

Liesegang Rings IV

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Ever since the attention of the scientific world was focused on the phenomenon of rhythmic precipitation by Liesegang in 1896, there have been numerous comparisons drawn between this phenomenon and many natural processes. Such matters as the structure of agates and flints, the rhythmic swarming of various bacilli, the banded structure of various concretions, the markings on wasps, tree rings, and many other geological and biological occurrences and processes have been mentioned in this respect¹⁻². Some writers even offer the Liesegang phenomenon as an explanation of many of these processes; and while there has been no immediate objection raised in the case of agates, there might be considerable skepticism displayed when the annular markings of trees are mentioned in this way.

In fact these very extremes have been examined critically by Jablczynski³; and he concludes that the former is a true Liesegang phenomenon, but the latter is not. The criteria employed were the quantitative requirements found to hold very exactly for synthetic Liesegang rings. These specifications are:

$$\frac{x}{\sqrt{t}} = k, \text{ and } \frac{X_n}{X_{n-1}} = \frac{\Delta X_n}{\Delta X_{n-1}} = A;$$

where x and t are the distance and time of formation respectively of the n -th rings or band. k and A are constants; known as the Morse and Pierce, and Jablczynski ratios respectively.

These relations are well known, and their accuracy fully warrants accepting them as criteria of the Liesegang phenomenon. Other than the instance cited above they have not been applied extensively to geological and biological cases. Perhaps the reason is that in most of these examples the bands are insufficient in numbers and definition, and the formulae are derived and con-

firmed for a large number of bands. To simulate the more natural condition, various Liesegang ring experiments were performed in which limited quantities of both inner and outer reactants were used; thus producing a limited number of bands. It is difficult to produce fewer than four or five distinct, measurable bands. In the cases of only a few bands there were definite deviations from the Jablczynski constant; the values diminishing with the larger band numbers. The change however is regular and neither erratic nor large.

To apply these quantitative ideas to natural objects, one may select the apparently infrequent sample with a large number of rings and expect a constancy of the ratios of successive positions of the bands; and, for the more common example of only a few bands, one would expect a regular and not too large change in these values. A few examples in the former class have been found in the literature, and in specimens available. Table I records the values of the Jablczynski ratio for these specimens and illustrations. Data on synthetic Liesegang rings of silver chromate and lead iodide are included for comparison. While a good many natural objects examined exhibit a multitude of rings, it is immediately apparent that only a few of these bands occur with any regularity. It is only these sections which are of interest.

There can be no question concerning the constancy of the values of the first three rows in Table I, and likewise concerning the variance of values in the last two. There is also an appreciable variation over the whole range in the case of the bacillus vulgare. On this same photograph in a southerly direction the measurements are about the same as presented. In other directions

however the five or six successive constants disappear and hence these best values presented may be ruled out as fortuitous and exceptional.

There is available much more data on systems with a smaller number of rings. Typical ratios of successive distances are given in Table II. These illustrations could be increased abundantly, but the results tabulated are typical of the measurements on hand and in the literature. The irregularity within a section selected as being most similar to the synthetic Liesegang phenomenon is sufficient to discourage any suggestion of both processes being the same. However it is possible to obtain results in synthetic cases very similar to the natural behavior, if the composition of the inculcating reactant is altered during the experiment.

In summary it may be stated that the natural cases of banded structures, other than agates and other geological illustrations, do not fit the quantitative requirements of the Liesegang ring phenomenon. While this disagreement does not eliminate the possibility that natu-

ral structures are the result of interrupted and occasional diffusional processes, it hardly justifies designating the result as a Liesegang phenomenon; for the process in such a case is merely the growth of the object. In gall stones it is undoubtedly a variable pathological environment which gives rise to the banded structure. Diffusion may be a secondary factor in this and similar cases, and the fact that Weiser⁹ has produced gall stones artificially in this way suggests this situation. Whether the actual deposition is by apposition or *in situ* can not be decided by the data given. If the instigating disturbance is constant in quality the former mechanism is indicated.

REFERENCES

- ¹Bhatnagar and Sehgal; Koll.Z. **39** 264 (1926).
²Hedges; "Liesegang Rings", Chapman-Hall, London, 1932.
³Hein, L. A. J. Botany **17** 143 (1930).
⁴Jablczynski, Roc. Chem. **3** 228 (1923).
⁵Liesegang Festschrift, Koll.Z. **89** (1939).
⁶Morse and Pierce, Z: phys. chem. **45** 589 (1903).
⁷Schade, in Alexander's "Colloid Chemistry" II 803 (1928), (N. Y.).
⁸Sweet, J.; Coll. Chem. Annual, **7** 249 (1929), (N. Y.).
⁹Weiser, H. J.; Phys. Chem. **36** 293 (1932).

TABLE I
Values of A

Ring No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Ag ₂ CrO ₄ —capillary	—	1.19	1.20	1.19	1.19	1.20	1.20	1.20	1.19	1.20	1.20	1.20	etc.	
PbI ₂ —petri dish	—	1.07	1.06	1.06	1.07	1.06	1.06	1.06	1.06	1.06	1.06	1.06	1.06	etc.
Agate, unknown source	—	1.11	1.14	1.12	1.13	1.12	1.15	1.12	1.12	1.10	1.11	1.11	etc.	
Bacillus Vulgare swarm, Knoll ⁵ , Fig. 3 (west)	—	1.43	1.30	1.19	1.11	1.14	1.09	1.12	1.08	1.06	1.07	1.06		
Gastrolith ⁷ , Fig. 44 (north)	—	1.23	1.19	1.95	1.28	1.26	1.14	1.44	1.52					
Gall stone (F. N. I) (FN. I)	—	1.18	1.31	1.60	1.43	1.32	1.30	1.24	1.31	1.11	1.19			

Dr. F. W. Ash of St. Joseph's Hospital, Paterson, N. J.; Dr. D. Loehr of Moscow, Idaho; and other physicians have presented me with a great number and variety of concretions. This one stone, of unspecified history, was the only one, of hundreds, which exhibited a large number of regular bands.

TABLE II
Values of A

Ring No.	1	2	3	4	5	6	7	8
Ag ₂ CrO ₄ , petri dish	—	1.71	1.57	1.53	1.49	1.44	—	—
Ag ₂ CrO ₄ , capillary	—	1.41	1.36	1.21	1.14	—	—	—
PbI ₂ , capillary	—	1.17	1.12	1.11	1.09	1.07	—	—
PbI ₂ , Petri dish	—	1.24	1.20	1.21	—	—	—	—
Gall stone, unknown history	—	1.27	1.61	1.64	1.43	1.42	—	—
Gall stone, Fig. I ⁸	—	1.69	1.29	—	—	—	—	—
Gall stone, Synthetic, Fig. V ⁹	—	2.04	1.43	1.22	1.11	1.10	1.10	—
Natural, Fig. III ⁹	—	2.15	1.38	1.43	—	—	—	—
Bacillus Vulgare swarm Knoll ⁵ , Fig. VII	—	2.08	1.69	1.40	1.25	1.17	1.19	—
Fungus ⁶ , Fig. 3	—	.82	1.03	1.30	—	—	—	—
Tree conk	—	1.07	1.19	1.08	1.34	1.26	—	—
Beet root markings ¹ Case D	—	.85	1.27	1.34	1.51	—	—	—