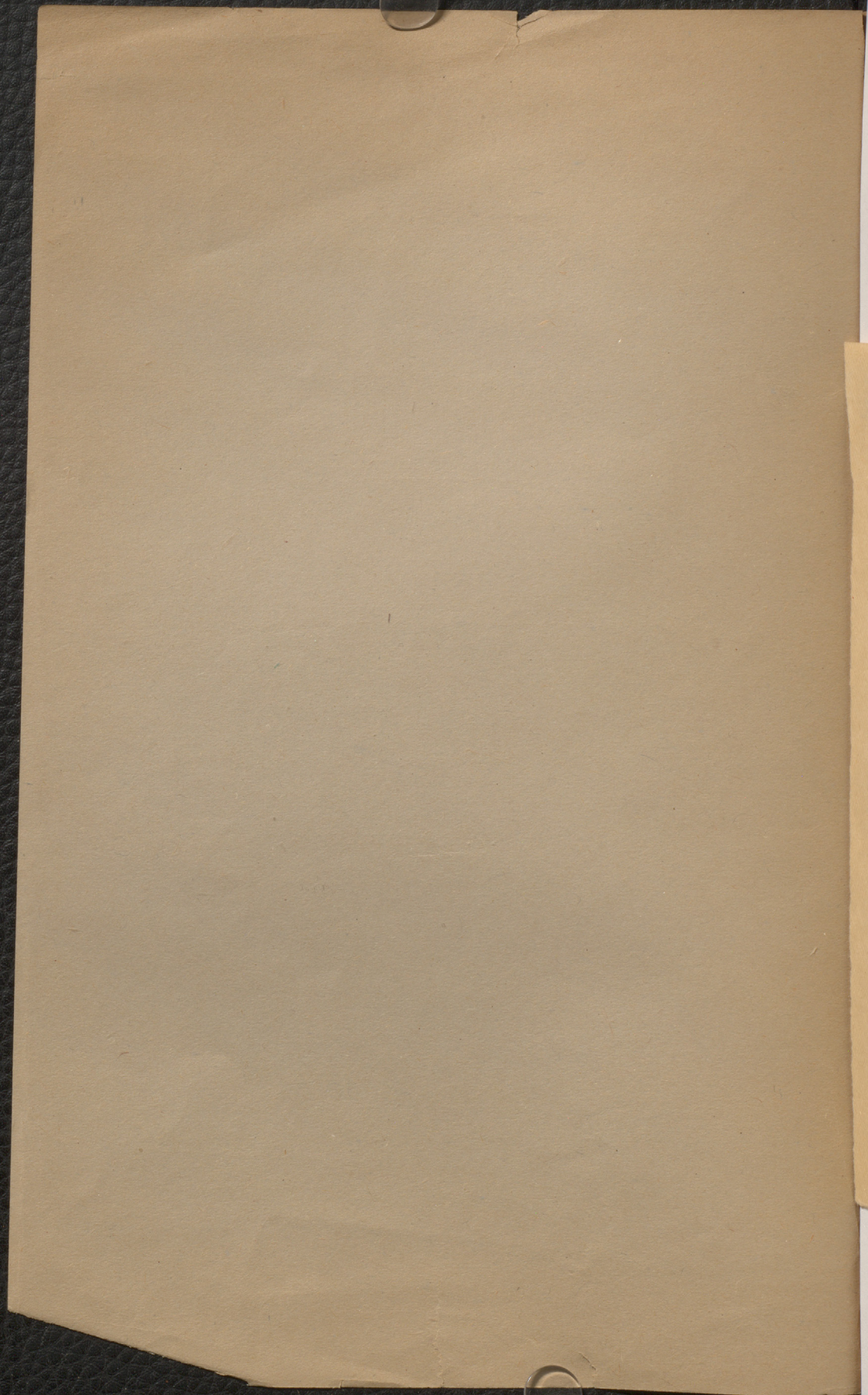


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ON AN INTERESTING VARIETY OF FETID
CALCITE AND THE CAUSE OF
ITS ODOR.

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Bertha, - Berlin

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ART. XXXVI.—*On an Interesting Variety of Fetid Calcite and the Cause of its Odor*; by B. J. HARRINGTON.

ABOUT fifty years ago, when Sir W. E. Logan was studying the geology of the Grenville region in Canada, he came upon an interesting variety of calcite in the township of Chatham (lot 10, range xi) which emitted "when rubbed an overpowering odor like that of sulphuretted hydrogen."* In the "Geology of Canada," published in 1863, Dr. T. Sterry Hunt again called attention to what is evidently the same material, as follows: "We may here notice a peculiar variety of fetid carbonate of lime, which forms a large bed in the Laurentian series, in Grenville. It is a very coarse-grained, cleavable, milk-white and apparently pure calcite, which when struck or very lightly scratched, evolves a most powerful and unpleasant odor, recalling somewhat that of phosphuretted hydrogen. It dissolves without residue in dilute acids, and the carbonic acid gas evolved does not affect solutions of lead or silver salts, so that it is difficult to say to what the peculiar smell of this singular rock can be due. It is entirely distinct from the bituminous odor, which is evolved by percussion from a great many of the limestones of the Palæozoic series, or from that produced by striking some siliceous rocks."

Specimens of this interesting calcite have long been in possession of the writer, and it was felt that it should be possible to arrive at some definite conclusion with regard to the cause of the fetid smell. Thin sections were in the first instance studied and showed under the microscope the presence of great numbers of very minute cavities, evidently containing a liquid, as moving bubbles due to the contraction of the liquid could occasionally be seen. These cavities suggested the presence of hydrogen sulphide in a liquid condition or possibly in solution in water. If the gas were present in either condition, it was obvious that it would be liberated either by solution of the calcite in an acid or by pulverizing the mineral; further, that the finer the degree of pulverization the more hydrogen sulphide would escape. This was fully confirmed by experiments made both by the writer and by Mr. Lloyd Lodge, demonstrator in the chemical department. It has been found, moreover, that Hunt's observation with regard to the action of the escaping gas upon solutions of lead or silver salts is erroneous, for in both cases black precipitates are obtained, while in the case of cadmium salts the characteristic yellow precipitate is produced. The inference would appear to be

* Geological Survey of Canada, Report of Progress, 1853-54-55-56, p. 23.

that Hunt worked with the finely pulverized mineral, from which most of the hydrogen sulphide had been liberated, or that the gases were not passed into the solutions of the salts in question for a sufficient length of time.

A specimen of the calcite was found to have a specific gravity of 2.713 and gave on analysis the following percentage composition :

Lime	55.330
Magnesia	0.540
Ferric oxide	tr
Carbon dioxide	43.925
Sulphur as H ₂ S	0.016
Phosphoric anhydride	tr
Insoluble matter	0.026
	99.837

The sulphur was determined by dissolving the mineral in dilute hydrochloric acid, passing the evolved gases into an alkaline solution of cadmium chloride and weighing the precipitate of cadmium sulphide. In the estimation of the phosphoric anhydride the mineral was dissolved in nitrohydrochloric acid, so that if any phosphorus were present as phosphide its oxidation to orthophosphate might be ensured. As the quantity of insoluble matter was insignificant, the determination was made upon about thirty grams of mineral—hydrochloric acid being the solvent. The filtrate from the insoluble matter was tested for sulphates, but gave no precipitate with barium chloride. In the analysis of another specimen of the calcite Mr. Lodge obtained results very similar to the above, but found a slightly higher percentage of hydrogen sulphide (0.021).

The following figures illustrate the different results obtained in determinations of the hydrogen sulphide according to the coarseness or fineness of the calcite :

	Lumps.	Powder of medium fineness.	Very fine powder.
H ₂ S from 29.45 } grams of mineral }	0.00471	0.00176	0.00035
Percentage of H ₂ S	0.01600	0.00560	0.00120

The figures show that the fine powder contained less than $\frac{1}{3}$ th of the amount present in the unpulverized material, and had the grinding been further prolonged there would no doubt have been a still greater difference.

On grinding a few fragments of the calcite under water in a porcelain mortar and filtering, the water contains sufficient hydrogen sulphide in solution to give the appropriate color

reactions with salts of silver, lead, cadmium, etc. If, again, the calcite be gently heated in a test-tube, hydrogen sulphide is liberated, and on heating somewhat more strongly the mineral generally decrepitates and gives off more hydrogen sulphide. On heating to 160° C. it shows a strong, deep yellow phosphorescence which persists for several minutes after removal from the source of heat.

From what has been stated it is evident that the hydrogen sulphide is the cause of the odor evolved when the calcite is scratched or rubbed, and although the quantity seems small when stated as percentage by weight it amounts to about 500 cubic inches of the gas per cubic foot of the mineral. Per cubic yard this would be about 13,500 cubic inches (a barrel and a half) of the gas, and the total quantity bottled up in the limestone of the region must be exceedingly large. It may exist in the calcite in a liquid condition, as in the case of the liquid carbon dioxide so frequently present in quartz, or in conjunction with water, or even with carbon dioxide. Mr. Douglas McIntosh, M.Sc., lecturer in chemistry, has kindly made some experiments for me which are interesting in this connection. He found that if solid carbon dioxide be dropped into liquid hydrogen sulphide and the tube sealed, as the temperature rises to that of the room the carbon dioxide dissolves and a homogeneous liquid is obtained, giving no evidence so far as appearance is concerned of the presence of two distinct compounds.

A small quantity of distilled water, again, was put into a tube and frozen, an equal volume of liquid hydrogen sulphide added and the tube sealed. When the ice melted, the two liquids could be seen to be separated by a distinct film—possibly of sulphur—which prevented their intermixing. In most cases when the tubes were heated they burst before the temperature reached 100° C. The same was also true if the tubes were inverted in position, that is with the water above the hydrogen sulphide; after standing for a short time the film gave way and the tube burst, possibly because of some sudden reaction between the two liquids. In one case, however, a tube which showed the distinct film separating the two liquids was forgotten and allowed to stand for some weeks. The film had then disappeared and, so far as one could tell by the eye, the two liquids had completely intermixed. On cooling the tube until the water crystallized out and then allowing it to gradually attain the temperature of the room, no separation of the two liquids took place. This would indicate that under the conditions of pressure in the tube, mutual solution of the water and hydrogen sulphide had taken place, and similar conditions may exist in the case of the fluid-cavities of the calcite.

Sir William Logan, judging from his description, regarded the fetid calcite as a local modification of one of the great bands of limestone belonging to the Grenville series. This modification might have been due to some form of solfataric action going on at the time of crystallization and introducing hydrogen sulphide, one of the usual accompaniments of such action. The crystals of pale green tourmaline (a boron mineral) which occasionally occur in the calcite might also point to solfataric action, though no such assumption is necessary to account for its presence. The hydrogen sulphide, again, might be taken as an indication of the existence of organic matter in the old sediments of the Laurentian series; for, as is well known, organic matter in presence of water reduces alkaline and earthy sulphates to sulphides, which reacting with water and carbon dioxide produce hydrogen sulphide. On the other hand, however, the hydrogen sulphide might have been produced from sulphides formed in the earth's crust quite independently of any organic agencies.

Associated with the fetid calcite there is also a white, translucent to subtranslucent quartz, which, on striking with a hammer or scratching with a knife, likewise evolves hydrogen sulphide. When fragments of the quartz are heated in a test-tube, considerable quantities of the gas are given off and readily darken lead acetate paper. No attempt has been made to estimate the proportion of the hydrogen sulphide in this case, nor does there seem to be any simple way of accomplishing this. In lump form the mineral would dissolve too slowly in hydrofluoric acid, while if powdered most of the hydrogen sulphide would escape. On heating the fragments, too, only a portion of the gas can be liberated and that in part at least is liable to undergo dissociation at the temperature of the experiment. The fluid-cavities in the quartz are, however, larger than in the calcite and more readily admit of study. Most of them afford no visible evidence of the presence of more than one liquid, and the moving bubble which they contain does not disappear on heating to 150°C —the highest temperature tried. In a few cases the bubbles disappeared at from 32° – 35°C ., indicating, no doubt, that the cavity contained liquid carbon dioxide whose critical temperature is 32°C . In one case the critical point was 40°C , and in several others from 60° – 65° , indicating, possibly, mixtures of carbon dioxide and hydrogen sulphide, the critical point of the latter being about 100°C . In cases where the bubbles did not disappear water is evidently present, accompanied no doubt by hydrogen sulphide and possibly by carbon dioxide as well. Some of the cavities, again, appear to contain two separate liquids with a bubble in one of them.

