409. *Basic Copper Carbonate and Green Patina.*

By W. H. J. VERNON.

IT is commonly stated in text-books that the green patina on copper after prolonged exposure to air consists of basic copper carbonate, and that a similar coating may be produced artificially by exposure of copper to a moist atmosphere containing carbon dioxide. The first part of this statement has already been shown, for conditions in this country (Vernon and Whitby, *J. Inst. Metals*, 1929, **42**, 181; 1930, **44**, 389) and in the United States (Freeman and Kirby, *Metals and Alloys*, 1932, **3**, 190), to be incorrect : the usual main constituent is basic copper sulphate—after long exposure $CuSO_4,3Cu(OH)_2$ (cf. mineral brochantite). Near the sea, basic copper chloride [ultimately $CuCl_2,3Cu(OH)_2$, atacamite] enters to an extent depending largely on prevailing winds (Vernon, *J. Inst. Metals*, 1933, **52**, 93). Basic copper carbonate [malachite, $CuCO_3,Cu(OH)_2$] is always in minor proportion; it is maximal in town (*e.g.*, 21% and 24% in typical London samples) and minimal in rural patina (consistently less than 3% in samples examined).

In the light of these results it seemed of interest to inquire into the origin of the foregoing statement, to ascertain by experiment whether a patina of basic carbonate can be produced by the action of carbon dioxide on copper in presence of air and moisture, and to elucidate the mechanism whereby basic carbonate enters into the composition of open-air patina.

Historical.—Clearly the idea that the green (aerial) patina consists of basic copper carbonate could not have arisen until the presence of carbon dioxide in the atmosphere had been recognised, *i.e.*, by Black in 1755. One of the earliest text-books in the modern sense, Baumé's " Chymie expérimentale et raisonée," 1773 (Vol. 2, p. 633; cf. English translation, Baumé's " Manual of Chemistry," 1778, p. 137) states that : " Cuivre, exposé à l'air, pousse à sa surface une efflorescence verte que l'on nomme *verd-de-gris*; mais il pourroit bien se faire que la prétendue influence de l'air sur ce métal ne fût pas plus âverée, que celle qu' on lui attribue sur le fer. La rouille de l'un et le verd-de-gris de l'autre paroissent également être le résultat de l'eau dont l'air est chargé."

Primary importance is here attached to the presence of water. Within a comparatively short space of time, however, the newer ideas were extended to explain, among other metallic " rusts," the green deposit on copper. This is shown by the following extracts from " Elémens d'histoire naturelle et chimie," by Fourcroy. [Actually they are taken from the fourth edition, 1791; but most of the matter occurs in earlier editions, and in particular the concluding passage (C'est . . . carbonique), the most vital from the present point of view, is in the second edition, 1786 (English translation, 1788, Vol. 3, p. 307).] " Les substances métalliques s'altèrent à l'air; leur surface se ternit, quelques-unes se couvrent de rouille. Les chimistes ont regardé la rouille comme un oxide métallique.

Nous aurons occasion . . . de faire voir que l'eau en vapeurs oxide plusieurs substances métalliques, et que l'acide carbonique contenu dans l'atmosphere s'y unit après leur calcination . . ." (Tome II, pp. 405—406).

" L'air attaque le cuivre d'autant plus facilement, que ce fluide est plus chargé d'humidité et plus altéré; il le convertit en une *rouille* ou oxide vert qui paroît avoir quelques qualités salines, car il a de la saveur, et il est attaqué par l'eau; * c'est pour cela que les anciens chimistes admettoient un sel dans la cuivre. Cette rouille a cela de remarquable, qu'elle n'attaque jamais que la surface du cuivre, et qu'elle semble même servir à la conservation de l'intérieur des masses de ce métal; comme on peut en juger par les médailles et par les statues antiques, qui se conservent très bien sous l'enduit de rouille qui les couvre. Les antiquaires appellent cette croûte *patine*, et ils en font beaucoup de cas, parce qu'elle atteste la vétusté des pièces qui en sont recouvertes . . ."

" L'oxidation du cuivre par l'air humide paroît être due à l'eau très divisée . . . il semble que ce métal soit plutôt oxidé par l'eau froide, car on sait qu'il est plus dangereux de laisser refroider des liqueurs dans les vaisseaux de cuivre, que de les y faire bouiller, parce que tant que la liqueur est bouillante et le vase chaud, la vapeur aqueuse ne s'attache point à sa surface; mais lorsque le vase est froid, les goutellettes d'eau qui adhèrent à ses parois, semblent le réduire en oxide vert. C'est à l'air et à l'acide carbonique qui y est répandu, qu'il faut attribuer cette oxidation; car en distillant cette rouille de cuivre à l'appareil pneumato-chimique, j'en ai retiré de l'acide carbonique" (Tome III, pp. 325—327).

This last statement is of great importance as being probably the earliest of its kind, and apparently the only one to claim a direct experimental basis. Two points should be emphasised: (i) the confusion between green patina produced simply by exposure to air, and that produced by contact with aerated water, or by long-continued burial in soil (carrying water charged with carbon dioxide); (ii) that Fourcroy's (qualitative) experiment had been carried out on a green deposit that had resulted definitely from contact of copper with water.

The natural consequence of this confusion of ideas is well brought out in a passage in Thomson's " System of Chemistry " (1802, Vol. I, p. 114): " Everyone must have remarked that when water is kept in a copper vessel, a green crust of verdegris, as it is called, is formed on that part of the vessel which is in contact with the surface of the water. When copper is exposed to the air its surface is gradually tarnished; it becomes brown, and is at last covered with a dark green crust. This crust consists of oxide of copper combined with carbonic acid gas."

The wording here strongly suggests a misinterpretation of Fourcroy's experiment, particularly as an English translation of the fifth edition of Fourcroy's book had appeared as recently as 1800. Another source which may also have influenced Thomson, however, is revealed in the following extract from the section on copper in Murray's " System of Chemistry " (1806—1807, Vol. 3, p. 260): " When exposed to humidity and to the action of air, its colour not only tarnishes, but it is soon covered with a green efflorescence or crust. This, according to Proust, is a carbonate of copper." Incidentally, under no conditions of ordinary aerial exposure does copper " soon " become covered with green. Interest now attaches, however, to the linking of the usual statement with the name of Proust.

In his " Recherches sur le cuivre " (*Ann. Chim.*, 1799, **32**, 26), Proust showed that the green basic salt (" sel au minimum d'acide "), whether of carbonate, chloride, or sulphate, formed by precipitation with alkali from a solution of the neutral salt, is similar chemically to the corresponding natural mineral. He further recognised that precipitated copper hydroxide would *absorb carbon dioxide from the air*, and he prepared basic copper carbonate by passing carbon dioxide into a suspension of copper hydroxide in water. His paper concludes with the statement: " Dans l'art, comme dans la nature, le cuivre ne s'oxide

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* This appears to refer to the presence of normal (soluble) copper salt in the early stages of exposure (see Vernon and Whitby, *J. Inst. Metals*, 1930, **44**, 394)—probably the chloride in the case of ancient specimens, but certainly not carbonate, since normal carbonate does not exist and basic carbonate is almost insoluble in water.

jamais qu'à 26 sur %. Quant aux couleurs bleues et vertes, que l'on a crue appartenir à différentes oxidations de ce métal, elles ne sont autre chose que le signe ordinaire d'une combinaison de l'oxide noir avec un corps connu ou inconnu."

In the light of these conclusions, and in view of the importance that would be attached to the recently discovered presence of carbon dioxide in the air, it is not surprising that the familiar green coating on copper *after exposure to air* should be attributed to the combination of copper oxide with carbon dioxide; but no one appears to have submitted this deduction to experimental test.

Following Murray (above), later text-books are unanimous in attributing the green patina to some form of carbonate of copper although the actual term " basic carbonate " is not yet employed [see, *e.g.*, Thenard (1817), Berzelius (1826), Dumas (1831), Graham (1842)]. Graham (" Elements of Chemistry," p. 579), referring to copper, says : " In damp air it acquires a green coating of sub-carbonate of copper, and its oxidation is remarkably promoted by the presence of acids."

In Gmelin's " Handbook of Chemistry " (Watts's translation, 1851, Vol. 5, p. 403) there occurs the following reference to the work of von Bonsdorff (1837) : " In contact with water and air containing carbonic acid, copper becomes tarnished, first with a blackish-grey, and then with a bluish-green colour : copper rust, also the so-called *verdigris* " (Bonsdorff, *Pogg. Ann.*, **42**, 337)."

This statement closely follows the investigator's own words and significantly there is no mention of the green *aerial* deposit consisting of basic carbonate. Curiously enough, after translating Gmelin's account of Bonsdorff's experimental work, Watts reverts to the older statement in his own " Dictionary of Chemistry " (1864, Vol. 2, p. 40) : " In damp air it acquires a green coating of basic carbonate, and its oxidation is remarkably promoted by the presence of acids." This is simply a copy of Graham's version, with " basic carbonate " substituted for " sub-carbonate "; from this time onwards, text-books use " basic carbonate " consistently in describing the green patina on copper.

In view of its importance, von Bonsdorff's description of his experiment (*loc. cit.*) is quoted *verbatim* : " Dünnes Kupferblech, das zum Theil in Wasser tauchte, zum Theil aus dessen oberfläche hervorragte, und unter einer Glocke ein mit Kohlensäure vermischten Luft ausgesetzt ward, erhielt nach Verlauf mehrerer Wochen einen schwarzgrauen Anlauf, und auch in geringerer Quantität einen bläulichgrünen Beschlag." Although this experiment cannot be regarded as justifying the traditional view, it was thought expedient to submit the matter to further investigation in order to determine under what conditions, if any, a patina of basic copper carbonate can be formed as the result of access of carbon dioxide, in solution or otherwise, to the metal.

EXPERIMENTAL.

Influence of Carbon Dioxide in Saturated Air and in Aqueous Solution.—Four specimens of electrolytic copper, each 5 × 5 × 0·05 cm., after a final polishing with Hubert No. 1 emery paper and cleaning with pure carbon tetrachloride, were suspended within a Hempel desiccator of 5300 c.c. capacity. Into the evacuated vessel, 53 c.c. of carbon dioxide (prepared from sodium carbonate and phosphoric acid, each of " A.R." purity) were admitted, and atmospheric pressure was restored by addition of purified air saturated with water vapour. Finally, by means of a tube sealed to the stop-cock, 200 c.c. of saturated solution of carbon dioxide were run into the annular space normally used for the desiccating agent. The atmosphere thus contained 1% of carbon dioxide, exclusive of that contributed from the solution. The apparatus was kept in an air-thermostat at 25°; and at intervals of three months both atmosphere and solution were replaced.

After nearly four years, the specimens had undergone little change beyond a slight general darkening. There was no green, but near the edges and around the suspension hole there was a trace of blue. The weight increments of three specimens (one had been removed earlier) were respectively, 1·5, 2·8, 3·2 mg., these erratic values corresponding with an irregular distribution of the blue " flecks."

In another group of experiments two specimens were suspended half immersed in an initially-saturated solution of carbon dioxide (contained in a crystallising basin, 9 cm. diam.) within a

10-litre bell-jar, whilst two other specimens were suspended in the atmosphere above; this contained no further carbon dioxide beyond that contributed from the solution, which was replenished at intervals of 3 months, the apparatus meanwhile being exposed to the fluctuating temperature of the laboratory. An experiment in which one specimen in each pair had been previously heated in air so as to give a pale orange interference colour, showed no appreciable effect due to pre-oxidation. There was a profound difference due to environment, green appearing on the immersed portions of the lower specimens; this matter is more fully discussed below. Weight increments on removal after 8 months, for the initially bright and pre-oxidised specimens, were 47·5 and 54·2 mg. (lower pair) and 0·07 and 0·02 mg. (upper pair).

In a parallel experiment in which a specimen of arsenical copper (0·45% As) was included in each (initially bright) pair, the partly-immersed specimens showed slight attack at the water-line in one day. After two months traces of green appeared on the immersed portions; and at 3½ years, when the specimens were removed, a green deposit (rather more developed on the arsenical specimen) extended from the water-line downwards and from the bottom edge upwards, leaving a narrow intermediate zone covered with a purplish-orange film which appeared to extend beneath the green. Weight increments, 54·4 and 168·0 mg. on electrolytic and on arsenical metal respectively, presented a greater difference than would have been expected from the appearance of the specimens. Analyses of the green deposit, after drying in a vacuum over concentrated sulphuric acid at room temperature for two days, gave the following results :

	Electrolytic.		Arsenical.	
	Cu.	CO_3''.	Cu.	CO_3''.
Found, %	53·9	27·9	57·0	29·2
Formula	$CuCO_3,0{\cdot}82Cu(OH)_2$		$CuCO_3,0{\cdot}84Cu(OH)_2$	
Total basic carbonate found, %	94·8		100·2	

Thus, both on electrolytic and on arsenical copper, and in close agreement, the deposit is a carbonate only slightly less basic than malachite; identity with the mineral would probably be realised after a longer period of immersion. The figures for total basic carbonate (derived from determined values of Cu and CO_3'') show that associated moisture is approximately 5% in the electrolytic and *nil* in the arsenical product. This is of interest in the light of previous work on basic sulphate corrosion product in which the presence of arsenic was found to reduce the hygroscopicity (Vernon, *Trans. Faraday Soc.*, **1931**, **27**, 269).

In striking contrast with the immersed specimens, the upper pair underwent very little change and gave no suggestion of green. Dark striations seen on the arsenical specimen within the first few days developed only slightly; a closer examination on removal at 3½ years showed that they consisted of isolated deep blue spots following the scratches left from the emery; they were especially marked (nearly black) in the neighbourhood of the suspension hole. On the electrolytic specimen, with the exception of a dark band surrounding the suspension hole, there was practically no change. Weight increments were 3·17 and 0·69 mg. respectively.

It was next sought to reverse the conditions of the previous experiment in respect to the initial distribution of carbon dioxide by employing distilled water in place of the saturated carbon dioxide solution, and an atmosphere containing carbon dioxide in place of the purified air; this arrangement reproduces approximately the conditions of von Bonsdorff's experiment (see p. 1855). As before, a pair of specimens was suspended in the upper part of the bell-jar and another pair partially immersed in the water in the vessel; conductivity water was used. After two preliminary evacuations of the bell-jar, refilling with purified air, it was again evacuated, and 100 c.c. of pure carbon dioxide introduced; purified air was finally admitted to bring the pressure to 1 atm., thus giving, initially, an atmosphere containing 1% of carbon dioxide. The experiment was continued for 6 months with the bell-jar on the laboratory bench, screened as far as possible from direct sunlight. In spite of the more limited period, the experiment had proceeded sufficiently far to show that the reversal in the distribution of carbon dioxide had caused no great change in the disposition of corrosion.; but the deposit on the immersed portions was not so good a green as obtained at a comparable stage of the previous experiment and it was more unevenly distributed. In some places it was bluish and in others a dark (olive) green, showing under the microscope a beautiful spheroidal structure. Neither specimen in the upper part had undergone any appreciable visible change beyond a few black dots and a slight incrustation near the suspension holes. Weight increments were as follows : lower pair (electrolytic and arsenical) 54·6 and 53·0 mg.; upper pair, 0·05 and 0·11 mg.

The conclusion therefore is that, so long as conditions are restricted to the simple reactants, actual immersion of the copper in the carbon dioxide solution is necessary for the development of green basic carbonate.

Influence of Sulphur Dioxide on Formation of Basic Carbonate.—An experiment has been described (Vernon, *loc. cit.*, 272), in which copper was exposed to a moist atmosphere containing both sulphur dioxide and carbon dioxide with the latter in great excess. (The investigation was concerned primarily with the influence of sulphur dioxide, *per se*.) Any effect of carbon dioxide from the point of view of corrosion was found to be quite negligible compared with that of much lower concentrations of sulphur dioxide simultaneously present. The experiment has since been repeated with the object of ascertaining whether under such conditions any basic carbonate enters into the composition of the product, even though no carbonate is formed in the absence of sulphur dioxide. Four specimens of electrolytic copper were suspended in a Hempel desiccator; the annular space contained a mixture of saturated solutions of carbon dioxide and sulphur dioxide in the ratio 400 : 1; into the atmosphere, 1% of carbon dioxide was admitted so as to ensure ample excess. Both atmosphere and solution were replenished every two days for the first eight days, and then once a week for a year, whereupon the specimens were removed. There was then a dark green undercoat with bright green patches; immediately next to the metal there was a red film, presumably cuprous oxide (a similar film is always found beneath natural patina of basic sulphate). The green deposit was dried in a vacuum, and then contained SO_4'', 31·5; CO_3'', 0·76%. This amount of carbonate, although small, is significant as showing that under conditions favouring attack on the metal *through other causes* the joint presence of carbon dioxide may lead to the presence of carbonate in the deposit. Presumably, it is hydrolysis of the sulphate, the initial product of attack, that enables carbon dioxide to compete with sulphur dioxide, although much less actively, for combination with the hydroxide.

Influence of Organic Acid Vapours.—The analyses of patina from copper structures after long exposure in a town atmosphere suggest that other indirect influences besides that of sulphur dioxide contribute to the presence of basic carbonate in the deposit. Thus, the patina from the copper roofs of Lancaster House (near St. James's Palace) and British Museum, London, contain 24·2 and 21·1% of basic carbonate—quantities that are difficult to account for on evidence so far adduced; rural samples are always very much lower in basic carbonate and correspondingly richer in basic sulphate. The suggestion arises that among the freshly-liberated products of combustion there may be constituents other than carbon dioxide or sulphur dioxide which, directly or indirectly, favour the formation of basic carbonate. A strong clue is provided by the presence of small amounts of combined carboxylic acids in open-air patina in almost direct proportion to the amount of basic carbonate jointly present (Vernon and Whitby, *J. Inst. Metals*, 1929, **42**, 184, 187). Thus, the highest proportions were found in town samples, traces only in rural samples, and in the one example from which basic carbonate was completely absent, combined carboxylic acids were also absent. It was decided therefore to test the influence of organic acid vapours on the formation of basic carbonate.

Four electrolytic copper specimens were suspended in a Hempel desiccator as before, the apparatus being kept on the laboratory bench. The atmosphere was prepared by the addition of 30% of carbon dioxide to saturated air; and 200 c.c. of an aqueous solution of the organic reagent under examination were run into the annular reservoir. Experiments with formaldehyde (included because of its presence in rain-water) and with phenol (as a representative of hydroxylic acids likely to be present in products of combustion) gave negative results; similarly with nitric and hydrochloric acids. The presence of formic acid (a 50% solution was used) caused appreciable attack; after 14 months, blue crystals were removed, analysis of which showed the presence of basic formate ($H\cdot CO_2'$, 7·65%) and basic carbonate (CO_3'', 1·24%).

The reaction in the presence of acetic acid vapour was much more vigorous; with a 50% solution of the acid in the vessel, a good green deposit was obtained in one day. Further experiments, using 0·5*N*- and 2·0*N*-acetic acid, were continued for 14 months; all specimens were then covered with a green patina, those from the 0·5*N*-acid being rather the poorer in appearance. Analyses gave the following results :

	0·5*N*.	2·0*N*.
Cu, %	57·7	41·15
$CH_3\cdot CO_2'$, %	10·8	45·7
CO_3'', %	24·4	4·4
$CuCO_3/Cu(OAc)_2$	50·2/16·6 = 3·0	9·0/70·3 = 0·13

Basic acetate in the patina is thus associated with basic carbonate, the proportion of which is significantly greater in the atmosphere containing the lower concentration of acetic acid vapour, where, assuming a proportional distribution of base (not shown above), basic carbonate predominates over basic acetate by approximately three times. The view that small amounts of carboxylic acid can give rise to much greater amounts of basic carbonate is thus amply confirmed (cf. " stack process " for manufacture of basic lead carbonate).

In order to decide whether acetic acid vapour alone is capable of producing basic carbonate, another experiment was conducted using $0{\cdot}5N$-acetic acid but omitting carbon dioxide. The experiment was continued for 12 months, with formation of a good green patina, which was found on analysis to contain no carbonate. The data for Cu and $CH_3{\cdot}CO_2'$ were 33·62 and 22·0% respectively, corresponding with a basic acetate of the formula $Cu(C_2H_3O_2)_2,1{\cdot}75Cu(OH)_2$. Evidently, for the formation of basic carbonate, the joint presence of carboxylic acid and carbon dioxide is necessary. As in the case of sulphur dioxide, the effect is probably due to the hydrolysis of the primarily formed normal copper salt; but it is very much more marked, so that the indirect effect, with formation of basic carbonate, now exceeds the direct effect with formation of the characteristic copper salt.

Influence of Chlorides.—Relatively high proportions of basic carbonate sometimes occur in patina high in basic chloride, in purely marine atmospheres. A good example is that of the patina on the copper spire of St. Joseph's Church, Guernsey, Channel Islands, where 16·5% of basic carbonate, $CuCO_3,0{\cdot}7Cu(OH)_2$, accompanies 55·0% of basic chloride, $CuCl_2,2{\cdot}1Cu(OH)_2$.* To investigate this, four specimens of electrolytic copper were sprayed twice daily for five days with fine sea-water spray, during which time they were exposed to the open-air; in this way a rather unevenly distributed green coating of basic copper chloride was obtained. They were then transferred to a Hempel desiccator (on laboratory bench) containing a saturated solution of carbon dioxide; this was replenished daily for two weeks, and then every two months for a year, the specimens then being removed. Analysis of patina gave the following results : Cu, 48·44; CO_3'', 22·24; Cl', 7·5%. Assuming excess of base to be distributed between carbonate and chloride with a three-fold preference for the latter (cf. malachite and atacamite), this corresponds to 60·8% basic carbonate and 27·1% basic chloride. Evidently chloride, as well as certain organic salts and to a smaller extent sulphate, permits the formation of basic carbonate in the presence of atmospheric carbon dioxide; hence a ready explanation is forthcoming for the relatively high proportion of basic carbonate in both marine and town examples of green patina.

SUMMARY AND CONCLUSIONS.

The usual statement that the green " aerial " patina on copper consists of basic copper carbonate has been traced to Fourcroy (1786). Failure to distinguish between the effects of purely atmospheric agencies and of immersion in water appears to have been originally responsible; the misinterpretation by contemporary writers of the work of Proust (1799) on the constitution of basic salts probably contributed to the perpetuation of the error in subsequent literature.

Basic copper carbonate in open-air patina is always in minor proportion; it is maximal in the town (sometimes also near the sea) and minimal in the country. Immersion of copper in an aqueous solution of carbon dioxide gives rise to green basic carbonate, but in air containing carbon dioxide and water vapour this substance is formed only in the presence of another reactant, *e.g.*, traces of carboxylic acid vapours; chlorides and traces of sulphur dioxide behave similarly but much less effectively. The mechanism probably consists in the formation initially of a normal copper salt which, by hydrolysis in the presence of carbon dioxide, permits the formation of basic carbonate.

Near the sea, chlorides are mainly responsible for secondary carbonate formation; sulphates, which contribute to the bulk of the patina under all inland conditions, are in this respect not so important as traces of combined carboxylic acids, the effects of which, however, are restricted to the immediate neighbourhood of the town. Basic copper carbonate is thus necessary either to basic copper chloride at the seaboard or to basic copper sulphate inland; but in the latter case it can reach appreciable dimensions only in urban districts.

Patina derived from immersion of copper in water or burial in soil may contain a pre-

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* In the reply to the discussion on a previous paper (*J. Inst. Metals*, 1932, **49**, 167) these values were incorrectly given as 24·9 and 48·9% respectively, the three-fold greater basicity of the chloride as compared with the carbonate having been inadvertently overlooked.

ponderance of basic carbonate. The so-called " malignant patina," which appears to be associated with excess of normal salt (usually chloride), falls outside the scope of the inquiry.

Acknowledgment is due to the Corrosion Research Committee of the Department of Scientific and Industrial Research, under the Chairmanship of Sir Harold Carpenter, F.R.S., for facilities afforded; to Professor J. R. Partington, M.B.E., and Mr. F. W. Clifford, Librarian of the Chemical Society, for advice and facilities in the historical search; to Mr. E. G. Stroud, B.Sc., for valuable experimental assistance; and to Professor G. T. Morgan, O.B.E., F.R.S., Director of Chemical Research, for his helpful interest and for permission to publish the paper.

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