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PREHISTORICAL PIGMENT MINING ON SANTORINI'S NEIGHBOURING ISLAND ANAFI (CYCLADES, GREECE)

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ABSTRACT

Abundant deposits of red chalk (hematite), ochre (goethite) and jarosite occur on several places of the island of Anafi. These pigments were produced by hydrothermal alterations in course of a young rhyolitic volcanism, and have been mined in ancient times. Anafi's natural pigments display close similarities with some pigments of the Bronze Age wall paintings that have been excavated in Akrotiri (Santorini). Arguments for a putative provenance of these prehistorical pigments from Santorini's neighbouring island Anafi are discussed in this article.

Reichliche Vorkommen von Röteln (Hämatit), Ocker (Goethit) und Jarosit wurden an mehreren Stellen der Insel Anafi entdeckt. Diese Pigmente sind durch hydrothermale Alterationen im Zuge eines jungen rhyolithischen Vulkanismus entstanden und in früheren Zeiten bergmännisch gewonnen worden. Die Erdfarben von Anafi weisen eine große Ähnlichkeit mit manchen Pigmenten der bronzezeitlichen Wandmalereien von Akrotiri (Santorin) auf. Argumente für die Herkunft dieser prähistorischen Pigmente von den Lagerstätten auf Santorini's Nachbarinsel Anafi werden in dieser Arbeit diskutiert.

1. INTRODUCTION

In 1939, the greek archaeologist Sp. Marinatos speculated that a major volcanic eruption of Santorini could have induced the destruction of the Minoan civilization on Crete. Close to Akrotiri (southern Thera), he discovered in 1967 a Bronze Age town, which had been buried under a thick cover of pumice. These excavations became an archaeological site of international importance – especially because of well preserved wall-paintings with close similarities to Minoan painting from Crete. In the meantime, much better archaeometric chronologies have shown, that the final decline of the Minoan culture on Crete postdates Santorini's main eruption by at least 300 years (cf. Broodbank, 2000, Fig. 1). Nevertheless, this so-called Minoan eruption had certainly a strong impact on the local settlements of the southern Cyclades.

The volcanic archipelago of Santorini (Fig. 1) is situated in the back-arc tectonic setting of the present-day Hellenic subduction zone. Santorini's volcanism has been reviewed by Druitt et al. (1999) with special emphasis to the pyroclastic activity. Geochronological data and long-term trends in magma composition demonstrate the existence of two major cycles of volcanic activity from about 360 ka onwards. Each cycle began with the effusion of mafic to intermediate magmas and terminated with violent eruptions of silicic tuffs. In course of the latter, gravitational collapse of the magma chamber resulted in the formation of large central calderas.

The second cycle was terminated by the so-called Minoan eruption, which has buried the Bronze Age town of southern Thera, and has created the final shape of the present-day caldera. In order to determine the precise time of this huge prehistorical eruption, archaeological chronologies and several dating methods were applied. Calibrated radiocarbon ages of 16 samples of carbonized material from the Thera excavations range close to 1625 BC (Fishman et al., 1977). This date is

supported by palaeo-climatological arguments, as for example frost rings in bristlecone pines from the upper timber line of the White Mountains in California, that were explained by a large volcanic eruption in the northern hemisphere (LaMarche & Hirschboeck, 1984). The dendrochronological date of these frost rings would correspond precisely to the year 1627 BC, but it should be noted that a date of 1626 BC was proposed in the original article, because LaMarche's computer was programmed to include a year zero between 1 BC and AD 1. Thus, his 1626 BC with a year zero can be corrected to 1627 BC without a year zero (cf. Kuniholm, 1990). The event which has caused the frost rings could have taken place a year earlier in 1628 BC. Such event is also recorded by the occurrence of narrowest growth rings in Irish bog oaks (Baillie, 1990; Baillie & Munroe, 1988) and by an acidity peak at 1644 ± 20 BC in ice cores from Greenland (Hammer et al., 1987). Three lines of evidence – bristlecone frost rings, Irish oak minimum-growth rings and ice-core acidity peaks – underline the high probability of a large volcanic dust-veil event in 1628 BC that has affected the whole northern hemisphere. None of these records implies necessarily that the dust veil must have been caused by the eruption of Santorini, but the coincidence with the radiocarbon data from the Thera excavations is striking.

The present article deals with a putative pigment source on Anafi island which could have been exploited as early as during the 2nd millennium BC. Pigments from Anafi could have been used for the wall-paintings of prehistoric Thera, and could have been involved in east-Mediterranean trade.

2. THE WALL PAINTINGS OF PREHISTORIC THERA

Various wall-paintings are the most spectacular findings of the Akrotiri excavations. Besides some striking analogies with

Minoan painting from Crete, they exhibit a distinct character of their own (Davis, 1990). They display many themes from cultural life and nature, as for instance religious ceremonies, persons in nearly life-size, animals and landscapes (Hejl, 2005; Vanschoonwinkel, 1990; Iliakis, 1978). All these pictures predate the Minoan eruption of Santorini but cannot be much older because of their good preservation. They were probably painted in the middle of the 17th century BC.

After a careful study of the technology of Thera wall-paintings, Asimenos (1978) concluded that they were made *al secco*, that is to say that the pigment layers were painted on a dry surface of lime plaster. In contrast to this technique, the Italian word *fresco* refers to wall-paintings performed on a still fresh surface of moist lime plaster (cf. Weissenhorn, 2002). Such fresh lime (Ca(OH)_2) reacts chemically with atmospheric carbon dioxide to produce calcium carbonate (CaCO_3), which encloses the pigments in the plaster. In the case of *al secco* paintings, the pigments are usually mixed with some kind of organic glue, that sticks them on the dry plaster. These binding agents can be aqueous solutions of either vegetable glues (for example fig milk or gums) or animal glues (for example gelatine or the white of egg).

According to Asimenos (1978), the following observations support the assumption that most wall-paintings of prehistoric Thera (Akrotiri) were made *al secco*:

1. String impressions at the edges of large colored areas. These string marks suggest that a whole wall was covered with lime plaster within one day. Given the large dimensions of the walls, it is rather improbable that they have been painted during the same day. The lime just started to dry, when the string impressions were made.
2. Incised preliminary sketches of a subject, which have been made on a dry wall. During the subsequent painting the surface must have been dry too.
3. Paintings on pre-existing colored walls (over-paintings). At least during the second painting the surface must have been dry.
4. Flaking of the paint indicating that the binding agent has decayed.

Filipakis (1978) has investigated pigments from the excavated wall-paintings by X-ray fluorescence, X-ray diffraction and microscopic observations. The results indicate that the pigments of prehistoric Thera are very similar to those of the Bronze Age paintings of Knossos in Crete (Profi et al., 1976). The blue pigments are Egyptian Blue, glaucophane or a mixture of both. The black pigments are either carbon or manganese oxide. The other pigments, red, pink, orange, yellow and brown are mainly composed of natural earth ochres, that is to say hematite and iron hydroxides (goethite) mixed with clay minerals. Noll et al. (1975) could also identify a red mixture of jarosite ($\text{KFe}_3[(\text{OH})_6(\text{SO}_4)_2]$) and hematite (cf. also Buchholz, 1980, and Noll, 1991, p. 200). In course of a recent study of Rasmussen et al. (2004) ten fragments of Bronze Age paintings from Akrotiri were examined by powder X-ray diffraction. Their samples comprise red, pink, white and grey colors. Two pink samples are composed of calcite, quartz, chlorite, hornblende, zinckite and albite. One red sample is composed of hematite, quartz, calcite, clinocllore, cordierite and

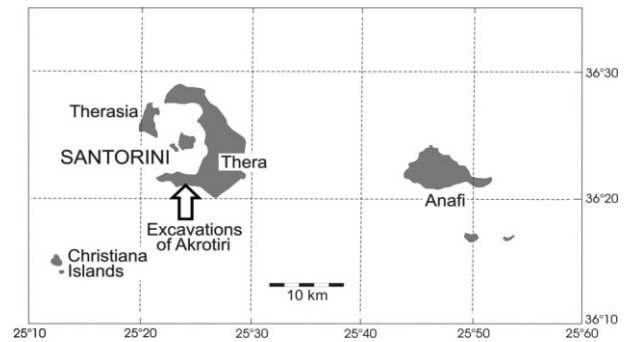


FIGURE 1: Topographic sketch map of the Santorini archipelago and its neighbouring island Anafi.

muscovite. Cordierite was also detected in a grey sample. Unfortunately, the colors of the studied samples have not been reported in a standardized nomenclature, as for example that of the Munsell® Soil Color Chart.

The social significance of Bronze Age wall-paintings has been discussed controversially by archaeologists, and one reason for the discrepancies could be, that the some published interpretations are influenced by the personal cultural background of the investigating archaeologist. Both function and individual perception of art have indeed changed during human history, and the meaning of pictorial themes for a Bronze Age society must not be obvious for a present-day observer.



FIGURE 2: The wall-painting of the Fisherman in the "West House" of prehistoric Thera.



FIGURE 3: The wall-painting of a standing priestess in the "House of the Ladies" in prehistoric Thera.

N. Marinatos (1987) argued that earliest paintings and sculptures with a purely decorative function were not produced before the end of the classical Greek period – in contrast to the art of former mediterranean societies, which did mainly reflect religious traditions or political power. Consequently, N. Marinatos tried to interpret the paintings of prehistoric Thera in the context of

presumable religious rituals of the Bronze Age society. According to her, the fisherman of the "Westhouse" (Fig. 2) is probably a young worshipper who served as a signpost in a ritual sacrifice, and the female figurines of the "House of the Ladies" (Fig. 3) could be maid-servants who delivered the ritual clothing for a priestess. In a later article N. Marinatos (1990) concluded that the religion of prehistoric Thera has emerged from a Minoan-Cycladic syncretism. Indeed, a local Cycladic tradition and a strong Minoan influence can be discerned by the analysis of cult equipment, architecture, and the iconography of the paintings. Especially the latter shows striking similarities to Minoan schemes. Such iconography could not have been known to Theran artists unless they had been taught in the Minoan tradition of painting (N. Marinatos, 1990).

On the other hand, Hejl (2005) could demonstrate that the so-called "Spring Fresco" of room Δ2 is most probably a rather naturalistic picture of a Cycladic landscape. It displays rock heads with different stages of tafoni development – very similar to those of the present-day Cyclades. However, such naturalistic scenery could have been integrated in a religious ceremony.

3. NATURAL OCCURRENCES OF RED CHALK, OCHRE AND JAROSITE ON THE ISLAND OF ANAFI

The Anafi island is situated 20 km to the east of Thera, has an area of about 38 km², and reaches a maximum altitude of 582 m at Mt. Vigla. Anafi's geology was mapped by Melidonis, and was published in 1962 at a scale of 1:50,000, as an individual sheet of the official geological map of Greece. Parts of the island were reinvestigated in course of some MSc. Thesis of the Univ. of Kiel (Germany). Essential results of these new studies were outlined in the articles of Reinecke et al. (1982) and Böger (1983). Apart from details, the new map of Reinecke et al. (1982) has mainly confirmed the regional geological descriptions of Melidonis (1962, 1963). Anafi consists of four major tectonostratigraphic units, that are from the base to the top (Fig. 5):

1. palaeogene flysch,
2. a series of greenschists,
3. high-temperature metamorphic rocks and granitoid intrusions of Latest Cretaceous age, and
4. the fluvial and lacustrine deposits of the Theologos formation (Plio-Pleistocene).

The three lower units were stacked by compressive nappe tectonics, but the Theologos formation is mainly delimited by extensional normal faults. Recently discovered dykes of altered rhyolite and volcanic breccias within the pre-Neogene basement on the one hand, and tuff layers in the basal part of the Theologos formation on the other hand, certify the existence of a young, most probably Plio-Pleistocene volcanic activity on the Anafi island.



FIGURE 4: Detail of the Lilies Fresco or Spring Fresco from room Δ2 of prehistoric Thera – now preserved at the National Museum of Athens.

These new discoveries complete our knowledge of the South Aegean active volcanic arc (SAAVA) and match very well with Anafi's position in the center of the arc. Leichmann and Hejl have studied Anafi's volcanic rocks in the field, as well as by petrological, chemical and stable isotope analysis. The results of their investigations will be published soon in an independent scientific article. The rhyolitic volcanism had a phreatomagmatic to phreatic character. It was triggered by tectonic extension and deep circulation of meteoric waters during the early stages of the Theologos sedimentary basin. Abundant water supply was responsible for a pervasive argillic and carbonatic alteration of the rhyolites and their country rocks. The hydrothermal alterations have also produced large quantities of ochre and red chalk, which are described in the present article.

Many outcrops of such hydrothermally altered zones with natural pigments occur in the central and western part of the island, as for example at the location Kammeni along the road from Anafi village to Vagia, or in the surroundings of Ag. Panteleimon (Prassa). Most pigment occurrences – especially those with yellow colors – are concentrated along the contact zone of the pre-Neogene basement and the Theologos formation or in the lowermost part of the Theologos formation itself. The samples of the present investigation were taken from a small basement area, approximately 800 m to the northeast of Anafi village. They were collected along a road outcrop, about 50 m to the southwest of the saddle with an elevation of 210 m. The sampling area extends over a length of about 20 m along the road. The central coordinates of this area were determined by a GPS measurement and verified on the official topographic map of Greece 1:50,000 (sheet Nisos Anafi). Latitude and longitude are: N 36°21'20"; E 25°46'30". The basement at this location consists of serpentinite and hydrothermal minerals, including opale and various types of ochre and red chalk. Fig. 6 shows a zone rich in hematite, in the southwestern part of the outcrop.

Eight homogeneous samples of different colors were taken from this outcrop and were treated as follows. First, they were sieved, and the fraction with a grain size of less than 1 mm was suspended in distilled water. The suspended material was

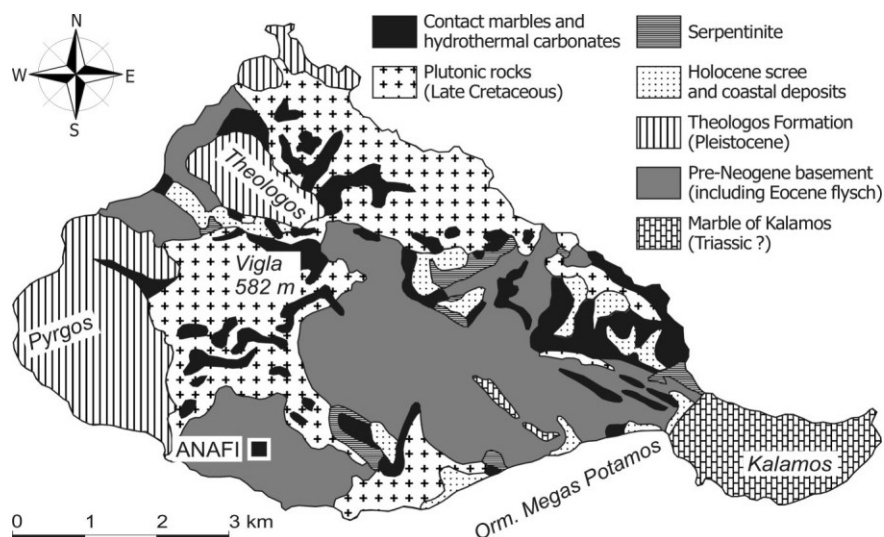


FIGURE 5: Geological sketch map of Anafi island (simplified after Melidonis, 1962, and Reinecke et al., 1982).

filled in sedimentation tubes, up to a water depth of 20 cm. The material, that was still in suspension after a fall time of 58 seconds at 20° C water and room temperature, was recovered and dried. For a mineral density of 2,6 g.cm⁻³, such fall times would yield grain size fractions of less than 63 µm (silt and clay). The resulting maximum grain size is even finer in the case of denser minerals, as for ex-ample hematite. Afterwards, these dried fractions were powdered in an agate mill, and their colors were determined under dry conditions.

The color names of the present article refer to the Munsell® Soil Color Charts. This collection of charts is a modified version of the collection appearing in the Munsell® Book of Color and displays only that portion needed for soils. The range of these colors is also well suitable for the comparison with pigments of natural ochre. Best working conditions are daylight in a cloudy day. Erroneous results would be obtained, when the energy distribution in the



FIGURE 6: Alteration zone rich in hematite. Road outcrop to the northeast of Anafi village, at about 200 m altitude (N 36°21'20"; E 25°46'30").

visible spectrum of the light source (wave lengths from 370 to 720 nm) is very different from sunlight, as for example in the case of candle light or yellowish light from an incandescent lamp. Nevertheless, correct measurements with the Munsell® Soil Color Chart are much better reproducible than any other verbal expression of individual color perceptions. For the color range under discussion (see paragraph below), we have found very similar color values for both daylight and for light from fluorescent tubes. Of course, the samples and the reference color chart must be exposed to the same light source and must be observed simultaneously during the comparison.

The Munsell® system of color nomenclature comprises three dimensions (notations): The HUE notation of a color indicates its relation to red, yellow, green, blue, and purple; the Value notation indicates the brightness; and the Chroma notation indicates the strength or departure from a neutral gray of the same lightness. The position of color in the three-dimensional color field is given by a combined notation, as for example: 10YR 6/4 = *light yellowish brown*. In this example HUE = 10YR, Value = 6, and Chroma = 4. The following colors occur among the eight samples from the road outcrop 800 m to the northeast of Anafi village: red, dark red, yellowish red, brownish yellow and yellow (cf. Table 1).

A qualitative phase analysis of the same eight samples has been performed by powder X-ray diffraction of randomly oriented material. X-ray powder diffraction patterns were measured with an automatic diffractometer (Siemens D500) with Cu K_α radiation (40 kV, 45 mA) between 2 and 75° 2θ (stepsize 0.02°, measuring

Sample code	Color code and name	Main constituents	Minor constituents and traces
AF 1	2.5YR 5/6 red	calcite, hematite	saponite, kaolinite, goethite
AF 2	10R 3/6 dark red	hematite	goethite, saponite
AF 3	2.5YR 3/6 dark red	hematite	goethite, montmorillonite
AF 4	5YR 4/6 yellowish red	quartz, hematite	kaolinite, magnetite, goethite
AF 5	10YR 6/8 brownish yellow	quartz, goethite	kaolinite, calcite, magnetite, hematite
AF 6	10YR 6/8 brownish yellow	goethite	jarosite, kaolinite, quartz
AF 7	2.5Y 8/6 yellow	jarosite, saponite	quartz, kaolinite, goethite
AF 8	2.5Y 8/6 yellow	jarosite	saponite, quartz, kaolinite, goethite

TABLE 1 : Color denotations and qualitative phase analysis (X-ray diffraction) of eight samples from the road outcrop to the northeast of Anafi village, at about 200 m altitude (N 36°21'20"; E 25°46'30").

time 5 seconds per step). The program EVA 3.0 (part of the software package Diffrac plus from BRUKER AXS) including PDF-2 database (from International Centre for Diffraction Data) was used for evaluating the diffraction data.

All identified phases are listed in Table 1, where they are classified in main constituents and others (minor constituents and traces). Three exemplary X-ray diffractograms are displayed in the Figs. 8, 9 and 10. It is evident from the phase analysis that hematite produces the red colors (samples AF 1, 2, 3 and 4), while goethite and jarosite produce brownish yellow (AF 5 and 6) and yellow (AF 7 and 8), respectively. The pigments are never pure, but several transitions occur even without artificial mixing of the natural materials. Goethite is never absent; minor amounts of this phase are also present in the yellow and dark red samples. On the other hand, hematite and jarosite seem to exclude each other: hematite is absent in the yellow samples (AF 7 and 8),

Sample code	SiO ₂ [%]	Al ₂ O ₃ [%]	Fe ₂ O ₃ [%]	MgO [%]	CaO [%]	Na ₂ O [%]	K ₂ O [%]	TiO ₂ [%]	P ₂ O ₅ [%]	MnO [%]	Cr ₂ O ₃ [%]	LOI [%]	Tot. C [%]	Tot. S [%]	SUM [%]
AF 1	36.43	9.87	18.06	2.08	9.67	.15	.21	.37	.05	.01	.25	22.3	2.91	.49	99.61
AF 2	23.75	.75	56.51	1.45	1.05	.07	<.04	.05	.13	.01	.75	15.0	.66	.18	99.79
AF 3	24.48	1.81	53.33	1.33	1.17	.02	<.04	.11	.13	.03	2.24	14.6	1.79	.08	99.53
AF 4	59.33	4.57	24.27	.62	.58	.10	.07	.05	.03	.02	2.07	7.5	.18	.06	99.27
AF 5	35.07	4.09	42.16	.99	1.67	.20	.20	.17	.08	.01	1.55	13.3	.45	.34	99.52
AF 6	19.50	8.07	50.72	.92	.54	.28	.51	.33	.12	<.01	.72	17.9	.15	1.45	99.64
AF 7	36.47	2.55	27.15	3.18	1.14	.61	1.55	.27	.07	<.01	.36	26.4	.09	3.64	99.76
AF 8	32.77	2.13	29.44	2.77	1.28	1.13	1.25	.28	.08	<.01	.72	27.9	.17	4.33	99.77

TABLE 2: Major element, Mn and Cr analyses of the same samples as in Table 1 (LiBO₂-Fusion, ICP-ES). LOI = Loss on ignition. Total C and Total S (both not included in the sum) were measured with a LECO Carbon/Sulphur determinator.

while jarosite is absent in the red samples (AF 1 to 4). The transition from brownish yellow to yellow correlates with decreasing goethite and increasing jarosite contents. At the present state of investigation we are not able to decide if hematite is replacing jarosite or vice versa, or if hematite is replacing goethite. The genetic relationship between the three minerals could be elucidated by textural investigations and could help to understand the role H_2O and K_2O in the stabilization of the paragenesis jarosite + goethite. Calcite in addition to hematite seems to increase the lightness (Value) of the red color: dark red (without calcite) changes into red (with calcite).

Powdered aliquots of the same eight samples were chemically analysed by Acme Analytical Laboratories Ltd. (Vancouver, BC Canada). The analytical results are listed in Tables 2 and 3. After $LiBO_2$ fusion of the powdered material, the main element concentrations (Table 2) were determined by ICP-ES. Total C and S contents were measured with a LECO Carbon/Sulphur determinator. The trace element concentrations of Ba, Co, Cs, Ga, Hf, Nb, Ni, Rb, Sr, Th, U, V, W, Zr, Y, La and REE were determined by ICP-MS on the same aliquots as the main elements. Most REE concentrations except of Ce were close to or under the limits of detection, and are not listed in Table 2. The trace element concentrations of As, Cd, Cu, Pb, Se, Sb and Zn were measured by ICP-MS on other aliquots that had been leached with 3 ml Aqua Regia ($HCl-HNO_3-H_2O$) for one hour at $95^\circ C$, and then diluted to 10 ml. Concentrations of most detectable trace elements are reported in Table 3.

The main element concentrations are quite consistent with the results of the qualitative phase analysis by X-ray powder diffraction (Table 1). Increasing sulphur content ($>1\%$) and increasing K_2O ($>.5\%$) correlate with increasing jarosite; the sample with the highest CaO content (9.67 %) is that with distinct calcite in the X-ray diffraction pattern; Al_2O_3 correlates mainly with kaolinite; Fe_2O_3 is never below 18 % and is mainly due to hematite, goethite or jarosite.

Some details of the trace element concentrations are worth to notice: A high Ni content (> 1400 ppm) is associated with a strong enrichment of hematite, and could hint to a hematite formation by



FIGURE 7: Sieved fractions (< 1 mm) of raw material from the pigment outcrops to the north-east of Anafi village. Same location as for Fig. 6.

Sample code	As ppm	Ba ppm	Co ppm	Cu ppm	Ga ppm	Hf ppm	Mo ppm	Nb ppm	Ni ppm	Pb ppm	Rb ppm	Se ppm	Sb ppm	Sr ppm	Th ppm	U ppm	V ppm	W ppm	Zn ppm	Zr ppm	Y ppm	La ppm	Ce ppm
AF 1	21	37	46.3	22	10.2	1.5	.3	7.6	951	195	3.1	1.4	1.0	55	1.1	1.2	206	7.6	201	48.9	1.3	1.5	2.5
AF 2	130	50	56.6	39	3.4	<.5	2.5	<.5	1428	447	<.5	.9	2.8	32	<.1	.7	422	1.4	105	<.5	.3	<.5	<.5
AF 3	127	29	113.8	27	4.9	<.5	4.7	<.5	1444	335	.5	.7	8.4	25	<.1	1.0	652	6.4	189	1.2	.7	<.5	<.5
AF 4	62	23	69.8	225	6.7	<.5	1.1	<.5	327	227	3.5	1.5	6.4	28	.2	.6	423	46.8	215	1.0	.1	<.5	<.5
AF 5	202	26	41.5	311	13.6	2.1	6.7	2.4	209	519	7.7	22.9	28.8	43	1.1	1.4	278	6.3	156	85.8	1.6	.9	1.4
AF 6	498	116	15.7	272	27.8	5.2	19.2	7.4	119	731	21.8	15.2	7.4	125	3.3	2.3	414	3.1	147	191.2	2.1	2.4	2.9
AF 7	288	329	6.8	15	15.0	6.1	1.5	4.8	91	825	30.0	3.5	5.3	189	2.1	3.0	26	8.4	71	222.8	1.7	2.8	3.0
AF 8	264	371	9.1	21	14.7	4.5	1.3	5.9	158	1310	21.0	3.3	.5	234	3.6	1.6	72	4.8	43	159.2	1.5	8.0	9.4

TABLE 3: Trace element analyses of the same samples as in Tables 1 and 2. All trace elements were determined by ICP-MS. The concentrations of Ag, Be, Bi, Sn, Ta and most REE are below or very close to the limits of detection, and are not reported in the Table. The Cs and Cd concentrations did not exceed 1.1 and 3.1 ppm, respectively. They are also not reported in the Table.

weathering or alteration of Fe-bearing sulfide ores. Higher As, Ba, Pb, Sr and Zr contents (> 250 ppm, > 100 ppm, > 700 ppm, > 120 ppm, and > 150 ppm, respectively) coincide with the presence of jarosite, but Zr must be present in an other mineral (probably zircon) because it does not fit in the jarosite crystal structure. A small amount of zircon could take up some Hf, Nb, Th, U, Y and La, that are also enriched in the samples with Zr > 150 ppm. The fact that higher Rb (> 20 ppm) coincides with the presence of jarosite is almost self-evident because of the substitution of Rb for K.

4. ANCIENT MINING PLACES ON THE ISLAND OF ANAFI, AND SOME REMARKS CONCERNING THE TERM “PREHISTORIC”.

Melidonis (1962, 1963) has reported some ore occurrences on the island of Anafi that had been mined in historical times. These ores are vein mineralisations of Zn, Pb, Fe and Cu in the granitoids and their contact aureole. They occur in the central western part of Anafi, in the vicinity of Mt. Vigla. One of these ore mineralisations has been mined to the S of the saddle of Stavros, i.e. approximately 1 km to the WSW of the summit of Mt. Vigla (582 m). Some other small ore workings are situated farther to the N. All these former mining areas are authenticated as official claims by the prefecture of the Cyclades (Nomos Kykladon, Ermoupolis, Syros). They have been exploited after the independence of modern Greece (AD 1822).

None of these ore mineralisations coincides with the pigment occurrences that we have mentioned in chapter 3. At least two of these places – i. e. the locations Kammeni and Ag. Panteleimon –

have certainly been mined, but these activities are not recorded by the official authorities (Nomos Kykladon) and are situated at the outside of the historical claims. Therefore, these mining activities must have taken place previous to the Greek independence. The biggest pigment mining place (Figs. 11 and 12) is situated at 160 m altitude, 100 m to the E of Ag. Panteleimon. This pigment excavation extends over a length of about 40 m in E-W direction and has a depth of about 10 m. The central coordinates of the location (latitude and longitude) are: N 36°22'17"; E 25°44'42". Without archaeological evidence we are not able to decide if this pigment occurrence has been exploited as early as during the late Bronze age. However, because of the quoted similarities with the pigments of the Akrotiri wall paintings we suggest that this place is a putative candidate for prehistorical pigment mining.

The term “prehistoric” can be misleading in the context of the Minoan culture, because it could suggest a period with no contemporaneous written documents or inscriptions. It is well known that the Minoan culture and the Cycladic population of the 2nd millennium BC have used a script system, the so-called Linear A writing (cf. Haarmann, 2003). It has evolved from an earlier hieroglyphic script, that has been used in Crete previous to Linear A. In course of time, this hieroglyphic script became more stylized and more linear, and finally developed into Linear A, which is a mixed writing system comprising both phonetic and semantic symbols. Linear A has about 60 phonetic symbols representing syllables, and 60 semantic symbols representing material objects or abstract ideas. However, these symbols are mostly undeciphered because the underlying pre-indoeuropean language is still unknown, and probably does not relate to any present-day

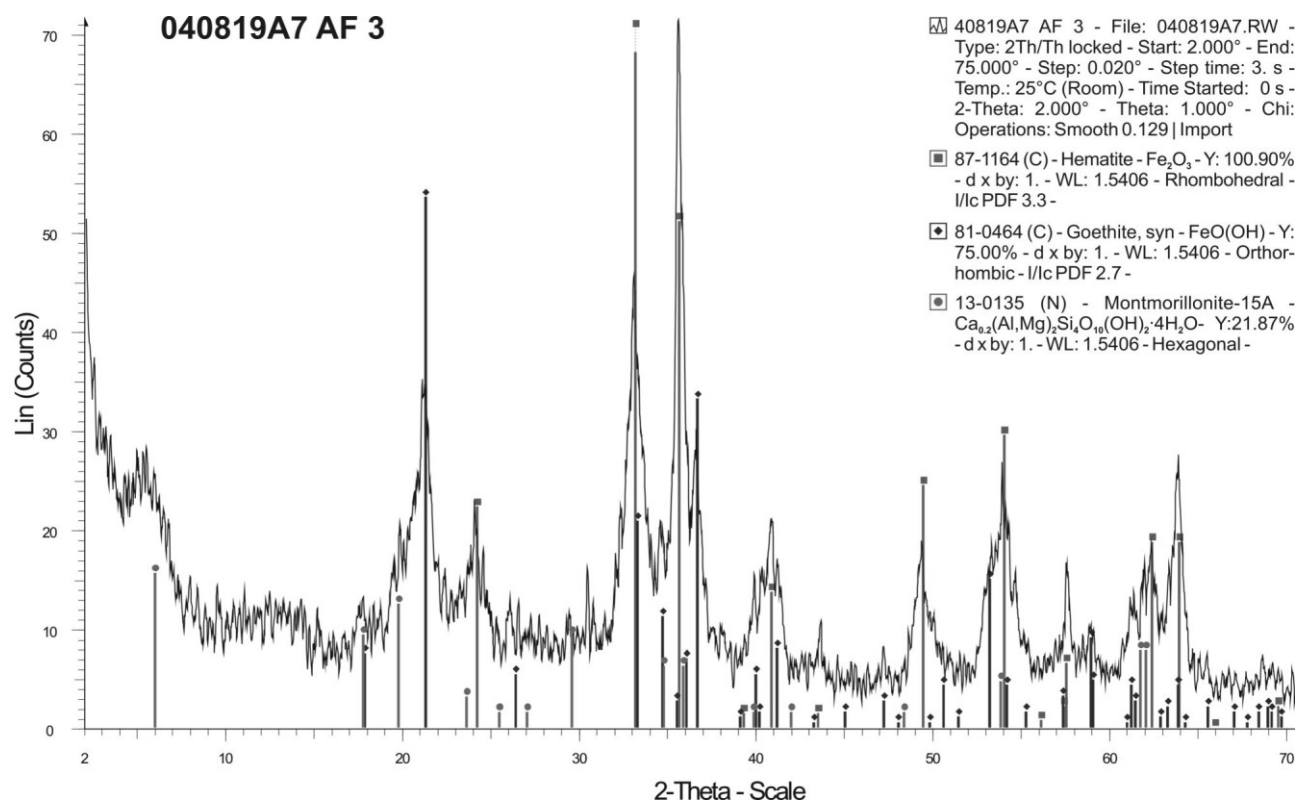


FIGURE 8: X-ray powder diffraction diagram of sample AF3.

language in Europe or western Asia. Only very few Linear A symbols have been identified, and these known symbols represent mainly dry measures or weight units (cf. Katsa-Tomara, 1990; Michailidou, 1990; Wass, 1971). Linear A has some similarities with the Mycenaean script Linear B (used between 1500 and 1200 years BC) but was certainly not a literal precursor of the Greek alphabetic writing, which was derived some centuries later from the Phoenician vocalised writing system (cf. Curtius, 2000). A continuous written tradition from the Minoan period until the early days of Greek writing around 900 BC can be excluded. The time gap between the latest Palace culture on Crete (around 1200 BC) and the earliest Greek scriptures exceeds 200 years. Therefore, the term prehistoric may be justified with regard to the Minoan period. It means that no intelligible written traditions from this period have come to us.

We have also no written documents concerning Anafi's pigment mines. If these mines were in use during the Bronze Age or the classical Greek period is simply not known. Only archaeological studies at the mining sites could solve this problem.

5. DISCUSSION

The pigments from Anafi and the wall-paintings of prehistoric Thera can be compared in three aspects: the general appearance of the colors (Hue, Value and Chroma according to the Munsell® nomenclature), the mineralogical identity of the colors, and the chemistry of individual pigment phases or mixtures of phases.

At present, a full comparison of Anafi pigments with Minoan or Thera wall-painting is not possible, because standardized color notations of the archaeological paintings are not available, and

the published photographs of these paintings do not render exactly the true colors. It must be also considered that any mixing or physical interaction of the pigments with white lime plaster or an organic glue could change the notations of Value (= brightness) and Chroma (= strength) with regard to those of the pure pigments. It can be expected that white lime will increase the brightness of the color, but will not essentially change the notations of Hue and Chroma. On the other hand, prehistoric wall-paintings are never in the same fresh conditions as at the moment when the ancient artist has completed the painting. The original painting layer can be covered with a thin layer of mineral deposits, as for example calcite or gypsum, that accumulated over the millennia. Also chemical weathering can produce secondary minerals and thus change the appearance of the colors (cf. Schiegl et al., 1990, 1991 a and b; El Goresy, 1997). In spite of these problems, we have tried to compare the Anafi pigments with the colors of some wall-paintings of the exhibition in the Museum of Prehistoric Thera (Phira, 847 00 Greece). We found that the degree of resemblance between the red and yellow colors of the paintings on the one hand and the Anafi pigments on the other hand is very high. However, this first appraisal would need a confirmation by precise mineralogical and textural investigations of millimeter-sized fragments from the wall paintings.

All the main pigments ranging from red to yellow colors, that we found on the island of Anafi, were also identified in the wall paintings of prehistoric Thera (Filippakis, 1978; Rasmussen et al., 2004). These pigment minerals are hematite, goethite and jarosite. The latter is not necessarily a primary phase of the

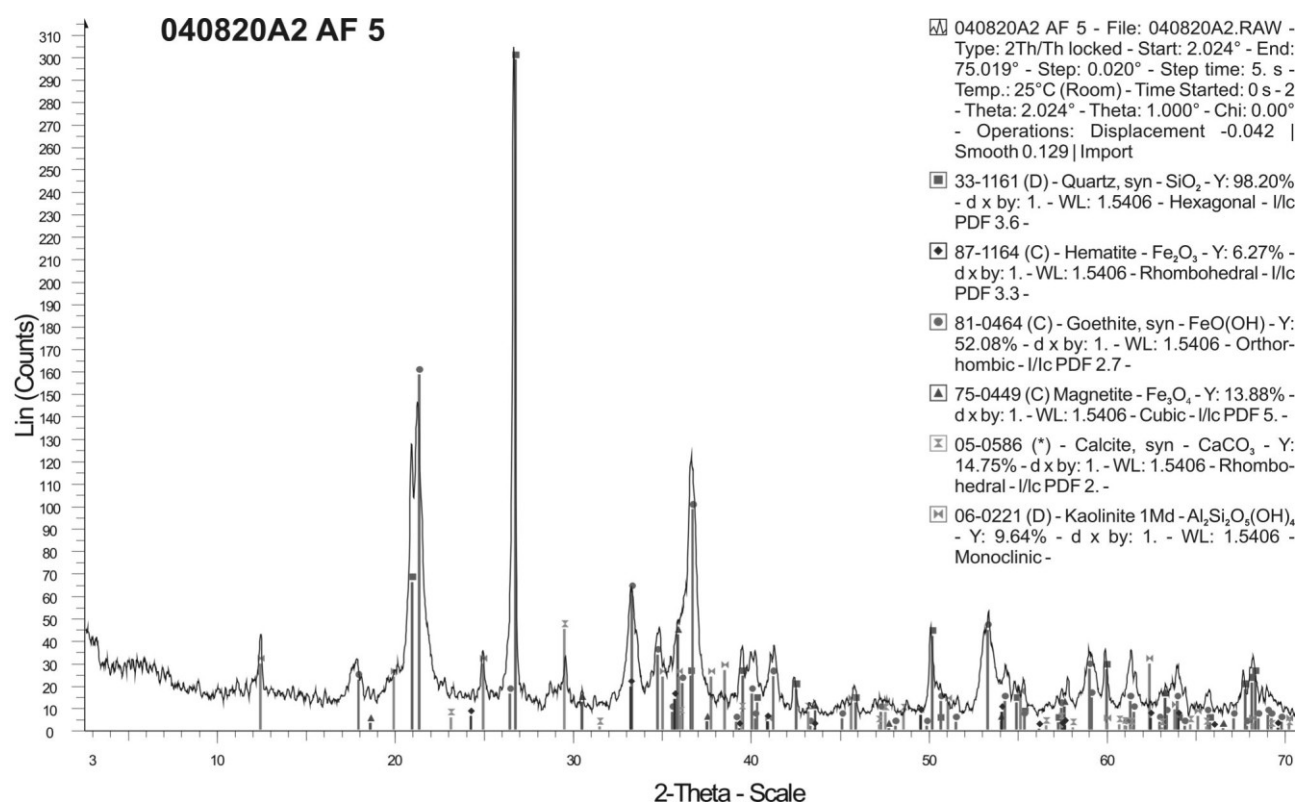


FIGURE 9: X-ray powder diffraction diagram of sample AF5.

original painting, but could be a secondary weathering product that has crystallized after painting. Schiegl (1991) has demonstrated that Jarosite in ancient Egyptian decorations has been formed by decomposition of an Fe-rich synthetic glass pigment (cf. also El Goresy, 1997). A distinction between primary jarosite, originating from a natural pigment source, and secondary jarosite, originating from weathering after painting, is not possible by X-ray diffraction of powdered samples. This important question could be only solved by electron microprobe analysis of impregnated polished sections of millimeter-sized fragments from the wall paintings. The presence of primary jarosite in the paintings of prehistoric Thera would be a strong argument for a pigment provenance from Anafi.

Also kaolinite, calcite and quartz are present in Anafi's natural earth ochres as well as in the wall paintings of prehistoric Thera, but are not indicative for discrimination of potential pigment sources. Nevertheless, the presence of cordierite in two samples from Akrotiri's frescoes (Rasmussen et al., 2004) is of particular importance for provenance studies. Cordierite is occasionally present in magmatites, but mainly in low-pressure high-temperature metamorphic rocks, as for example those of Anafi. It was found in metapelitic gneisses of Anafi, that have been metamorphosed during a late Cretaceous high-temperature metamorphism (Reinecke et al., 1982), but it seems to be absent on most other islands of the Cyclades. There is no doubt, that cordierite must be absent in the unaltered part of the Eocene blueschist belt. However, we did not find cordierite in the eight samples from Anafi that we have analysed for the present article.

Only the blue colors of prehistoric Thera must originate from

other sources than Anafi. They are essentially composed of glaucophane and Egyptian Blue (Filipakkis, 1978). Glaucophane is very abundant in the Eocene blueschist belt of the western and northern Cyclades, for example on Siphnos and Syros (Avigad & Garfunkel, 1991). Egyptian Blue is a synthetic pigment composed of cuprorivaite ($\text{CuCa}[\text{Si}_4\text{O}_{10}]$), cuproan wollastonite ($(\text{Ca,Cu})_3[\text{Si}_3\text{O}_9]$), silica polymorphs (tridymite, cristobalite or quartz), tenorite or cuprite (CuO or Cu_2O , respectively), and an alkali- and chlorine-bearing cuproan glass phase (Schiegl et al., 1990; Schiegl, 1991; El Goresy, 1997; and personal communication of El Goresy). It is possible to produce Egyptian Blue by heating of a mixture of malachite, quartz (sand) and limestone to about 1000 to 1100 °C (Noll, 1991), but in pharaonic times it has been manufactured with Cu-bearing metal scrap instead of malachite and with an addition of natron in order to lower the melting temperature (cf. Marcus Vitruvius Pollio, about 33-22 B.C., and El Goresy, A.D. 1997). Most authors assume that the Bronze Age population of Thera has imported Egyptian Blue from a distant source.

Red chalk (hematite pigment) was used by the early Homo sapiens, and was mined systematically at least since the Neolithic period (Goldenberg et al., 1998). It is probably the first pigment that was used for painting on ceramics (Noll, 1991, p. 160 and 190). Red chalk occurs in many places of the east Mediterranean region, for example in Cyprus and the Aegean island of Lemnos. Also ochre (goethite pigment) is available from several places, and was certainly not an extremely rare pigment during the Bronze Age. Nevertheless, it should be borne in mind that the transport costs were not negligible at this time, and that com-

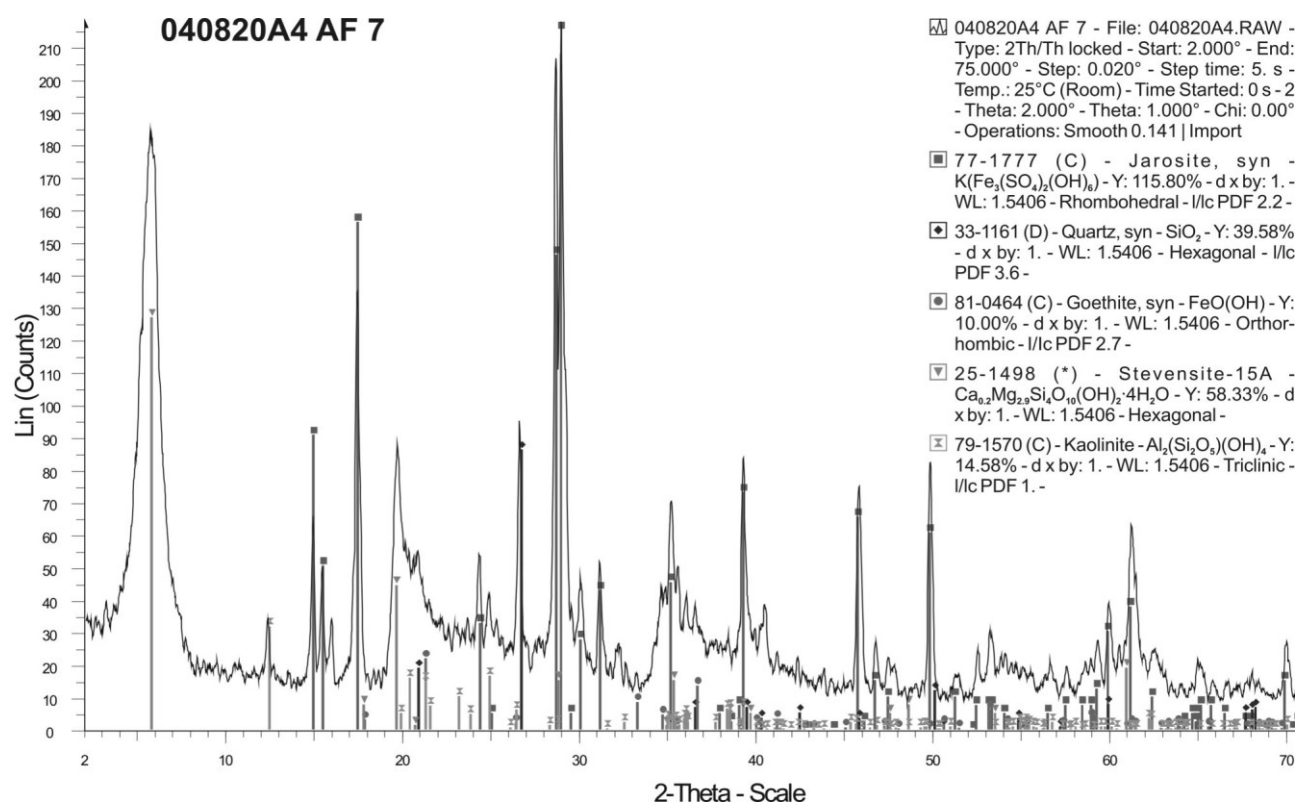


FIGURE 1 □: X-ray powder diffraction diagram of sample AF7.

mercial goods were only shipped over long distances when it was necessary or economically efficient. It is almost certain that the natural pigment occurrences of Anafi were known to the prehistoric population of Thera, and it is reasonable to assume that these pigments were used by the local population. They may have been exported in exchange for other materials, as for example ores or metallic artefacts. Especially tin must have been imported from distant sources, because of the scarcity of tin ores in the Aegean region (cf. Skarpelis, 2001). The geographical position of Thera and the results of lead isotope analyses of excavated bronze artefacts suggest that this site was an important trading post for Late Bronze Age commerce (Stos-Gale & Gale, 1990). Because of the prosperity of prehistoric Thera it is rather improbable that this community has imported all kind of raw material. Therefore, we suppose that some high-quality pigments could have been exported and exchanged for tin or other goods.

Exploitable pigment deposits of jarosite are less common than such of hematite and goethite. Jarosite has been identified in few ancient colors and paintings: a pigment mixture of jarosite and hematite was found in prehistoric Thera (Noll, 1991), and secondary jarosite is present in ceramic paintings from El Tarif (Egypt, 11th dynasty; cf. Schiegl, 1991, after misinterpretation as primary pigment by Noll, 1978). At the moment, it is not yet clarified if the jarosite from prehistoric Thera is of primary or secondary origin. Natural jarosite occurs in the alteration zone of pyrite deposits in Cyprus. Noll (1991) has assumed that this pigment from Cyprus has been exported to Thera. In view of the big jarosite deposits of Anafi, such a distant jarosite source as Cyprus is improbable for the Akrotiri wall paintings, even if it could be demonstrated that the jarosite of the paintings is of primary origin.

Quantitative chemical analyses of Thera wall-paintings are not yet available. Besides X-ray diffraction data, Filippakis (1978) has only published a qualitative element determination by X-ray fluorescence. Of course, the red and yellow colors of the paintings con-

tain always Fe (mainly from hematite and Fe-Hydroxides) and Ca (from the lime plaster). In addition, Filippakis (1978) found Cr, Ni, Zn, Pb, Mn and Cu. An elevated content of Cr, Ni, Zn and Pb would fit well to a putative pigment source on Anafi island. On the other hand, the pigments from Anafi have not elevated concentrations of Mn and Cu. This apparent discrepancy is relativated by the fact that Cu is a major element of cuprorivaite ($\text{CuCa}[\text{Si}_4\text{O}_{10}]$) and other phases of Egyptian Blue, and by the fact that manganese oxide has been used for the black colors. Elevated contents of Cu and Mn in the red to yellow colors can be easily explained by a contamination with Egyptian Blue and manganese oxide during the painting procedure (color pots and/or brushes).



FIGURE 11: Ancient mining place close to Ag. Panteleimon, between Vagia and Prassa in the western part of Anafi island (Koordinates: N 36°22'17"; E 25°44'42"; altitude 160 m).



FIGURE 12: Detail of the mining place close to Ag. Panteleimon. The artificial excavation has a maximum depth of about 10 m. The wall rocks consist of hydraulic fractured marble and hydrothermal alteration products. No samples were taken from this presumable archaeological place.

6. CONCLUSION

Natural occurrences of red chalk, ochre and jarosite on the Aegean island of Anafi display close mineralogical similarities with red to yellow pigment mixtures that were used for the Bronze Age wall-paintings in prehistoric Thera (Santorini).

Anafi's pigment deposits have been mined in ancient times, previous to the Greek independence. Because of the short distance of only 20 km between Santorini and Anafi, it is almost certain that these natural earth ochres were known to the Bronze Age inhabitants of both islands. Besides the domestic use of the local population, these high-quality pigments could have been involved in the east-Mediterranean trade of the late Bronze Age.

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REFERENCES

- Asimenos, K., 1978. Technological observations on the Thera wall-paintings. – In: C. Doulmas (editor), *Thera and the Aegean World I*, pp. 571-578, London.
- Avigad, D. and Garfunkel, Z., 1991. Uplift and exhumation of high-pressure metamorphic terrains: the example of the Cycladic blueschist belt (Aegean sea). – *Tectonophysics* 188, 357-372.
- Baillie, M. G. L., 1990. Irish tree rings and an event in 1628 BC. – In: D. A. Hardy and A. C. Renfrew (editors), *Thera and the Aegean World III. Volume Three (Chronology)*, pp. 160-166, The Thera Foundation, London.
- Baillie, M. G. L. and Munro, M. A. R., 1988. Irish tree-rings, Santorini and volcanic dust veils. – *Nature* 332, 344-346.
- Böger, H., 1983. Stratigraphische und tektonische Verknüpfungen kontinentaler Sedimente des Neogens im Ägäis-Raum. – *Geologische Rundschau* 72, 771-814.
- Broodbank, C., 2000. *An island archaeology of the Early Cyclades*, XX + 414 p., Cambridge University Press.
- Buchholz, H.-G., 1980. Some observations concerning Thera's contacts overseas during the Bronze age. – In: C. Doulmas (editor), *Thera and the Aegean World II*, pp. 227-240, The Thera Foundation, London.
- Curtius, E., 2000. *Griechische Geschichte. Von den Anfängen bis zum Tode des Perikles*. – 749 S., Vollmer, Essen.
- Davis, E. N., 1990. The Cycladic style of the Thera frescoes. In: D. A. Hardy et al. (editors): *Thera and the Aegean World III. Volume One (Archaeology)*, 214-228, The Thera Foundation, London.
- Druitt, T. H., Edwards, L., Mellors, R. M., Pyle, D. M., Sparks, R. S. J., Lanphere, M., Davies, M. and Barriero, B., 1999. *Santorini Volcano*. – Geological Society London, *Memoirs* 19, VIII + 165 p., Bath.
- El Goresy, A., 1997. Polychromatic wall paintings in monuments of Pharaonic Egypt: compositions, chronology, and painting techniques. – Invited lecture, 33 p., *The First International Symposium on the Wall Paintings of Thera, August 30th to September 4th, 1997, Santorini* (organized by The Thera Foundation, Piraeus, Greece).
- Filippakis, S. E., 1978. Analysis of pigments from Thera. – In: C. Doulmas (editor), *Thera and the Aegean World I*, pp. 599-604, London.
- Fishman, B., Forbes, H. and Lawn, B., 1977. University of Pennsylvania radiocarbon dates XIX, *Radiocarbon* 19/2, 188-228.
- Goldenberg, G., Kaiser, M. and Maass, A., 1998. Neolithischer Hämatitbergbau bei Sulzberg, Kreis Breisgau-Hochschwarzwald. – *Archäologische Ausgrabungen Baden-Württemberg* 1997, 33-35.
- Haarmann, H., 2003. *Geschichte der Sintflut. Auf den Spuren der frühen Zivilisationen*. – 208 S., C. H. Beck Verlag, München.
- Hammer, C. U., Clausen, H. B., Friedrich, W. L. and Tauber, H., 1987. The Minoan eruption of Santorini dated to 1645 BC? – *Nature* 328, 517-519.
- Hejl, E., 2005. A pictorial study of tafoni development from the 2nd millennium BC. – *Geomorphology* 64, 87-95.
- Iliakis, K., 1978. Morphological analysis of the Akrotiri wall-paintings of Santorini. – In: C. Doulmas (editor), *Thera and the Aegean World I*, pp. 617-628, London.
- Katsa-Tomara, L., 1990. The pottery-producing system at Akrotiri: an index of exchange and social activity. – In: D. A. Hardy et al. (editors), *Thera and the Aegean World III. Volume One (Archaeology)*, pp. 31-40, The Thera Foundation, London.
- Kuniholm, P. I., 1990. Overview and assessment of the evidence for the date of the eruption of Thera. – In: D. A. Hardy and A. C. Renfrew (editors), *Thera and the Aegean World III. Volume Three (Chronology)*, pp. 13-18, The Thera Foundation, London.
- LaMarche, V. C. and Hirschboeck, K. K., 1984. Frost rings in trees as records of major volcanic eruptions. – *Nature* 307, 121-126.
- Marcus Vitruvius Pollio, 33-22 B.C., reprinted in 1981. *De architectura libri decem* [in latin language]. 248 p., Wissenschaftliche Buchgesellschaft Darmstadt.
- Marinatos, N., 1987. *Kunst und Religion im alten Thera: Zur Rekonstruktion einer bronzezeitlichen Gesellschaft*. 128 p., I. Mathioulakis + Co. KG, Athens.

- Marinatos, N., 1990. Minoan-Cycladic Syncretism. – In: D. A. Hardy and A. C. Renfrew (editors), *Thera and the Aegean World III. Volume One (Archaeology)*, pp. 370-377, The Thera Foundation, London.
- Marinatos, S., 1939. The volcanic destruction of Minoan Crete. – *Antiquity* 13, 425-439.
- Melidonis, N. G., 1962. Geological map of Greece, 1:50 000, Anaphi sheet. – Institute for Geology and Subsurface Research, Athens.
- Melidonis, N. G., 1963. Die Geologie der Insel Anaphi (Stratigraphie- Tektonik- Petrologie- Lagerstättenkunde) – IGSR, Geol. and Geophys. Res., v. 3, 308 p., Athens.
- Michailidou, A., 1990. The lead weights from Akrotiri: the archaeological record. – In: D. A. Hardy et al. (editors), *Thera and the Aegean World III. Volume One (Archaeology)*, pp. 407-419, The Thera Foundation, London.
- Noll, W., 1978. Mineralogie und Technik der bemalten Keramiken Altägyptens. – *N. Jb. Miner. Abh.* 133, 227-290.
- Noll, W., 1991. Alte Keramiken und ihre Pigmente. VI + 334 p., Schweizerbart (Nägele u. Obermiller), Stuttgart.
- Noll, W., Born, L. and Holm, R., 1975. Keramiken und Wandmalereien der Ausgrabungen von Thera. – *Naturwissenschaften* 62, 87-94.
- Profi, S., Weier, L. and Filipakkis, S. E., 1976. X-ray analysis of Greek Bronze Age pigments from Knossos. – *St. in Conservation* 21, 34-39.
- Rasmussen, S. E., Grundvig, S. and Friedrich, W. L., 2004. Composition of pigments of Santorini's frescoes: The Rietveld method as an aid in qualitative phase analysis. – *Powder Diffraction* 19, 145-148.
- Reinecke, Th., Altherr, R., Hartung, B., Hatzipanagiotou, K., Kreuzer, H., Harre, W., Klein, H., Keller, J., Geenen, E. and Böger, H., 1982. Remnants of a Late Cretaceous high temperature belt on the island of Anafi (Cyclades, Greece). – *N. Jb. Miner. Abh.* 145, 157-182.
- Schiegl, S., 1991. Altägyptische Pigmente und Glasuren: Phasenbestand, chronologische Evolution, Zersetzungsmuster und deren Ursachen. – Dissertation Univ. Heidelberg, 297 p.
- Schiegl, S., Weiner, K.-L. and El Goresy, A., 1990. Zusammensetzung und Provenienz von Blau- und Grünpigmenten in Altägyptischen Wandmalereien: Ein Beitrag zur exakten Chronologie der Bronzetechnologie in Altägypten. – *Erzmetall* 43/6, 265-272.
- Schiegl, S., Weiner, K.-L. and El Goresy, A., 1991. Das Mosaik eines archäologischen Desasters. Teil I – Die Geowissenschaften 7, 199-209.
- Schiegl, S., Weiner, K.-L. and El Goresy, A., 1991. Das Mosaik eines archäologischen Desasters. Teil II – Die Geowissenschaften 8, 241-246.
- Skarpelis, N., 2001. Ancient potential tin sources in the Aegean. – Acts of the XIVth UISPP congress, Université de Liège, Belgium, 2-8 September 2001: Section 11, Symposium 11.2 (The Problem of Early Tin), BAR International Series 1199, 159-164, Hadrian Books Ltd., Oxford.
- Stos-Gale, Z. A. and Gale, N. H., 1990. The role of Thera in the Bronze Age trade in metals. – In: D. A. Hardy et al. (editors): *Thera and the Aegean World III. Volume One (Archaeology)*, pp. 72-89, The Thera Foundation, London.
- Vanschoonwinkel, J., 1990. Animal representations in Thera and other Aegean arts. – In: D. A. Hardy et al. (editors): *Thera and the Aegean World III. Volume One (Archaeology)*, pp. 327-347, The Thera Foundation, London.
- Wass, D. A., 1971. Numerical fractions in Linear A. – *Kadmos* 10, 33-51.
- Weissenhorn, R. G., 2002. Chemie in der Freskomalerei. – *Chemie in unserer Zeit*, 36. Jg., Heft 5, 310-316.

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