

XI.—*Note on Thierschite.*

BY J. LIEBIG.

(FROM A LETTER TO DR. HOFMANN.)

Some time ago, I received from Dr. F. von Thiersch, General Conservator of the scientific collections of Bavaria, a fragment of a white marble column from the Parthenon, for the purpose of analyzing the incrustation with which the external surface of the column was covered, the chief object of the examination being to decide whether the column had been painted with a colour of a still determinable nature.

The incrustation was about  $\frac{1}{10}$  of an inch thick, and possessed the hardness of fluor-spar. Under the microscope, when illuminated by sun-light, it appeared as a lustrous, opaline aggregate of warty nuclei, exhibiting a concentric structure. When seen by the naked eye, it appeared an uneven layer of a dingy-grey colour, covering the whole outer surface of the stone.

A portion of the detached crust dissolved in acetic acid with effervescence; the solution contained nothing but lime. The greater portion was insoluble in acetic acid, but was readily dissolved by nitric acid, only a trifling residue remaining behind.

The nitric solution gave, upon addition of ammonia, a snow-white precipitate, insoluble in ammonia. After addition of acetate of soda, it furnished, with salts of silver and lead, a white precipitate. This deportment pointed towards oxalic acid, and indeed a more minute examination soon convinced me that the chief mass of the incrustation, which had been taken for a pigment used in painting the column, consisted of crystallized oxalate of lime.

I treated the precipitate produced by ammonia in the nitric

solution with chloride of copper, which converted it into a bluish powder, whilst the lime was dissolved. The copper precipitate dissolved readily in ammonia; and this solution yielded, after the copper had been thrown down, a beautiful crystallization of oxalate of ammonia which was decomposed, without deposition of carbon, into carbonic acid and carbonic oxide when heated with concentrated sulphuric acid, and from which oxalic acid, with all its properties, was prepared in sufficient quantity for an analysis, if such had been considered necessary.

Dr. Sendtner, Adjunct to the Botanical Gardens in Munich, who has a great deal of experience in researches of this kind, was unable to discover any organic structure, either in the incrustation itself or in the residue insoluble in nitric acid. I believe, therefore, I am justified in considering this incrustation, which will probably be found upon many lime-stones, as a mineral species; and since Sandall has observed crystallized oxalate of lime between metastatic calc-spar crystals in Hungary, without proposing a mineralogical name for it, I have great pleasure in coupling with this mineral the name of the learned man whose labours have so successfully contributed to the elucidation of antiquities, and who has given rise to the present observations.

The origin of this oxalate of lime can scarcely be doubtful; it is evidently derived from lichens vegetating upon the lime-stone; it is the residue of a series of generations, following each other during centuries, until the whole surface of the stone—in consequence of the gradual destruction of former vegetations, whose organic matter decayed, while the oxalate of lime produced during their vitality remained unaltered—was so completely covered, that new germs of lichens no longer found the soil of carbonate of lime necessary for their development. The residue of the incrustation, insoluble in nitric acid, when heated in a glass tube, was slightly charred; it contained traces of a humus-like substance, evidently the last residue of the lichens, protected by the oxalate of lime from entire destruction.

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