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Colour and composition of nodules from the Calabrian clay deposits: a possible raw material for pigments production in Magna Graecia

Domenico Miriello[1]*, Andrea Bloise[1], Anna Maria De Francesco[1], Gino Mirocle Crisci[1], Francesco Chiaravalloti[2], Donatella Barca[1], Mauro Francesco La Russa[1] and Elisa Marasco[1]

[1]Dipartimento di scienze della terra, università degli studi della Calabria, Ponte P. Bucci cubo 12B, 87036 Arcavacata di rende (Cs), italy
[2]C.n.r - irPi istituto di ricerca per la Protezione idrogeologica, via Cavour, 87036 rende (Cs), italy

Abstract - Pliocene clays in rocca imperiale (north Calabria - italy) and monasterace (south Calabria- italy) have oxide and hydroxide iron nodules of a range of colours, varying from brown to red. it is likely that the inhabitants of some colonies in magna Graecia (who already used the clay deposits to produce bricks) had detected the presence of the above-mentioned raw materials and decided to use them to produce mineral pigments and to decorate polychrome artefacts. the nodules were pulverized and analysed through sEm-EDs, XrPD and colorimetric analysis; further, they were heated at 275°C, 400°C, 550°C e 750°C, monitoring their mineralogical and chromatic transformations. our study pointed out that it is possible to chemically differentiate the nodules of monasterace from the nodules of rocca imperiale. Furthermore, our study proved that it is possible to produce mineral pigments by using such raw materials.

Riassunto - le argille Plioceniche di rocca imperiale (nord Calabria - italy) e monasterace (sud Calabria- italy), contengono noduli di ossidi e idrossidi di ferro di colore variabile dal marrone al rosso. È molto probabile che gli abitanti di alcune colonie della magna Grecia, le quali già utilizzavano gli stessi depositi argillosi per la produzione di laterizi, avessero notato la presenza di queste materie prime e le avessero utilizzate per la produzione di pigmenti minerali, impiegandoli per decorare manufatti policromi. i noduli sono stati polverizzati e studiati attraverso analisi sEm-EDs, XrPD e colorimetriche; inoltre, sono stati riscaldati alle temperature di 275°C, 400°C, 550°C e 750°C, monitorando le trasformazioni mineralogiche e cromatiche. lo studio ha evidenziato che è possibile differenziare chimicamente i noduli di monasterace da quelli di rocca imperiale e ha dimostrato che è possibile produrre pigmenti minerali usando queste materie prime.

Key Words: *Ochres; Iron oxides; Iron hydroxides; Kaulon; Monasterace; Rocca Imperiale; Greek colonies; Policoro; Amendolara.*

Introduction

since prehistory, man has always tried to express himself through art forms, in some instances using mineral pigments extracted from natural deposits with a high content of iron hydroxide and oxide (marean *et al*., 2007; iriarte *et al*., 2009), commonly known as “ochres“ (from the Greek word ochrós = yellow). the ochre owes its pigmenting capacity to various iron composites, which determine its variety of colorations (red, yellow, orange, brown and green).

Generally ochres contain more than 10-12 % of iron oxides. the percentage of Fe_2O_3 ranges between approximately 10 and 20 % up to more than 90 % in the deep red ochres (Benbow, 1989).

As centuries went by, man learnt how to transform such raw materials improving their aesthetic features, thus obtaining mineral pigments of various colours. Around 2000 B.C., man realised that a range of browns and reds could be obtained by calcining raw ochres in air (Cornell and schwertmann, 1996). Probably the Greek populations that settled in the magna Graecia (Arena, 1996) - south of italy - between viii and vii century B.C. were also aware of this. in magna Graecia, art expressed itself through the realisation of numerous polychrome artefacts, making a wide use of mineral pigments to decorate plasters, pottery and other handmade objects. vitruvius talks about the use of “natural earth pigments” in Greek art in his book vii of “De Architectura” (vitruvius, 1990). he points out that, in Athens, when an ochre vein was found in the silver quarry, it was followed and extracted as if it were a precious raw material.

in particular, many artefacts, decorated with

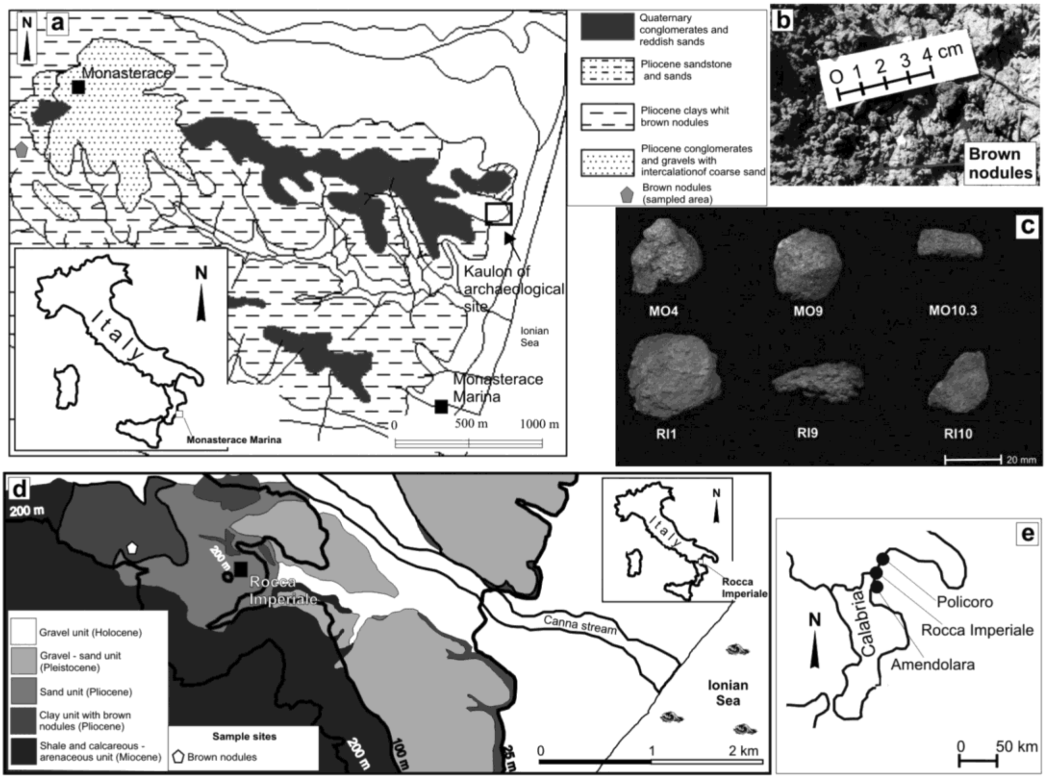

Fig. 1 - a) semplified geological map of monasterace area (by De Francesco *et al*., 2009 modified); b) image of monasterace nodules in clay sediments; c) studied samples (mo= monasterace, ri = roccaa imperiale); d) semplified geological map of rocca imperiale area - by miriello and Crisci, 2006 modified; e) location of some Greek archeological sites near rocca imperiale.

Fig. 2 - Decorated heads of lion (v sec. B.C.) discovered on the "Colle della Passoliera" at monasterace - Calabria, italy (monasterace museum).

mineral pigments, were found, during excavations, in the archaeological area of the ancient Greek colony called Kaulon, located in Calabria - south of italy - on the ionian coast, near the village of monasterace marina (Fig. 1a). Among the findings above, we may mention architectonic earthenware dating back to v century B.C. (Greco, 1996; raco, 2000) relating to a roof of the "colle di Passoleria", where we find representations of leonine heads decorated with pigments of various colours-black, brown and red (Fig. 2). looking at these beautiful works of art, many archaeometric questions and scientific issues arise. the present study will attempt to shed new light on some of these questions and, in particular if raw materials potential source of mineral pigments could be locally found. the same pigments will be reproduced in laboratory and the mineralogical transformations as well as chromatic alterations taking place during the heating process will be monitored.

SAmPlinG oF thE noDulEs

literature only mentions few Calabrian areas where ochre quarries exist. some historical quarries have been signalled in Pazzano, a village in the province of reggio Calabria (scarzella and natale, 1989) and in the "Grotta della monaca", a karstic cave located in the village of sant'Agata d'Esaro in the province of Cosenza (Dimuccio *et al.*, 2005). however, in an area few kilometers away from Kaulon, we found outcrops of Pliocene clay sediments (Fig. 1a) of the monte narbone Formation (Cavazza *et al.*, 1997). the clay sediments closer to the archaelogical site of Kaulon are generally affected by moderate agricultural activities. on the contrary, the clay sediments found approximately 3.5 kilometres north-West from the archaeological area have a lower degree of anthropisation, which allowed us to detect numerous, centimetric size, brown nodules (Fig. 1b and 1c). some of these (samples mo4, mo9, mo10.3) were easily sampled on the surface of the clay sediments. the location of the sampled area is shown in Fig. 1a. the nodules have a coarse sand aspect (Wentworth, 1922) and some of them crumble easily producing a brownish/ reddish powder. it is likely that their aspect, which is very similar to the one of typical ochres, attracted the attention of Greek colonists, who had already used the same kind of clay to produce bricks (De Francesco *et al.*, 2009); and it is also likely that they used the nodules for the production of mineral pigments.

Brown nodules, similar to the ones sampled near the village of monasterace, were detected in the village of rocca imperiale, in the province of Cosenza (Fig. 1d). Also in rocca imperiale the nodules are easily found in Plio-Pleistocene clay sediments (Fig. 1c and 1d) on top of the "rocca imperiale thrust" (ogniben, 1969; Ghezzi, 1973; Cucci and Cinti, 1998). some of these nodules (samples ri1, ri9, ri10) were sampled by the area shown in Fig. 1d. Plio-Pleistocene clay of rocca imperiale was used during the middle Age to produce bricks (miriello and Crisci, 2007) and we may assume that also Greek colonists of the close areas of Amendolara and Policoro (Fig. 1e) used the nodules to produce pigments.

our research does not aim to study the geological genesis of monasterace and rocca imperiale nodules, but it aims to prove that they can be used to produce mineral pigments, starting from the study of their chemical composition and mineralogical and colorimetric changes that take place during the heating process in air. however, iron-manganese nodules and concretions may form in soils after reduction and subsequent oxidation of Fe and mn, as a result of seasonal changes in soil moisture (liu *et al.*, 2002; scarciglia *et al.*, 2003). under reducing conditions, Fe and mn release Fe(ii) and mn(ii) ions to the soil solution. When the soil dries out, Fe(ii) and mn(ii) oxidize and precipitate, forming new metal oxides.

the present study may be considered as a preliminary phase of a future research, which will be carried out on a higher number of nodules.

ExpErimEntAl AnD AnAlytiCAl mEthoDs

Each nodule was pulverised in an agata mortar and heated in air at a controlled temperatures (275°C, 400°C, 550°C and 750°C) for 8 hours.

major chemical composition of the natural nodules was performed by sEm-EDs (scanning Electron microscopy with Energy Dispersive X-ray spectroscopy) on pressed pellets, which were representative of the powder bulk sample (tABlE 1).

the mineralogical composition of natural and heated samples was studied using a Bruker D8 Advance XrD Diffractometer operating at 40 kv and 40 mA, Cu Kα radiation, monochromated with a graphite sample monochromator. scans were collected in the range 3 - 60° 2θ using a step interval of 0.02° 2θ, with a step-counting time of 3 seconds. the EvA software programme (DiFFrACplus EvA) was used to identify the mineral phases in each X-ray powder spectrum, by comparing experimental peaks with 2005 PDF2 reference patterns. the qualitative mineralogical

tABlE 1
SEM-EDS microanalysis of Monasterace (MO) and Rocca Imperiele (RI) nodules.

	sio_2	tio_2	Al_2o_3	Fe_2o_3	mno	mgo	Cao	na_2o	K_2o	so_3	sum
mo4	23.74	0.55	8.21	31.79	0.25	1.97	8.65	1.25	3.83	19.76	100.00
mo9	26.77	0.55	7.51	25.17	0.20	2.06	14.27	1.88	1.80	19.80	100.01
mo10.3	35.72	0.50	8.61	45.27	0.34	2.17	1.13	2.55	1.67	2.03	99.99
ri1	27.21	0.61	7.57	33.97	0.26	1.31	4.18	1.05	1.82	22.02	100.00
ri9	2.94	0.16	1.27	59.19	0.24	0.66	0.48	0.44	0.21	34.42	100.01
ri10	6.21	0.17	2.50	46.82	0.19	0.48	0.40	0.46	0.60	42.16	99.99
standard deviation	12.95	0.20	3.20	12.37	0.05	0.74	5.59	0.83	1.26	13.84	

composition of each mineralogical phase detected in the XrPD spectrum was calculated with the EvA support programme. the results are summarised in Fig. 3.

in order to study the variations in colour produced by the heating process, we carried out - on pulverised nodules in agata mortar, sieved through Astm sieve no. 200 (size 75 μm) - colorimetric measurements with a Konica minolta spectrophotometer Cm- 2600d under standard illumination D65, including the specular component (measuring area: 8 mm). this process determined the trichromatic colorimetric coordinates in the CiE-$L^*a^*b^*$ space (L^* represents brightness: 0 = black, 100 = white; +a^* = red; -a* = green; +b* = yellow; -b* = blue) as defined by the *Commission International de l'Eclairage* (CiE). the results are shown in tABlE 2. the colour difference between the natural sample and the sample heated at 750°C was measured by the calculation of ΔE^* (tABlE 3), which is defined as: $\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta \alpha^* +) + (\Delta b^*)^2}$.

rEsults AnD DisCussion

Chemical composition

the definition of ochres in scientific literature is rather vague. they are typically composed of two types of iron oxide (Fe_2o_3 and Feo), mixed with varying proportions of clay, silicates and other minerals (Popelka-Filcoff *et al.*, 2007). however, we may say that the monasterace and rocca imperiale nodules, which have more than 10-12 % of Fe_2O_3 (tABlE 1), may be classified as ochres (Benbow, 1989). in Fig. 4a and in tABlE 1, it is possible to observe nodules with a content of Fe_2o_3 varying from 25.17 % of sample mo9 to 59.19 % of sample ri9. Also extremely variable are sio_2, Cao and so_3 (Fig. 4a and tABlE 1). An important difference between the monasterace and rocca imperiale nodules lies in the content of mgo, so_3 and Al_2o_3. monasterace nodules clearly differ from the rocca imperiale ones because of their higher content of mgo (tABlE 1 and Fig. 4b). Furthermore, rocca imperiale nodules generally have a lower content of Al_2O_3 (except for sample ri1) and a higher content of SO_3. these clear differences (Fig. 4b) could allow the determination -in future studies- of the provenance of mineral pigments used to produce archaeological artefacts, provided that they were produced with mineral pigments prepared using rocca impariale or monasterace nodules.

Mineralogical composition of natural and heated samples

Generally, ochres are composed of variable quantities of iron oxides, such as hematite (α-Fe_2o_3) or/and goethite (α-Feoo) together with some minerals called "white pigments", eg.

Samples		Natural	275 °C	400 °C	550 °C	750 °C
MO4	Max.	Jarosite	Jarosite	Anhydrite	Anhydrite	Anhydrite
		Quartz	Quartz	Quartz	Hematite	Hematite
		Gypsum	Muscovite	Muscovite	Quartz	Plagioclase
		Chlorite	Anhydrite	Plagioclase	Muscovite	Quartz
		Muscovite	Plagioclase	Rutile	Plagioclase	Muscovite
	Min.	Plagioclase			Rutile	Rutile
	Powder's image					
MO9	Max.	Quartz	Hematite	Hematite	Anhydrite	Anhydrite
		Gypsum	Quartz	Anhydrite	Hematite	Quartz
		Plagioclase	Plagioclase	Quartz	Quartz	Hematite
		Muscovite	Anhydrite	Plagioclase	Rutile	Rutile
		Goethite	Muscovite	Chlorite	Muscovite	Muscovite
		Chlorite	Chlorite	Muscovite	Plagioclase	Plagioclase
	Min.		Rutile	Rutile		
	Powder's image					
MO10.3	Max.	Goethite	Quartz	Quartz	Muscovite	Quartz
		Quartz	Muscovite	Muscovite	Quartz	Hematite
		Muscovite	Hematite	Hematite	Plagioclase	Plagioclase
		Rutile	Plagioclase	Plagioclase	Hematite	Muscovite
		Plagioclase	Rutile	Rutile	Rutile	Rutile
	Min.	Montmorillonite				
	Powder's image					
RI1	Max.	Goethite	Plagioclase	Anhydrite	Anhydrite	Anhydrite
		Quartz	Hematite	Hematite	Hematite	Hematite
		Plagioclase	Anhydrite	Muscovite	Plagioclase	Plagioclase
		Gypsum	Muscovite	Quartz	Quartz	Quartz
		Chlorite	Quartz	Plagioclase	Muscovite	Muscovite
	Min.	Muscovite				
	Powder's image					
RI9	Max.	Goethite	Hematite	Mikasaite	Mikasaite	Hematite
		Quartz	Pyrrhotite	Hematite	Hematite	Quartz
		Pyrrhotite	Quartz	Quartz	Quartz	
		Pyrite				
	Min.	Rosickyite				
	Powder's image					
RI10	Max.	Goethite	Hematite	Hematite	Hematite	Hematite
		Quartz	Quartz	Quartz	Quartz	Quartz
		Gypsum	Anhydrite	Anhydrite	Anhydrite	Anhydrite
		Chlorite	Illite	Illite	Plagioclase	Plagioclase
		Illite	Plagioclase	Plagioclase		
	Min.	Plagioclase				
	Powder's image					

Fig. 3 - mineralogical associations of natural nodules and of those heated at 275°C, 400°C, 550°C and 750°C as detected by XrPD analysis. mineralogical composition is supported by the image of the natural powder and of that heated at 275°C, 400°C, 550°C and 750°C.

TABLE 2
*CIE-L*a*b* colorimetric coordinates of the natural nodules' powder and of that heated at 275°C, 400°C, 550°C and 750°C.*

	natural	275°C	400°C	550°C	750°C
L*					
mo4	65.83	51.08	45.02	44.33	45.74
mo9	57.15	48.36	47.70	46.40	46.38
mo10.3	46.26	34.25	33.37	34.14	36.50
ri1	57.78	38.67	37.85	39.33	48.92
ri9	48.82	34.49	25.66	35.05	38.77
ri10	40.86	33.70	32.52	34.42	37.73
a*					
	natural	**275 °C**	**400 °C**	**550 °C**	**750 °C**
mo4	10.74	18.50	20.00	27.20	32.74
mo9	14.60	16.64	17.40	19.91	23.36
mo10.3	20.08	20.32	19.11	20.21	23.09
ri1	12.66	21.62	22.33	27.21	29.21
ri9	13.78	24.16	19.42	23.89	31.13
ri10	13.92	21.51	21.79	27.32	28.98
b*					
	natural	**275 °C**	**400 °C**	**550 °C**	**750 °C**
mo4	31.78	26.87	28.35	31.04	34.99
mo9	27.79	19.81	20.52	21.42	23.98
mo10.3	29.49	18.30	16.82	16.78	18.96
ri1	35.21	22.82	22.84	26.10	27.40
ri9	30.44	25.84	15.23	18.86	26.00
ri10	31.63	21.26	20.93	24.04	22.86

TABLE 3
Color difference between natural sample and that heated to 750°C calculated by ΔE.*

	ΔE*(natural-750 °C)
mo4	29.97
mo9	14.40
mo10.3	14.67
ri1	20.33
ri9	20.54
ri10	17.71

aluminium-silicates, quartz, anhydrite, calcium compound and gypsum etc. (Elias *et al*., 2006).

As regards the nodules analysed in the present study, the mineralogical composition may sometimes be more complex. Fig. 3 shows the qualitative mineralogical composition of natural nodules and of their powder heated for 8 hours at 275°C, 400°C, 550°C and 750°C.

All natural and unfired samples, except for mo4, contain goethite, being the main phase in samples mo10.3, ri1, ri9, and ri10. The lowest amount of goethite was detected in sample mo9. hematite only occurs after the heating process. Quartz is present in all natural samples, whereas gypsum and chlorite were detected in

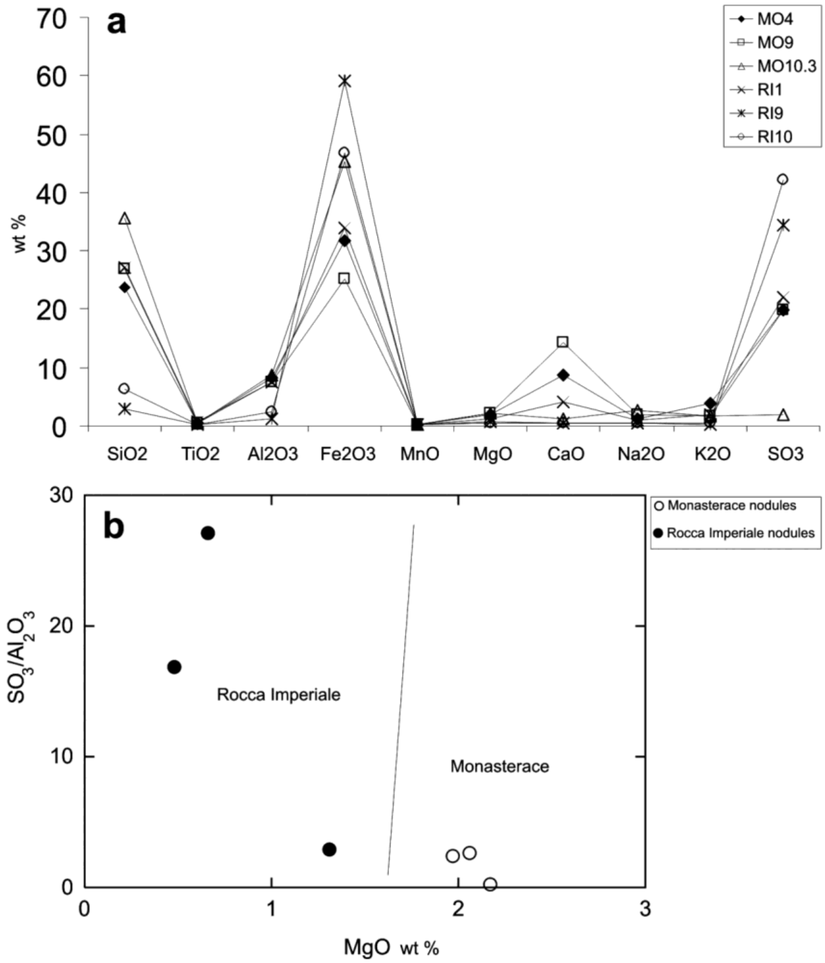

Fig. 4 - a) major chemical element distribution pattern of the nodules by sEm-EDs analysis; b) Bivariate plot of mgo vs. so_3/Al_2o_3 for nodules.

samples mo4, mo9, ri1and ri10. Plagioclase is present in samples mo4, mo9, mo10.3, ri1, ri10 and muscovite was detected in all samples except for ri9 and ri10; other minerals are present only in single samples, such as jarosite (in mo4), rutile (in mo10.3), pyrite, pyrrhotite and rosickyite (in ri9), illite (in ri10) and montmorillonite (in mo10.3). the mineralogical composition of natural samples explains the high content of so_3 detected mainly in the rocca imperiale samples. this is due not only to the presence of gypsum, but also to the presence of pyrrhotite, pyrite and rosickyite in sample ri9.

the heating of natural nodules may produce substantial mineralogical transformations compared to the original raw material (Fig. 3). this kind of transformation accounts for the chromatic changes of the pulverised nodules.

When goethite is heated at 250 °C, it dehydrates transforming to hematite, with an evident change in colour (Pomiès *et al*., 1998; 1999). As a matter of fact, the lowest heating temperature (275 °C) determines the crystallization of hematite in all the samples in which goethite had been initially identified. in sample mo4 (initially lacking goethite) hematite appears only after heating at 550°C.

in all the samples with gypsum, anhydrite appears after the heating process, because of the dehydration of the gypsum itself.

Particularly interesting is the neoformation of rutile and mikasaite after the heating process.

the rutile in samples mo9 and mo10.3 appears after heating at 275°C (Fig. 3), while in sample mo4 it only appears after heating at 400°C.

the mikasaite, a ferric sulphate mineral $Fe_2(so_4)_3$ that was found in ikushunbetsu, mikasa city, hokkaido, Japan (miura *et al*., 1994), is found only in sample ri9 after heating at 400°C (Fig. 3), and it disappears after heating at 750°C.

Colorimetric measurements on powder samples

Among variables which may significantly influence the colour of the powder, we may mention particle size and different crystal shapes (hund, 1981; Cornell and schwertmann, 1996). therefore, in order to reduce the effects of the above mentioned variables, colorimetric measures were carried out on powders which were sieved through an Astm no. 200 sieve (size 75 μm).

the colour of natural pulverised nodules varies from light to dark brown. this pigmentation is probably due to the presence of goethite in samples mo9, mo10.3, ri1, ri9 and ri10. Jarosite likely affects the colour of sample mo4, as natural jarosite generally varies from yellow to brown. Fig. 5 reports the trend of trichromatic colorimetric coordinates in the CiE-l*a*b* space as a function of temperature.

Fig. 5a shows how *L** decreases significantly up to 400 °C in the samples mo10.3, ri1, ri9

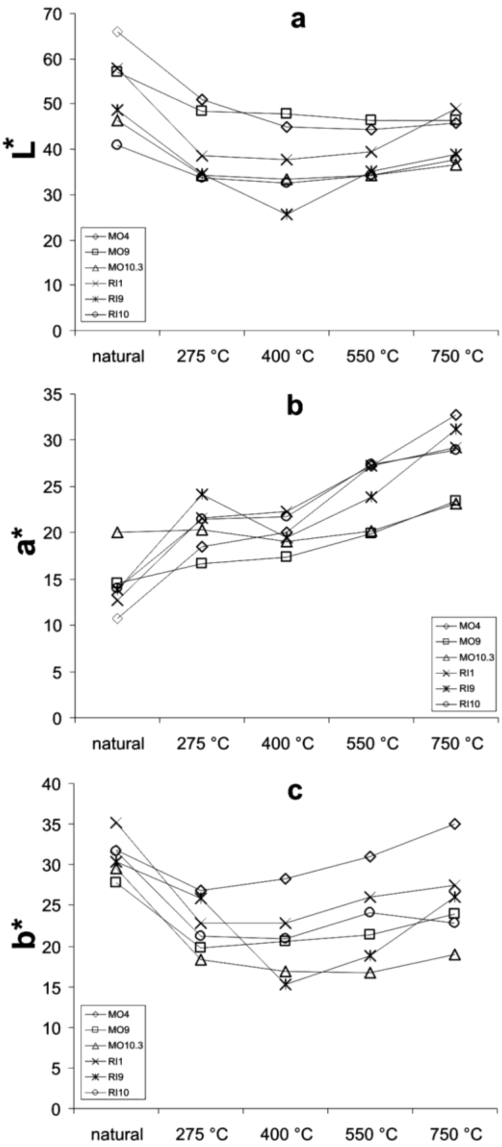

Fig. 5 - Graphic representation of trichromatic colorimetric coordinates in the CiE-l*a*b* space of the natural nodules' powder and of that heated at 275°C, 400°C, 550°C and 750°C. a) trend of l* as a function of temperature; b) trend of a* as a fuction of temperature; c) trend of b* as a fuction of temperature.

and ri10; after 400 °C *L** slightly icreases. in the sample mo4 *L** decreases up 550 °C and subsequently it increases again. only in the sample mo9 *L** constantly decreases up 750°C.

Coordinate *a** gradually increases up to 750°C (Fig. 5b), thus leading to a shifting of the colouring of samples towards the red (Fig. 3), again due to the increase of hematite (nagano *et al*., 1994). sample ri9 denotes a significant reduction of *a** from 275°C to 400°C followed by a prompt increase up to 750°C. this anomalous behaviour may be explained by the crystallization of mikasaite at 400°C which ranges in colour from yellow to brown, thus producing an appreciable fall of *a**.

Coordinate *b** falls significantly up to 275°C for the samples mo4, mo9 and ri1; subsequently it increases up to 750°C. in the sample ri9 *b** decreases up to 400°C and then rises. in sample ri10, *b** has a behaviour which is completely different from the one of all other samples. As a matter of fact, *b** decreases up to 400°C, increases at 550°C, and then decreases again. the behavior of the sample mo10.3 is also interesting, where *b** decreases up to 550°C and subsequently it slightly increases.

*ΔE** between the natural sample and the one heated at 750°C is particularly significant. in tABlE 3, it is possible to observe that the highest *ΔE** was found in mo4, ri1 and ri9 samples. this data confirms that the heating of the powders made with the monasterace and rocca imperiale nodules may lead to significant chromatic variations, which may be employed in the production of mineral pigments.

ConClusions

the present study has shown how brown monasterace and rocca imperiale nodules may be used to produce mineral pigments, varying in colour from brown to red. the heating of the powders leads to significant chromatic variations, mainly due to the formation of hematite, which takes place after heating at 275°C. hematite relatively increases up to 750°C, shifting the colouring of samples to red.

in the future, it will be possible to determine the provenance of some mineral pigments used to produce polychrome artefacts in magna Graecia, by combining the different mineralogical associations, obtained at different temperatures, to chemical data (eg. mgo content) and to trichromatic colorimetric coordinates in the CiE-l*a*b* space.

however, the idea that Greek coloners in Kaulon, Amendolara and Policoro may have used these nodules to decorate polychrome artefacts remains an hypothesis. only future comparisons between archaeological pigments and pigments produced by monasterace and rocca imperiale nodules, will lead to the solution of the archaeometric problem. our future research will attempt to clarify the question through a study of archaeological artefacts and the implementation of the chemical analysis of trace elements.

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rEFErEnCEs

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