2/_3$) and occur in conjunction with crossovers which are distributed in a Poisson manner, the latter tending to randomize the intensity of the *T*-distribution. [In this connection the term 'randomize' means to cause a distribution to be nearer (deviate less from) the *N*-distribution, $^1/_6$ I + $^1/_6$ II + $^2/_3$ III.] Additive chromosome maps have been obtained from *T*-distributions by means of a mapping function which measures this degree of randomization and solves for the Poisson mean as a metric. *T*-distributions are common in the tetrad analyses of *Saccharomyces* (they cannot be detected in single strand analysis), indicating that localized crossovers are prevalent among these chromosomes. If a chromosomal region in which a localized crossover occurs is appended to a region in which only Poisson-distributed crossovers occur, the distal pairs of markers bounding the total composite region also exhibit a *T*-distribution which is not as extreme as the original *T*-distribution of the sub-region since the effect of the latter is now randomized by a larger average number of Poisson distributed crossovers. This relationship is written $T \cdot L = T$, where the left-hand symbols refer to the tetrad-distribution type of the two sub-regions, and the right-hand symbol refers to the distribution type of the total region. The relations $T \cdot F = T$ and $T \cdot R = T$ also hold[7] on the hypothesis that recombination occurs independently in both sub-regions. The relation $L \cdot L = T$ (or $F \cdot F = T$) would not be predicted on this basis. In fact the high frequency of tetratype tetrads for the total region can occur only because, when one region is type III, the other region is type I or type II, that is, the apparent occurrence of chromosomal interference. Since the total region exhibits a *T*-distribution this must be interpreted as a localized crossover distributed over two regions as is illustrated in the Figure.