ANCIENT GREEK PIGMENTS FROM THE AGORA

IN THE academic year 1935-36 S. W. Midgley, Jr., a student of chemistry at Princeton, undertook as a senior-thesis project under the writer's direction the identification of a number of specimens of ancient Greek pigments scraped mostly from objects of terracotta, or fragments of such objects, found in the course of excavations at the Athenian Agora and vicinity. In the first half of the year 1937 the writer examined and identified a number of specimens of pigments from the Agora while serving as the chemist of the excavation staff. Unlike those examined by Mr. Midgley, these were not decorative pigments detached from terracottas or other objects but for the most part were substantial specimens or small remains of bulk pigments found in the vessels, or the remains of the vessels, in which these pigments had been stored or in which they had been mixed for application. Subsequent to these two investigations a few other specimens of ancient Greek pigments were examined and identified by the writer. The present report is a much-belated summary of the most interesting and significant results of all this work.

It seems unnecessary to discuss here in any detail the technical procedures by which the identity of the various specimens was definitely established. More or less conventional physical and chemical methods were used. These included microscopic examination and qualitative analysis, and occasionally when the quantity of material permitted quantitative analysis also. A principal difficulty often encountered in the scientific examination of specimens of ancient pigments is the small amount of material available. This requires that the investigator work carefully on very small quantities for individual tests or determinations, usually by microchemical manipulation. This kind of manipulation was largely employed in obtaining the results here reported. However, such a restriction on the method of examination does not imply that the final results are any less trustworthy than those which would have been obtained had larger quantities of material been available. It only means that more careful and tedious work was required.

In Table I are summarized the principal results obtained by Mr. Midgley, and in Table II those obtained by the writer. It will be noted that quantitative results are given for the ferric oxide content of the red iron oxide pigments listed in Table I. These results are indicative of the purity or quality of these pigments. Quantitative estimations actually were made of the principal components of all five such pigments listed in this table, and as an example of a nearly complete quantitative analysis made on a very small quantity of an ancient pigment the results obtained on one of them (Table III) may be of more than passing interest. In this analysis the silicon dioxide, the aluminum oxide, and some of the water represent chiefly the sand and the kaolin or clay admixed with the iron oxide in the natural ochre. The unusually high proportion of calcium oxide revealed by the analysis is possibly an indication of a deliberate admixture of lime or chalk with the ochre when it was applied, or the use

TABLE I. PIGMENTS FOUND MOSTLY ON TERRACOTTA OBJECTS

No.	*Description*	*Approximate Date B.C.*	*Identification*
1	Dark brick red pigment on uncatalogued leg of horse, Agora	VII Cent.	Red Ochre (About 48% Fe_2O_3)
2	Yellow pigment on same fragment as No. 1	VII Cent.	Yellow Ochre
3	Dull red pigment, Agora, T 197	VII Cent.	Red Ochre (About 15% Fe_2O_3)
4	Bright red pigment on lekythos, Pynx	IV Cent.	Cinnabar, Natural Mercuric Sulfide
5	Green pigment on draped female figure, Pynx	IV Cent.	Malachite, Natural Basic Copper Carbonate
6	Light red pigment, Agora T 363	III Cent.	Red Ochre (About 17% Fe_2O_3)
7	Yellow pigment, Agora, T 364	II Cent.	Yellow Ochre
8	Red pigment on sherd, Agora	III-II Cent.	Red Ochre (About 13% Fe_2O_3)
9	Pink pigment, Agora	III-II Cent.	Red Ochre diluted with Gypsum, Natural Calcium Sulfate (About 3.5% Fe_2O_3)
10	Blue pigment, Agora	III-II Cent.	Blue Frit

TABLE II. SPECIMENS OF BULK PIGMENTS

No.	*Description*	*Approximate Date B.C.*	*Identification*
1	Roughly spherical ball of medium blue pigment weighing 13 grams	VI-V Cent.	Blue Frit
2	Heavy coating of dull red pigment on inside of fragment of base of pot, P 5342	VI-V Cent.	Red Ochre
3	Dull red pigment adhering to inside of three vase fragments, P 3448, a, b, c	V Cent.	Red Ochre
4	Traces of bright red pigment on part of inner side and on adjacent part of rim of small black bowl, P 9516, X 391	V Cent.	Cinnabar, Natural Mercuric Sulfide
5	Lumps of smooth white pigment found in grave with remains of vessel, OX 219	V-IV Cent.	White Lead, Artificial Basic Lead Carbonate
6	Small amount of medium blue pigment in half of small black glaze bowl, P 1537	IV Cent.	Blue Frit
7	Specks of red pigment imbedded in design of fragment of black glaze stamped plate, P 6783	IV-III Cent.	Red Ochre
8	Small amount of bright red pigment contained in a scallop shell, BI 217	III Cent.	Cinnabar, Natural Mercuric Sulfide
9	Deposit of red pigment on bottom of ribbed kantharos fragment, P 1433	II Cent.	Red Ochre

No.	*Description*	*Approximate Date B.C.*	*Identification*
10	White pigment coating inside of bottom of fragment of black glaze bowl	II-I Cent.	Chalk, Impure Calcium Carbonate
11	Heavy coating of yellow pigment on inside of two fragments of black glaze bowl or dish	II-I Cent.	Yellow Ochre diluted with Chalk
12	Dark brownish red pigment coating inside of fragment of bottom of a pot, P 8933	I Cent.	Red Ochre

Table III. Quantitative Analysis of Specimen No. 8 of Table I

(Total quantity used for analysis, 0.0469 gram)

Silicon Dioxide (SiO_2)	36.5%
Aluminum Oxide (Al_2O_3)	15.6%
Ferric Oxide (Fe_2O_3)	13.0%
Calcium Oxide (CaO)	15.8%
Magnesium Oxide (MgO)	2.3%
Loss on Ignition (Mostly Water)	16.4%
Summation	99.6%

of a lime wash as an undercoat for the application of this pigment in the form of a tempera paint. Considerable proportions of calcium oxide were found in some of the other red iron oxide pigments, though sometimes it was entirely absent, as in No. 1 of Table I. In No. 9 of Table I a considerable part of the calcium was present as the sulfate, a compound that is not normally a component of natural red ochre. Moreover, from the pink color of this pigment it would appear that the calcium sulfate in the form of gypsum was mixed with it before application, though it may have been contained in an undercoat consisting of a plaster wash. Of the various pigments listed in Tables I and II only the blue frit and the white lead are clearly of artificial origin. It is possible that some of the specimens of red ochre were pigments manufactured by the roasting of yellow ochre, but no evidence for this could be found in the course of their examination. All the other pigments are simply natural mineral products used directly in their native state, or after having been subjected to some sort of a mechanical refining process. Since cinnabar, for example, is usually found admixed with rocky material, it is highly probable that this pigment was obtained by a process of mechanical separation such as that described by Theophrastus.[1] The production of certain of them by mixing together natural products is also very probable as has been previously indicated. Moreover, the existence of such a practice in Greece during the classical period is evident from certain remarks of Theophrastus.[2]

[1] *De Lapidibus,* 58, 59.

[2] *Op. cit.*, 53.

Some of the pigments here identified were undoubtedly imported products. Since there is no evidence for the present or past occurrence of cinnabar in Greece proper, that found in the Agora or vicinity was almost certainly imported. The nearest source, as indicated by Theophrastus [3] and shown by modern geological exploration, was western Asia Minor, and certain much more distant sources in Transcaucasia, also mentioned by this author, may well have been the source of the pigment. The blue frit was in all probability imported directly or indirectly from Egypt. This beautiful blue pigment was made there as early as the Fourth Dynasty, and became common shortly after.[4] Its Egyptian origin is specifically mentioned by Theophrastus,[5] who also notes that it was a manufactured product. Apparently, it was only at a time later than the date of the specimens here identified that this artificial blue pigment came to be manufactured anywhere on the continent of Europe. According to Vitruvius [6] it was first manufactured at Puteoli by Vestorius. There is no evidence that it was ever made in Greece. The shape of the bulk specimen found at the Agora is of considerable interest as indicating the probable form in which this pigment was sold for use. Moreover, from the description of Vitruvius it seems certain that it was manufactured in just such roughly spherical balls. Possibly some of the ochres were of distant origin, though no concrete evidence for this can be given. Theophrastus [7] mentions the island of Ceos as being the source of the best red ochre, and the province of Cappadocia in Asia Minor as a source of both red and yellow ochre. However, ochres of good quality occurred anciently on the mainland of Greece, particularly in Attica, and still can be found there today, so that the specimens here identified may well have been of local origin. It is uncertain whether the white lead was of local or distant origin. Theophrastus [8] describes the process for manufacturing white lead concisely and clearly as though it were well-known to him from personal observation, and he apparently wrote this account while residing at Athens. Moreover, abundant lead for its manufacture at Athens could have been readily obtained from the mines at Laurion. On the other hand, ancient writers do not specifically state that white lead was ever manufactured at Athens, though they do mention other places where this pigment was manufactured. Dioscorides,[9] for example, remarks that the best grade was made at Corinth, in Lacedaemon, and on the island of Rhodes. Unlike the other pigments discussed here, white lead was apparently never used as a decorative paint pigment but only as a cosmetic.

Certain kinds of pigments known from other investigations to have been used by the ancient Greeks are not among those here identified. No specimen of either orpiment or realgar, the two native sulfides of arsenic, has been found at the Agora,

[3] *Op. cit.*, 58.
[4] Lucas, *Ancient Egyptian Materials and Industries*, London, 1934, p. 285.
[5] *Op. cit.*, 55.
[6] *De Architectura*, VII, 11, 1.
[7] *Op. cit.*, 52.
[8] *Op. cit.*, 56.
[9] *De Materia Medica*, V, 103.

though a few specimens of one or the other have been occasionally found at other sites in Greece. Rhousopoulos [10] identified as orpiment a specimen of a yellow pigment found in a Greek grave of the Fifth or Fourth Century, and Foster [11] identified as realgar a quantity of a red pigment contained in a pot excavated at Corinth. No specimen of any black pigment has been found at the Agora, though specimens of a particular black pigment have been found elsewhere. Samples of this taken from lekythoi have been identified by Rhousopoulos [12] as pyrolusite, a native oxide of manganese. From their sporadic occurrence the sulfides of arsenic and the black oxide of manganese were apparently not much used.

The correlation between the pigments listed by Theophrastus [13] and those actually found in modern excavations in Greece is remarkably good. As red pigments he lists cinnabar, realgar, and red ochre, the latter in three shades, dark red, medium red, and pinkish. Red ochre is described as either natural, or of artificial origin from the roasting of yellow ochre. The yellow pigments are two, orpiment and yellow ochre. The green pigments are malachite, chrysocolla, and verdigris, the last being manufactured. There are also three kinds of blue pigments, azurite, powdered lapis lazuli, and Egyptian blue frit. Four different shades of blue are said to have been produced by different degrees of grinding. Except for white lead, the white pigments were evidently natural white earthy substances such as chalk and earthy gypsum. He fails to mention any black pigment, but from the rarity of such in excavations black was evidently not much used as a decorative paint pigment in ancient Greece. Only one of the pigments he lists has clearly not been found in modern excavations and identified. This pigment is verdigris, the preparation of which is so clearly described by him that there can be no doubt that it was made for use as a pigment in his day. That ancient specimens of this artificial basic copper acetate will ever be found, however, is perhaps too much to expect since it is an unstable pigment that is readily transformed by the action of air and water into the basic copper carbonate. This chemical instability may be the source of a curious error since it is by no means improbable that some of the specimens of ancient Greek green pigments which have been identified as basic copper carbonate were originally in the form of verdigris. All the other pigments used by the Greeks in painting were very permanent.

For providing the samples of the pigments here identified and for giving information about their provenance the writer hereby acknowledges his indebtness to Professor and Mrs. T. Leslie Shear, to Professor and Mrs. Homer A. Thompson, and to Mr. Rodney S. Young.

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[10] *Beitrag zum Thema über die chemischen Kentnisse der alten Griechen* in Diergart, *Beiträge aus der Geschichte der Chemie dem Gedächtnis von Georg W. A. Kahlbaum*, Leipzig und Wien, 1909, p. 187.

[11] *Journ. Chem. Ed.*, X, 1933, p. 276.

[12] *Op. cit.*, p. 181.

[13] *Op. cit.*, 50-67.