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(ERASMUS MUNDUS MASTER IN ARCHaeological MATerials Science)

Laurea Magistrale

Colour of the past. First Archaeometric investigations of Caucasian rock art paintings in Georgia

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''Colour and sound are both wave phenomena: colours are electromagnetic, while sounds are mechanical waves. Both influence our feelings. With some colours we have the impression of energy, while others calm us down; the same applies to sound. We also communicate our feelings through colours. Colour is also probably part of modern human behaviour. Colours have the potential to be very powerful symbols'' (Foreman, 2019).

Contents

Abstract

This research presents the first archaeometric investigation on Damirgaya and Trialeti Rock art sites and the Neolithic settlement Khramis Didi Gora, South Caucasus, Georgia. The aim is to characterize rocks and pigments, to assess painting technology, including the possible identification of organic binders and the compatibility of inorganic pigments with those locally available.

In order to build up our awareness and solve scientific curiosity, the research questions are cleared up through the comparison with adjacent archaeological sites, from Armenia, Azerbaijan and Anatolia, where traces of monochromatic red pigment were recovered in settlements, barrows, on artifacts, such as grinding tools and mainly on rock art. Several analytical techniques, specifically Optical Microscopy (OM) on samples as such and thin sections, X-ray Powder Diffraction (XRPD), and Scanning Electron Microscopy with Energy Dispersive X-ray analysis (SEM-EDX) were used to obtain mineralogical and chemical composition of the samples. Moreover, with the contribution of Fourier-Transform Infrared (FTIR) and Raman Spectroscopy, inorganic compounds were better characterized in both rock paintings and grinding tools. On the contrary, it was not possible to define organic compounds such as binders, possibly due to their low amount or absence. In terms of compatibility with local supplies, with the help of thin section and cross section analysis, it was possible to deduce that the mineralogical composition of the rocks is relatively similar to pigment samples.

In terms of pigments, hematite was the major pigment used for rock art and grinding tools, while in terms of rock samples, that of Trialeti is an igneous basaltic dacite, whereas that of Damirgaya is a rock mainly composed of quartz, but it is also characterized by other minerals, such as iron oxides are likely present, as well as phyllosilicates.

Key words: Hue, Pigment, Archaeometry, Rock Art, South Caucasus Georgia, Neolithic Settlement, Grinding Tools, Comparisons with adjacent sites and Ethnography.

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List of abbreviations

ARCHMAT	Archaeological material science
B.P.	Before present
FTIR	Fourier-Transform Infrared Spectroscopy
OM	Optical microscopy
SEM-EDS	Scanning electron microscopy with energy dispersive X-ray spectroscopy
KA	Kura-Araxes Culture
E.g.	For example
A.s.l	Above Sea Level

1. Introduction

1.1 The history of Rock Art in Caucasus

The Caucasus is characterized by vast intertwist mountains, steppes, marshes, and valleys, compressed by the Black and Caspian Sea (Sagona, 2017). Today, this territory includes the Republic of Georgia, Azerbaijan, and Armenia, and in geographical terms the Greater and Lesser Caucasus Mountains, and the intra-Caucasus depression, along with the Sioni and Kura River basins (Chataigner et al., 2014).

For what concerns archaeology, the Caucasus has a significant presence of Prehistoric and historic archaeological sites, where material culture is well expressed on settlements, barrows, and rock art sites.

Paintings (pictographs) and engravings (petroglyphs) on natural rock surfaces, which include caves, rock shelters, rock walls, or portable rocks are widespread, with significant variations in chronology, production, and cultural contexts (e.g., Whitley, 2001).

Rock art in the Caucasus is scarcely known and includes almost exclusively petroglyphs and a few examples of pictographs (Figure 1.1). The most significant rock art sites are known in five districts of the Azerbaijan Republic: Gobustan, Shikhov, Apseron, Gemigaya (Nakhchivan), and Kelbajar (Anati, 2014). In particular, the rock art sites in Gobustan are the most important, where more than 6000 petroglyphs representing humans, animals, various symbols, and inscriptions were revealed, covering the period from the Upper Palaeolithic to the Middle Ages (Sigari et al., 2019).

Other engravings and paintings have been discovered in the Syunik region and at the Kasakh River gorge (Geghamavan-1 cave) in Armenia (Khechoyan et al., 2015), as well as engravings at Ughtasar (Hermann, 2011). Likewise, copious prehistoric traces of art are well known in Anatolia, at Keçe Cave (Yaman, 2019), Tırşin Hill (Tümer, 2018) or in the engravings of Çatak, Hakkari, Cevaruk (Anati, 1972), Palanli (Anati, 1968), and pictographs in Çildir, Inkaya Cave (Donmez, 2019), and Deraser Cave (Soydan & Korkmaz, 2013). Further rock art sites have been reported at – Dagestan, near the towns of Buynaksk and Chiyana-Khit (Sagona, 2017).

Figure 1.1 - Map of the Caucasus depicting the presence of prehistoric painted and engraved rock art sites (https://earth.google.com/web/@40.31178899,41.41326722,1306.27364972a,2596591.37215108d,30.00002781y,360h,0t,0r/data=MicKJQojCiExR1FBMUVGMDFIM3MyUlFUSjZ3MWxxRV9ndnRpN3BJR3U)

South Caucasus Georgia has a little amount of rock art sites, such as in west Georgia, specifically in the Apkhazeti village Anukhva, where human hand contours, crosses, and circles have been found. Also, at Chiatura, Mghvimevi art impressions belong to the Palaeolithic period (Ksica, 1994). The noticeable rock art of Georgia is in Patara Khrami/Trialeti petroglyphs (Sagona, 2017). Sometimes engravings are depicted in Middle Bronze Age barrows at Zurtaketi mound (Meskheti region), where there is the presence of mobile petroglyphs which were inserted in the walls of burial chambers. Here, common depictions are deer, goats, scratched lines, rhomboids, and other geometric signs (Goguadze, 2010).

In the Trialeti area, about 100 petroglyphs have been recovered near the gorge of river Patara Khrami, including animal figures such as deer, horses, camels, and ambiguous animals. There are snakes, birds, fishes, crosses and sun depictions, and hunters with their arrows too. Based on archaeological findings on the site of Trialeti and iconographic investigation of the rock art, the petroglyphs have been relatively dated from the Mesolithic to the Bronze-Iron Age (Gabunia et al., 1980).

Besides petroglyphs in the south Caucasus, Georgia has painted rock art sites too, such as the recently discovered rock art sites which will be the subject of the present research: Damirgaya and Trialeti.

1.2 Geological and archaeological settings

The Republic of Georgia's geological, structural, and stratigraphic history is congruent with the observable depositional sequences and lithologies (Adamia, 1992). Because of the subsequent extensional separation during the early Mesozoic with the development of Jurassic Island arc volcanic and narrow oceans, Georgia can be treated as a single unit during the Palaeozoic, up to the Hercynian collisional event. However, four primary morphological and tectonic units can be identified in the Caucasus: (1) the Ciscaucasian plain (Scythian platform), which includes the Greater Caucasus' foredeeps. (2) the Greater Caucasus itself, which stretches WNW-ESE. (3) the Transcaucasian intermontane basin system (4) The Lesser Caucasus, which has the most varied structure and an arcuate N-convex shape (Eppelbaum and Khesin, 2012). Paleozoic rocks can be found in the Khrami, Dzirula Salient, and Loki massifs. Likewise, it should be told here that due to the obvious interplay of minor block movements, block accretion, and the complexities imposed by sea-level variations, Georgia's Mesozoic-Cenozoic stratigraphic history is complicated. A detailed geological map of Georgia (Figure 1.2) was published by Adamia in 2004. It shows that breccia and conglomerates are present in Marneuli (Figure 1.3), while volcanic tuff, basalt and andesite are in Trialeti Plato.

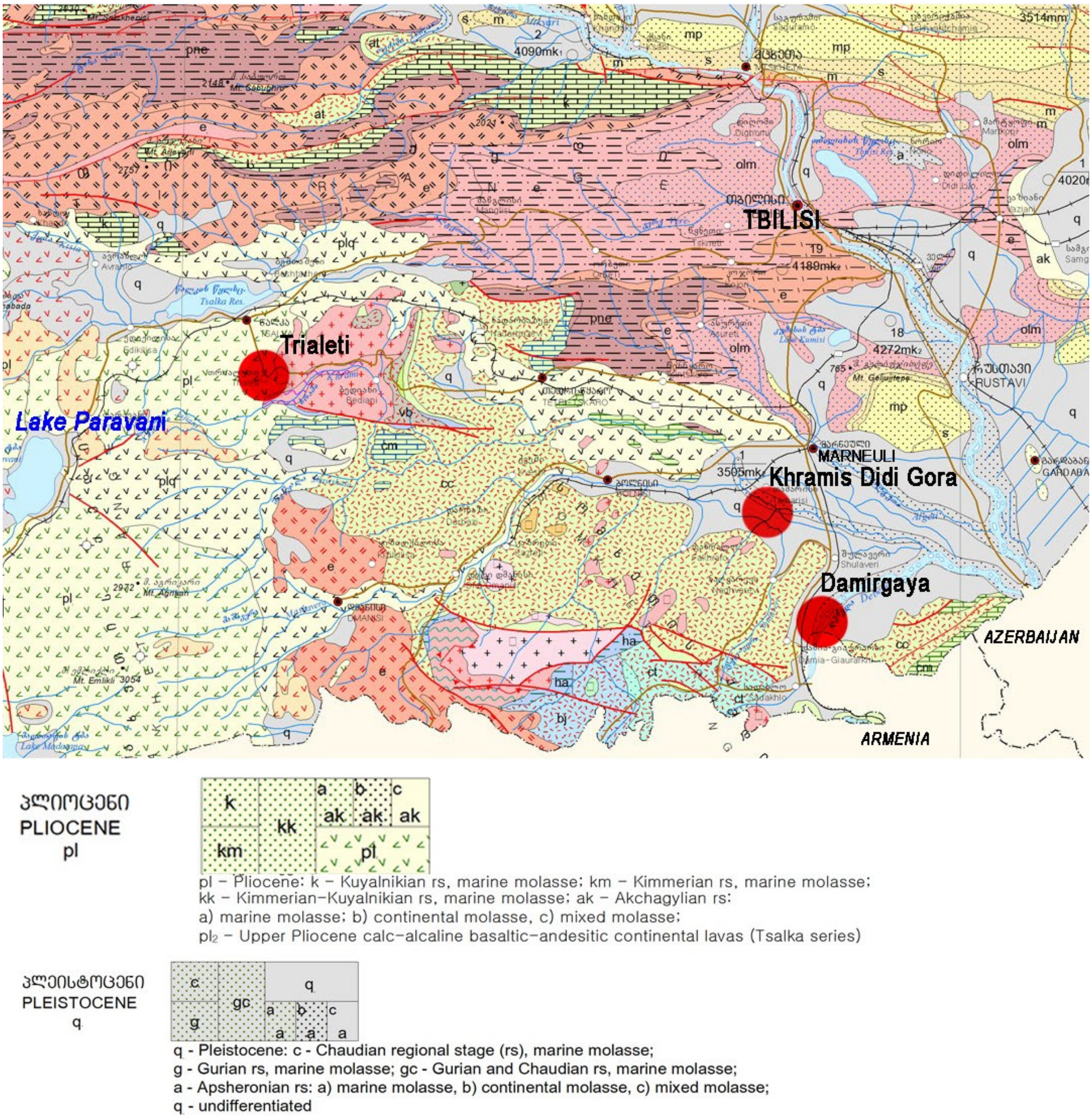

Figure 1.2 - Geological map, modified after Adamia, 2004, with location of the archaeological sites under investigation.

Damirgaya

Damirgaya is a rock shelter located in southern Georgia in the northern foothills of the Lesser Caucasus, 3 km south of the village Kasumlo, on the ridge of Berduji, at an altitude of 687 m a.s.l. The site is one of the rock shelters that originated in the sediments of the Marneuli block, which is structured from Jurassic-Quaternary age terrigenous, carbonate, and volcanogenic deposits (Figure 1.3). The Marneuli block consists of sedimentary and igneous deposits, namely lava breccia, andesite-basalts, and dacites (Mrevlishvili, 1997). Geological processes, i.e., weathering and erosion, with post-volcanic activities such as moving hydrothermal solutions with consequent cooling of the superheated lava, led to form boulders with dimensions of 5-10 m. Additional erosion formed the rock shelters.

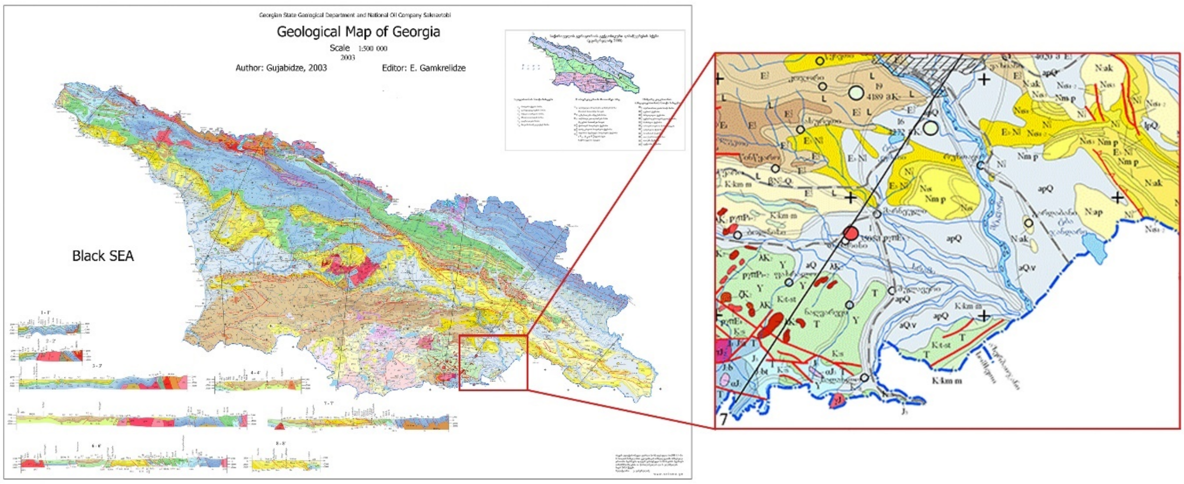

Figure 1.3 - Geological map of Marneuli (modified after Gujabidze, 2003). For more visibility please follow the link: http://science.org.ge/newsite/wp-content/uploads/Geology_Georgian_A0.gif?fbclid=IwAR2iZHGMC0W-3Vh1WJkMfgX7yREfp11AXEd6x-L4GAokdbCQjVayB7QOQ0Y

Azeri people settled there in late medieval times and gave this site the name of Damirgaya, which means ''iron rock''. The site was surveyed in 1980 by Tamaz Kiguradze (Menabde et al., 1986), while the first archaeological investigation was carried out by the archaeologist Levan Losaberidze in 2017 (Losaberidze, 2020). The rock shelter (5.5 m height; 7.3 m width) opens towards the north. Red paintings are located on the central and western parts of the inner wall and spread about 3-3.5 m. The images are 10-20 cm wide and are divided into three groups: 1) Geometric; 2) Zoomorphic; 3) Indeterminate (Figure 1.5a). Painted rock art is depicted and well preserved, despite contemporary graphite damage performed by local herdsmen (Figure 1.4b).

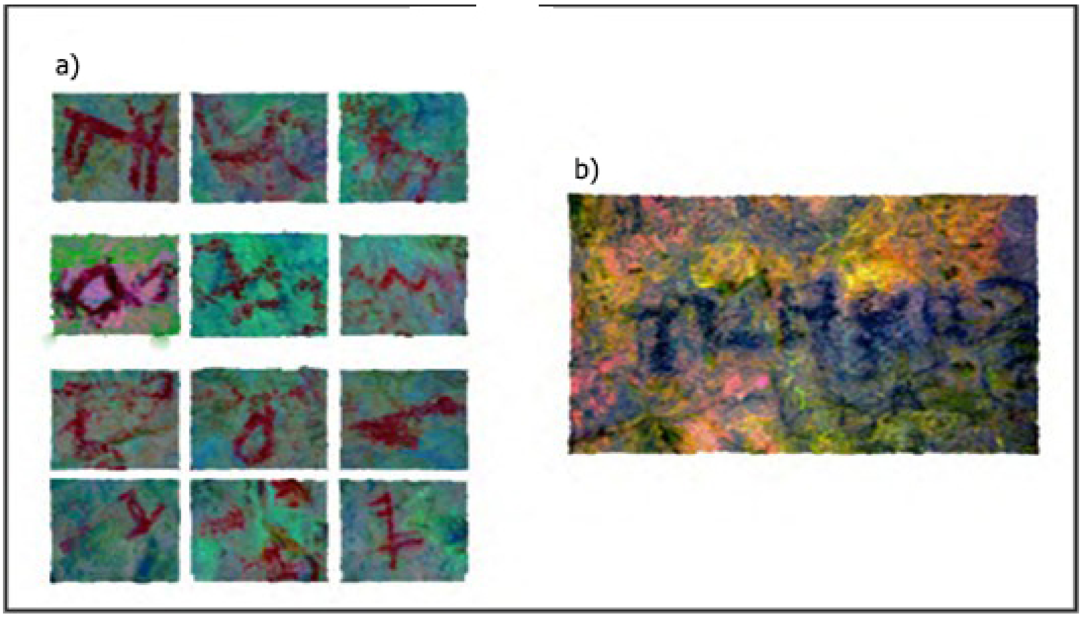

Figure 1.4 - a) Damirgaya, DStretch image of zoomorphic and geometric figures; b) Damirgaya, contemporary artificial damage (Losaberidze, 2020)

For what concerns the dating of Damirgaya, Tamaz Kiguradze (Menabde, 1986) suggested dating the site broadly from Neolithic to Early Bronze Age, but there are no other studies regarding the subject (Losaberidze, 2020). Furthermore, in 2020 a small test excavation was carried out in the surroundings of the site, where archaeologists discovered lithics that might be dated to the Prehistoric period, whilst pottery fragments and bones might be from the Middle Ages. An archaeological survey carried out in the nearby area allowed to identify seven sites with materials dating to the Neolithic period (Chilingarashvili, 2020).

Trialeti

The Adzharo-Trialet stands out in the northwest of the Lesser Caucasus. The Adzharo-Trialet ridge, which has summits up to 2,850 meters, is made up of Albian-Lower Senonian island-arc volcanics, Upper Senonian limestone, Paleocene-Lower Eocene tuffaceous flysh, and Middle-Upper Eocene subalkaline and alkaline intermediate volcanics. The last Eocene folding was followed by small syenite-diorite intrusions. The sequence of the Adzharo-Trialet zone is strikingly similar to the Talysh Mountain fold zone, which includes Upper Cretaceous limestone, Paleocene-Lower Eocene tuffaceous flysch, Middle-Upper Eocene subalkaline and alkaline andesite-basalt volcanics, and Middle-Upper Eocene subalkaline and alkaline andesite-basalt volcanics (Eppelbaum, 2012).

Trialeti pictographs were discovered in 2019 as part of a survey conducted by the Georgian Culture Agency. Paintings were discovered in gorges developed by pseudotachylyte, which was formed during the Late Pleistocene by lava defects and unequal internal erosion, resulting in andesite and basalt rocks. Conversely, groundwater washed layers of rocks, and the traces of drowned strata were well illustrated during archaeological investigations in 1974-75. Archaeologists also recovered numerous obsidian artifacts with faunal remains (Gabunia, 2020). The paintings are depicted in the Kvemo Kartli region, the southern section of village Gantiadi, and the river Avdriskhevi. Motifs are two: three horizontal parallel lines and animal-like figures, all in monochromatic red pigment (Figure 1.5).

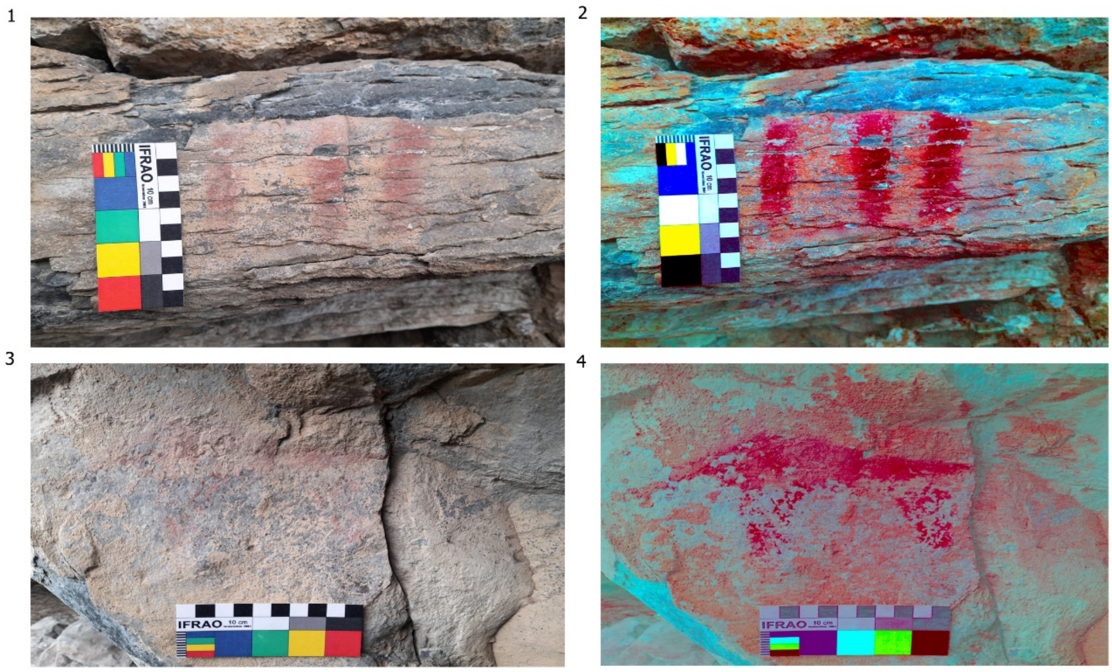

Figure 1.5 - (1) Tiraleti three lines; (2) Three lines with DStretch; (3) animal-like figure; (4) animal-like figure with DStretch; (By Losaberidze, 2020)

The site is still unpublished, and the present research constitutes the first archaeometric study of the context.

Khramis Didi Gora

The Khrami Massif is a granitoid with crystalline slates on its surface. Large wedges of fossiliferous limestone containing Visean and Namurian corals and foraminifera, as well as sandstone with Bashkirian plant remains, may be found within the massif. Graphitic, chloritic, muscovite, biotite, and andalusite schists and gneisses with amphibolites, marble, and quartzites make up the lithology of Khrami. Most of the Paleozoic rocks in Khrami have suffered considerable metamorphism during the Hercynian period (Adamia, 1992).

The Neolithic settlement of Khramis Didi Gora shows common features with the other two sites, such as the use of red monochromatic pigments which have been recovered on several grinding tools.

The Neolithic of the central and southern Caucasus is often referred to as the 'Shulaveri-Shomutepe' culture, after two key sites were excavated in the late 1950s and early 1960s: *Shulaveris Gora*, on the Marneuli Plain in Georgia, and *Shomutepe*, situated in the Kazakh region of Azerbaijan. In the case of Georgia, Shulaveri culture is represented by the following archaeological sites: Shulaveris Gora, Imiris Gora, Gadachrili Gora, and Khamis Didi Gora (Figure 1.6).

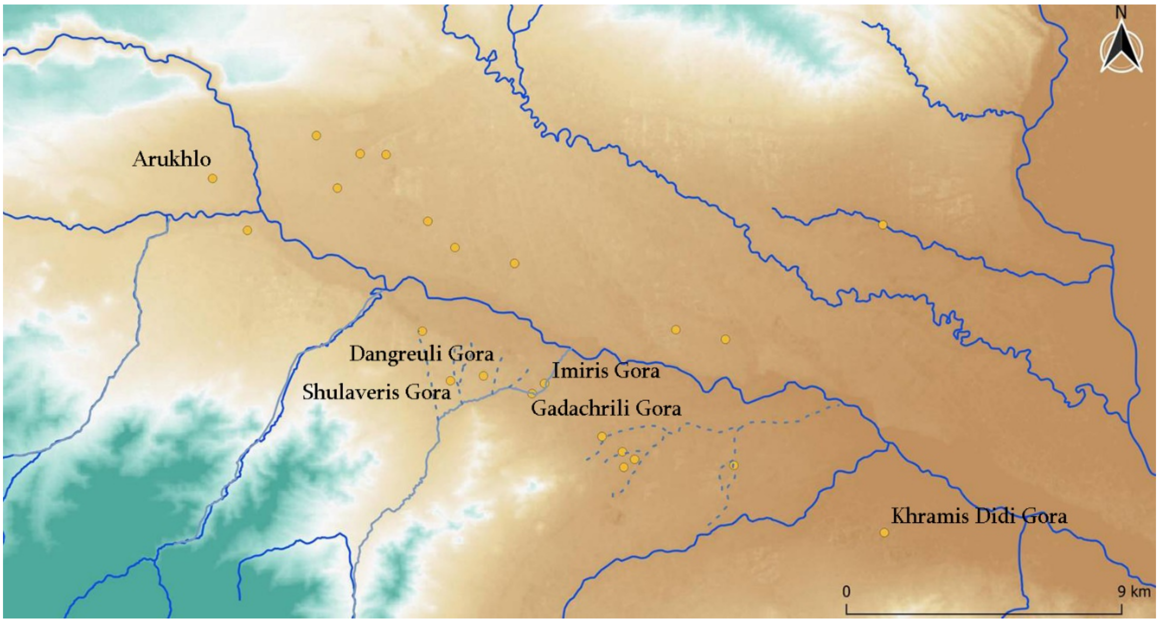

Figure 1.6 - Map of Neolithic sites in Georgia: Shulaveris Gora, Imiris Gora, Gadachrili Gora, and Khramis Didi Gora (QGIS Software)

Though Khamis Didi Gora is the largest Neolithic mound site, measuring about 4.5 ha, most of these archaeological sites are typically small hamlets averaging about 1–1.5 ha in size. The architecture of the settlements is of round shape, made with clay and mudbrick (Japaridze, 2003). The yards of the settlements contain a lot of agricultural artefacts: rubbers and saddle querns, grinding slabs, wasted hammers and edge-ground axes, sling stones and polishing tools, as well as bun-shaped grooved stones possibly used as spoke-shaves, and perforated stone weights, made from sandstone, basalt, and granite. All these indicate systematic farming and an agriculture life (Sagona, 2017).

Most of the grinding tools are made of vesicular basalts. Its minerals, such as hornblende and quartz, have been identified by XRPD analysis, although sandstones were utilized too, and its mineral composition has been determined by the same analysis (Hamon, 2008). Most tools have a semi-circular shape, their sides are shaped by chipping and the ends often show two or three steps of flaking. Pecking was used to smooth the back and side edges and allow a better grasp. The flat to plano-convex working surfaces were often pecked transversely. A polishing zone of 2-to-3 cm wide occupies the ends and sides, if not the whole periphery, of the working surface of these grinders (Hamon, 2008). A crucial part of the present investigation will be dedicated to the traces of red pigments on these grinding stone, mortars, and hand stones.

1.3 Some parallels with adjacent rock art sites

In 2002, noticeable rock art paintings were recovered near the Kasakh River gorge (Geghamavan-1 cave) in Armenia, in the proximity of the newly founded village of Geghamavan at the western foot of Mt. Ara, showing several common features with Damirgaya rock art (Khechoyan et al., 2015).

The name comes from locals and Geghamavan means ''Red Cave'', since most of the interior of the cave – ceiling, walls, and facade – and the surfaces of broken rock slabs retain red ochre paintings. The cave is made of basalt and tuff, the latter showing iron oxides, and hence possibly being the source of the red pigment. Red ochre was utilized to create these perceptible monochromatic rock paintings, which occupancy is outwards and in most of the shelter, but also outside of it, part of the pictographs is affected by direct light. The motifs of Geghamavan-1 even point out similarities with Damirgaya, in the case of animal and human depictions from the Neolithic period, where schematic characteristics can be seen (Figure 1.7). Concerning chronology, the earliest paintings in Geghamavan-1 cave date from the Late Mesolithic/Proto-Neolithic period. Inside the shelter of Geghamavan-1, archaeologists carried out excavations, and they recovered medieval scattered pottery fragments, faunal remains and obsidian tools (Khechoyan et al., 2015). A similar scenario was also portrayed in the case of Damirgaya (Chilingarashvili, 2020).

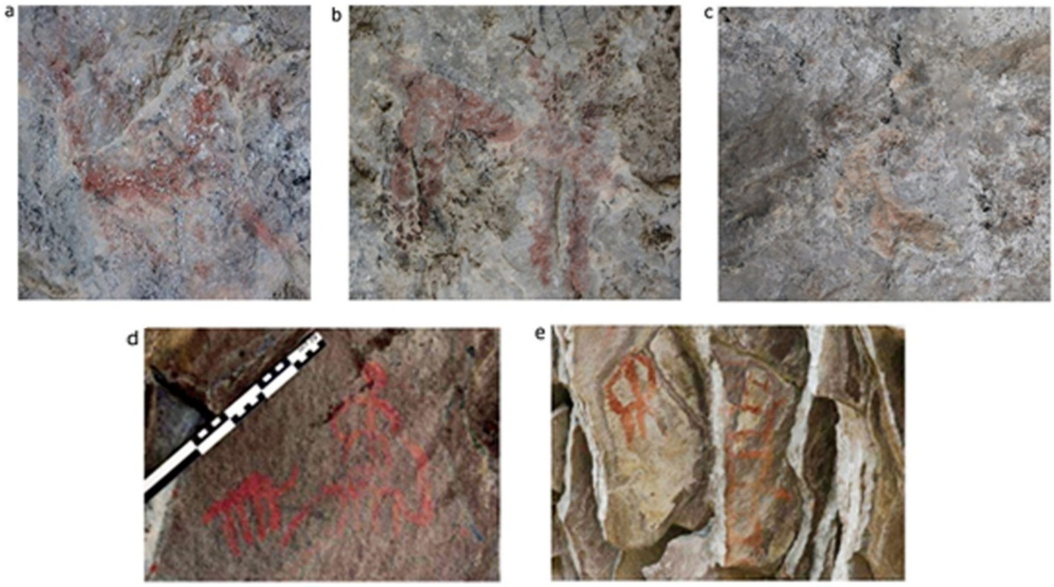

Figure 1.7 - (a-c); Animals and human motifs from Damirgaya (By Losaberidze); (d-e) Animal and human sings from Geghamavan-1 cave (Khechoyan et al., 2015)

Moreover, Damirgaya has some common features with the Neolithic/Early Bronze Age phase at Gobustan rock art site, in Azerbaijan (Anati, 2014), such as animal motifs, mostly cervids and goats, and human depictions, too. A well depicted human figure which has common features with Damirgaya (Figure 1.8 B) is found here (Figure 1.8 A, in Anati, 1984).

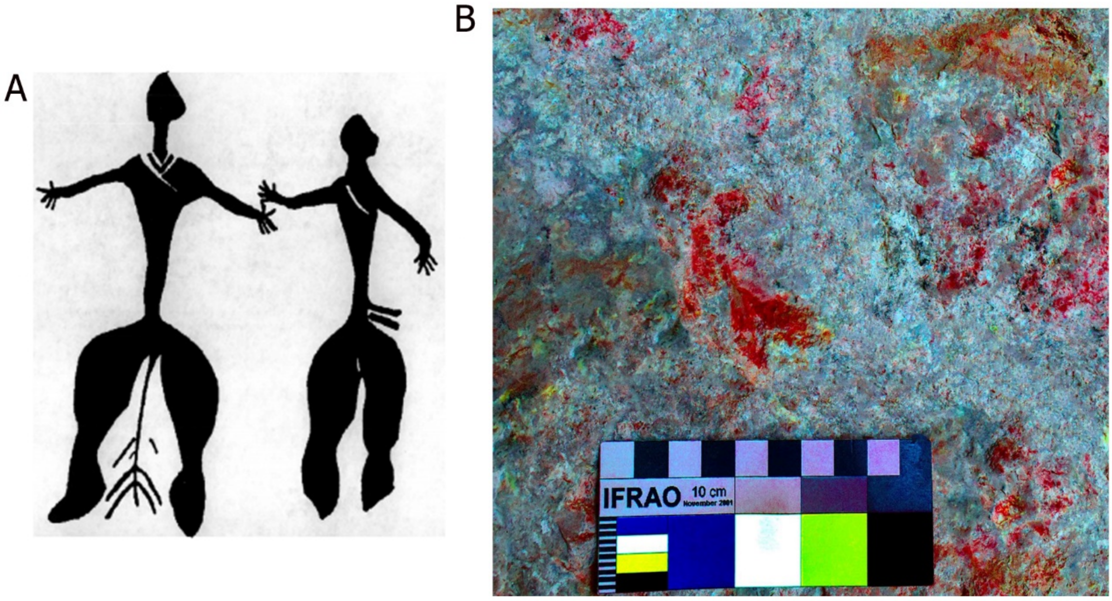

Figure 1.8 - (A) Gobustan rock art (Anati 1984); (B) Human depiction from Damirgaya (By Losaberidze)

Also, it reveals certain related characteristics for what concerns geometric motifs including zigzag lines, linear motifs, rhombus, etc. detected on the wall paintings of the Neolithic settlement of Çatalhöyük (Anatolia) (Figure 1.8 f) (Schotsmans et al., 2020). Wavy lines are also depicted on Neolithic pottery coming from Aruchlo (Georgia) (Figure 1.8 d) (Lyonet, 2012). In case of humans and animal defections, the site also shows common features with goats and deer at Damirgaya (Figure 1.7 a), Imiris Gora (9b) and Khramis Didi Gora (Figure 1.9c). Additional compatibilities can be found with rock art sites in Turkey: engravings from Palani, Hakkari (9e, A and B in Anati, 1968); Çildir (9e (C), in Ceylan, 2015); Tirsin (9e (D) in Donmez, 2019); paintings from Keçe Cave (9g in Yaman, 2019), Inkaya Cave (Donmez, 2019), and Deraser Cave (Soydan & Korkmaz, 2013).

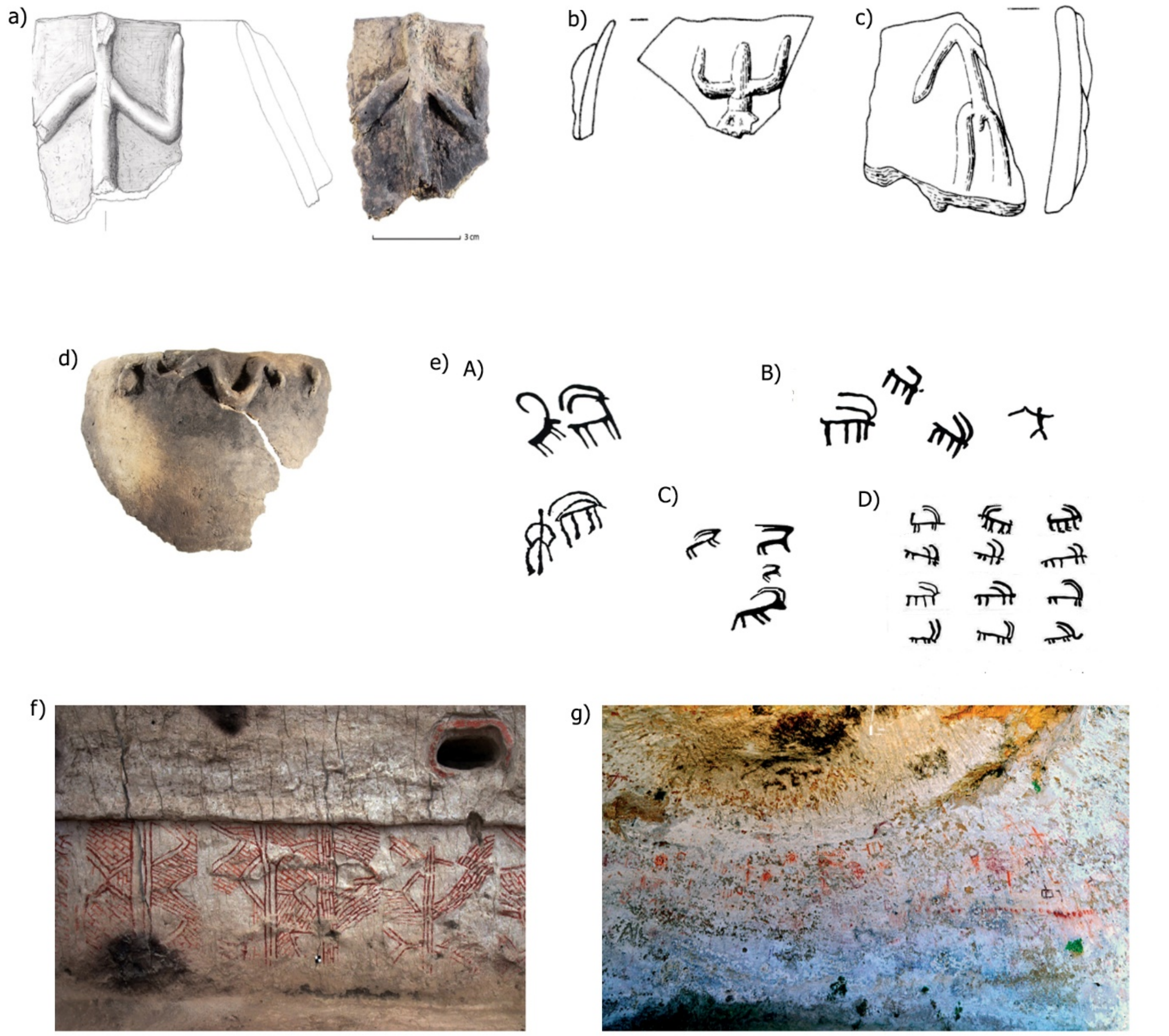

Figure 1.9 - (a)Aruchlo; (b)Imiris Gora; (c) Khamis Didi Gora; (d) Aruchlo, pottery with wavy motif (Lyonnet, 2012); (e) A) Palanli; B) Hakkari (Anati, 1968); C) Cildir (Ceylan, 2015); D) Tirsin (Donmez, 2019); (f) Çatalhöyük (Schotsmans, 2020); (g) Keçe Cave (Yaman, 2019)

Concerning Trialeti rock art, there is the presence of an unclear zoomorphic figure, interpreted as a wild boar (Figure 1.10a), which was also recovered at the Neolithic Beyukdash Mountain in Gobustan, Azerbaijan (Farajova, 2018) (Figure 1.10, a-b).

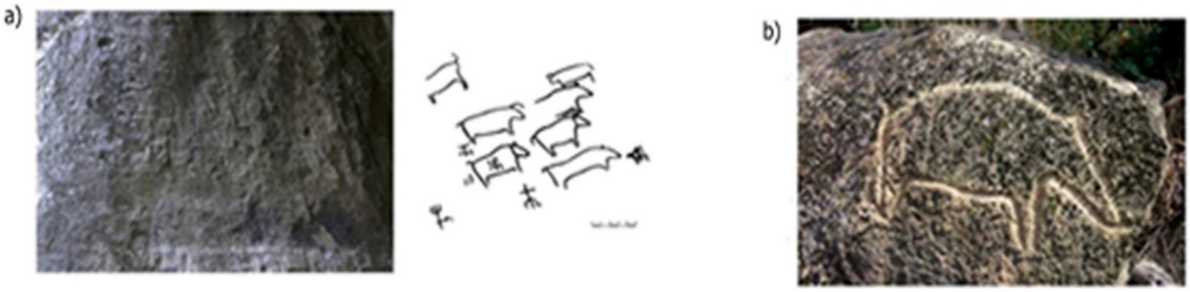

Figure 1.10 - (a-b) Wild boar sketch on Gobustan rock art, Beyukdash mountain, in Azerbaijan (Farajova, 2018)

1.4 Designation of colour in archaeology and ethnography

Based on archaeological recoveries and ethnographic studies, colour from Prehistoric times and up to present expresses art, gender, funerary and religious practices, status, power, festivities, markers for location, etc.

Minerals are usually found to be used as pigments in Stone Age sites, especially in the Upper Palaeolithic period. Mostly, they correspond to inorganic earth pigments and are recovered on rock art sites. A few examples can be cited in particular: the Palaeolithic Kapova Cave with well-sketched animal figures, where hematite and calcite have been used as recurring pigments (Pakhunov et al., 2014). Another famous example of this art is in the neighbouring South Ural Mountains of the Russian Palaeolithic Ignatievka cave, where geometric figures are grouped into two panels, ochre for red and charcoal for black (Haarmann, 2007).

The first emergence of tint in the South Caucasus Georgian archaeological sites is documented in the Palaeolithic Dzudzuana Cave, where flax fibres have been modified, and dyed grey, black, turquoise, and pink, most likely with natural plant pigments (Bar-Yosef et al., 2011).

Furthermore, inorganic pigments were found in the Apiancha Cave (Georgia). It is located on the right bank of the Kodori river, near the village of Tsebelda, or its southern-eastern part, below the mountain range of Apiancha. In the stratigraphic layer of Apiancha L. Soloviov discovered lumps of ochre in 1940. Later, more investigations have been carried out in this cave and archaeologists found Palaeolithic layers where a grinding bowl was discovered with trace of ochres, together with a bear bone, which was revealed to be for rubbing. It was confirmed that life in the Apiancha cave was from Mousterian until the Neolithic period

(Korkia, 2001). Six clods of ochre have also been detected in another Georgian territory, at Khergulis Klde Cave. The stratigraphic layer where they have been found dates to the Neolithic-Bronze Age period (Szymczak, 2020).

So far, ochres have been observed on the settlement of Shulaveri mound, Georgia, where houses are round in shape, floor made of clay, and most of the time surfaces are decorated with ochre (Japaridze, 1971). Imiris Didi Gora and Khramis Didi Gora belong to the same period and geographical settings of Shulaveri mound, and the archaeologists revealed a palette: it is a massive ovoid cobble (26 x 19 x 4 cm) with a wide zone covered by longitudinal striations and peripheral traces of ochre, and with it, a lump of ochre was detected too (dimensions are the following: 6.2 x 5.8 x 2.4 cm) (Hamon, 2008).

The presence of ochre is seen in many Neolithic settlements and burials in Prehistoric Anatolia, where red ochre was used for both ceremonial and mortuary purposes, and it played a crucial role in discourse. The use of red ochre in the Prehistoric architecture of Central Anatolia appears to have a symbolic meaning and it is potentially linked to ritual activities. The red-coloured terrazzo floors of some ritual houses, such as ‘the Terrazzo House' in Çayönü, eastern Anatolia, are distinctive (Erdogu, 2011).

Moreover, traces of red colour were depicted on various grinding tools from Göbekli tepe (Anatolia) which indicates the processing of ochre in ancient times (Dietrich & Haibt, 2020). In parallel, in Neolithic burials of Körtik Tepe the deceased bodies were defleshed and coated with plaster, then coloured with ochre (Erdal, 2014).

Another example is the large and dense site of Aşikli Höyük, Anatolia, dating to 8500–7450 BC, in the Aceramic Neolithic period, where some parts of buildings and floors were painted in red. The same scenario of red paintings was recovered in the Pre-Pottery Neolithic site of Musular (Erdoğu & Ulubey, 2011).

Furthermore, excellently preserved red paintings were discovered in almost all buildings at Neolithic Çatalhöyük (Anatolia), especially in buildings referred to as "ritually elaborated buildings," which Mellaart referred to as "shrines"(Erdoğu & Ulubey, 2011) and Hodder and Pels as “History houses’’ (Hodder & Pels, 2010). Platforms, walls, niches, and space thresholds were all painted red as well. The red colour can also be found in graves, typically on skulls. In all these examples, red represents blood and life, and it has a defensive role in Çatalhöyük (Erdoğu & Ulubey, 2011). Correspondingly, red pigments have been used to decorate objects in Çatalhöyük: one of the most notable is a plaster head adorned with ochre and obsidian (Schotsmans et al., 2020). Likewise, traces of red hue were identified on the floor at the Neolithic site of Yumuktepe (Caneva, 2020). The presence of ochre is also abundant in barrows of the Neolithic period: for instance, several burials related to the Neolithic period present traces of ochre, e.g., the burials of Mentesh Tepe, in Azerbaijan, where there is the delineation of myriad traces of ochre on the deceased bodies and on the floor of barrows (Lyonnet et al., 2016).

A further use to be mentioned is that many potteries Neolithic sites have been decorated with red hue. After the Neolithic period, red hues are again detected in Eneolithic sites such as the Arukhlo I settlement located in the Kvemo Kartli region, Bolnisi Municipality. The buildings is made of clay and mudbrick, and it has a circle shape. The site is foremost and crucial with its archaeological discoveries, one of the most interesting being a round-shaped stone with a human face depiction made in light red pigments, discovered along with numerous pottery fragments (Chikovani, 2015).

Moreover, in some Early Bronze Age cultures, such as the Kura Araxes (KA), the chance of finding traces of red pigments is noticeable: for instance, in the Areni-I cave, in southern Armenia, vessels are painted with ochre and fired to high temperatures, which results in a reddish yellow and grey coloration (Wilkinson et al., 2012). Likewise, the association of ochres to the ceramic production in the KA culture has been also revealed at Khashuri Natsargora site (Georgia), where archaeologists, based on an archaeometric investigation, found that people belonging to the Kura Araxes culture used ochre for pottery decoration (Babetto et al., 2021).

Traces of pigments have been recovered also on Early Bronze Age barrows of Georgia (Bedeni barrows) but due to a lesser interest in pigments investigation, there are no data available (Gobejishvili, 1981).

Again, red pigment is depicted in historical periods too, such as portable rock art with the depiction of a deer, recovered in the Jokhtaniskhevi village site, which is in Tbilisi municipality, northeast of the village of Gldani and based on Numismatic discoveries it was dated at the end of 13th century or at the beginning of the 14th century AD (Chikovani, 2015).

As can be deduced from the traces left on several artifacts in various archaeological sites, red (or more generally, shades of red) pigmentation used in pictograms, were produced by adding different minerals such as goethite or hematite and the possible application of certain organic and inorganic binders.

To sum up, the creative tradition of rock art is reflected in contemporary folk art, and in some areas of the Caucasus people believe in the magic of various figural and non-figural symbols, found in the rock carvings and in the cut stones of masonries. Also, nowadays there are myriads of rock etchings inside of towers in the mountain area of the South Caucasus, and people are still living there (Ksica, 1994).

In the following map (Figure 1.11) all the places mentioned above are listed.

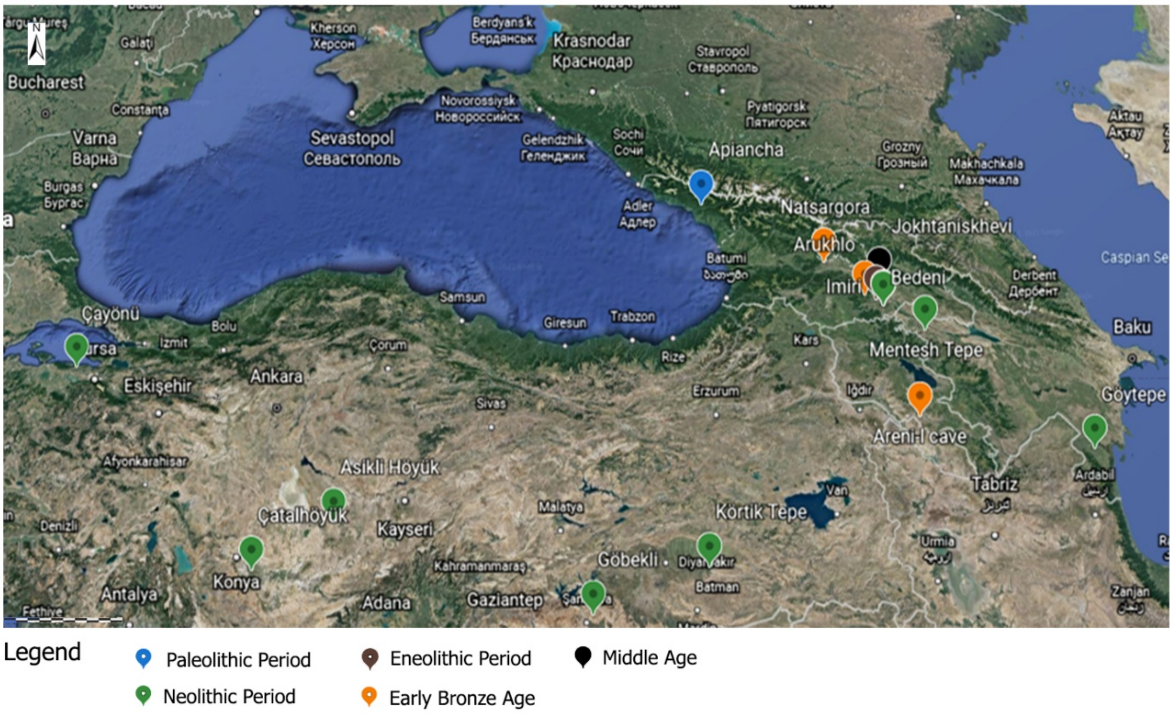

Figure 1.11 - Diffusion of ochre among South Caucasus and adjacent regions from Palaeolithic until Middle Ages (https://earth.google.com/web/@41.37760489,41.20076629,569.60888507a,1922531.66087508d,35y,0h,0t,0r/data=MicKJQojCiExYllzVG9zVmlfZXYyVXB4X2tWMnJvOEc3T0RNZlBwNUw)

1.5 Aim of this work

With the investigation of rocks and monochromatic red pigment samples from the prehistoric rock shelters of Trialeti and Damirgaya, it will be plausible to understand rock and pigment chemical and mineralogical composition, their compatibility with local sources, and eventually the use of organic binders.

Furthermore, it is the first time that the archaeometric investigation is applied to the pigments sampled from grinding tools found at the Neolithic settlement of Khramis Didi Gora, thanks to the collaboration with the Georgian National Museum. Specifically, pigment samples provided from grinding stones, which have relative chronology, can contribute to solve dating issues, and compare Neolithic technological awareness at Khamis Didi Gora with rock art makers in nearby sites.

Particularly, FTIR and Raman spectroscopy were combined to characterise inorganic and organic compounds in the pigments of all sites. In addition, the mineralogical assemblage was confirmed for pigments and further defined for rock samples coming from Trialeti and Damirgaya, by X-ray Powder Diffraction analysis (XRPD). Finally, optical (OM) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDX) were applied on thin and cross sections: on thin sections, they contributed to the identification of the parental rock in Trialeti or Damirgaya; on cross sections, they led to describe in detail the morphology and composition of the pigment layers in the samples from Damirgaya.

2. Materials and Methods

2.1 Materials

2.1.1 Sampling

Samples come from three different archaeological sites (Figure 1.2). Two are Prehistoric rock shelters, Damirgaya (Figure 2. 1 A-B) and Trialeti (Figure 2.1 C). Four pigment and four rock samples were chosen from the two described rock shelters. Additionally, a third sampling was carried out at the Georgian National Museum: six micro-samples of pigments were taken from grinding tools (pestles/hand stones, mortars and grinding stone) coming from the Neolithic settlement of Khramis Didi Gora (Figure 2.2).

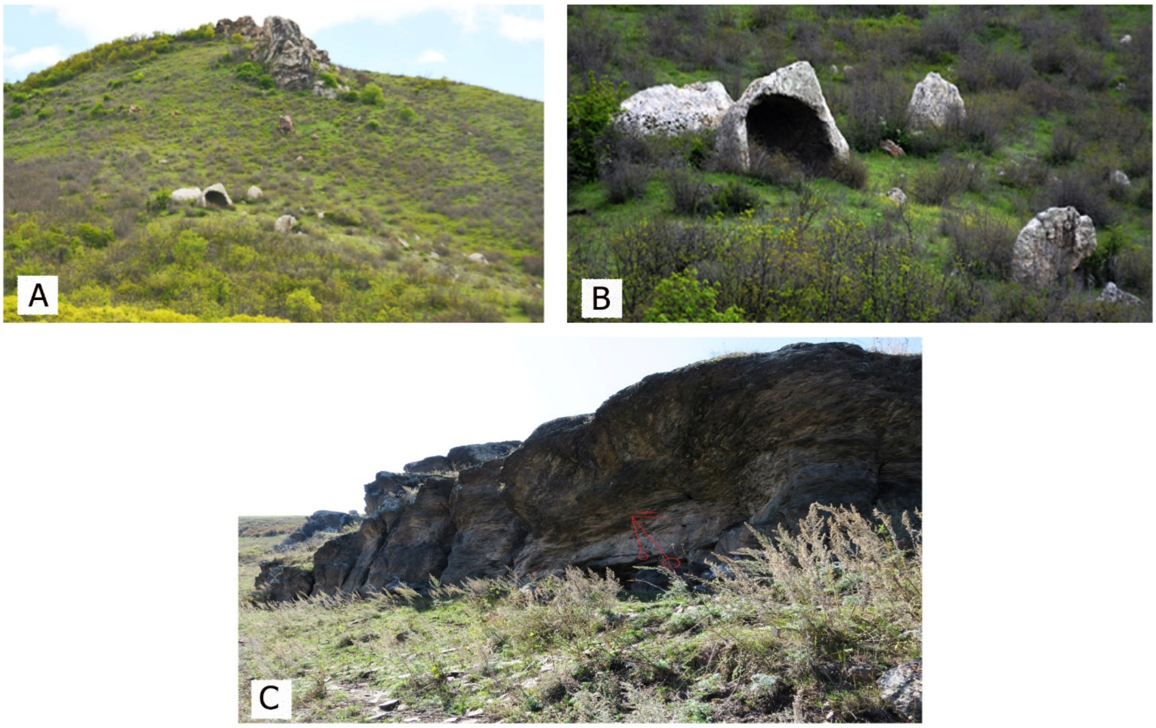

Figure 2.1 - (A) - (B) Damirgaya (Losaberidze & Eloshvili, 2020); (C) Trialeti (Culture Agency, 2019)

The samples were labelled as follows: the two rock-painting pigment samples from Damirgaya are DS1 and DS2 (Figure 2.2) while those from Trialeti are TS1 and TS2 (Figure 2.3), rock samples from Damirgaya are DRS1 and DRS2 while those from Trialeti are TRS1 and TRS2; the six powdered pigment samples from Khramis Didi Gora are KDG 1149, KDG

898, KDG 1718, KDG 1208, KDG 816/817 and KDG 884 (Figure 2.5). My colleagues MA Levan Losaberidze and MA Mariam Eloshvili gathered samples from the sites, as well as from the Georgian National Museum.

Figure 2.2 - Sampling from Damirgaya (1) DS1 before sampling; (2) DS2 before sampling; (3) DS1 after sampling; (4) DS2 after sampling (by Losaberidze)

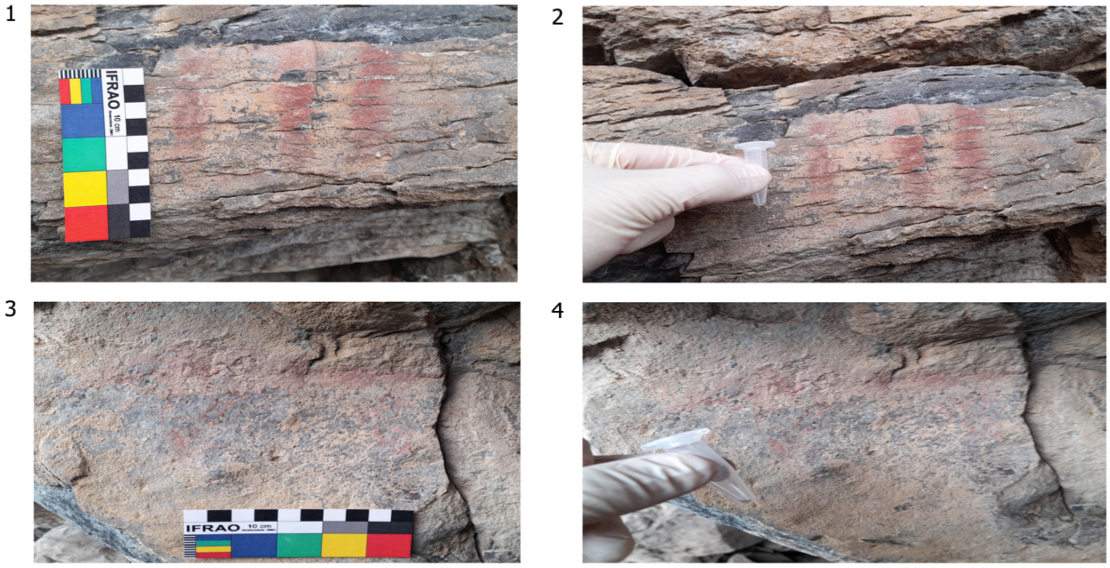

Figure 2.3 - Sampling from Trialeti (1) TS1 before sampling; (2) TS1 after sampling; (3) TS2 before sampling; (4) TS2 after sampling (by Losaberidze)

Both Damirgaya (Figure 2.3) and Trialeti (Figure 2.4) have a monochromatic red hue and pigment samples were scraped from two spots with plastic knives and placed in test tubes, while rock samples were ripped off nearby the paintings (Figure 2.4).

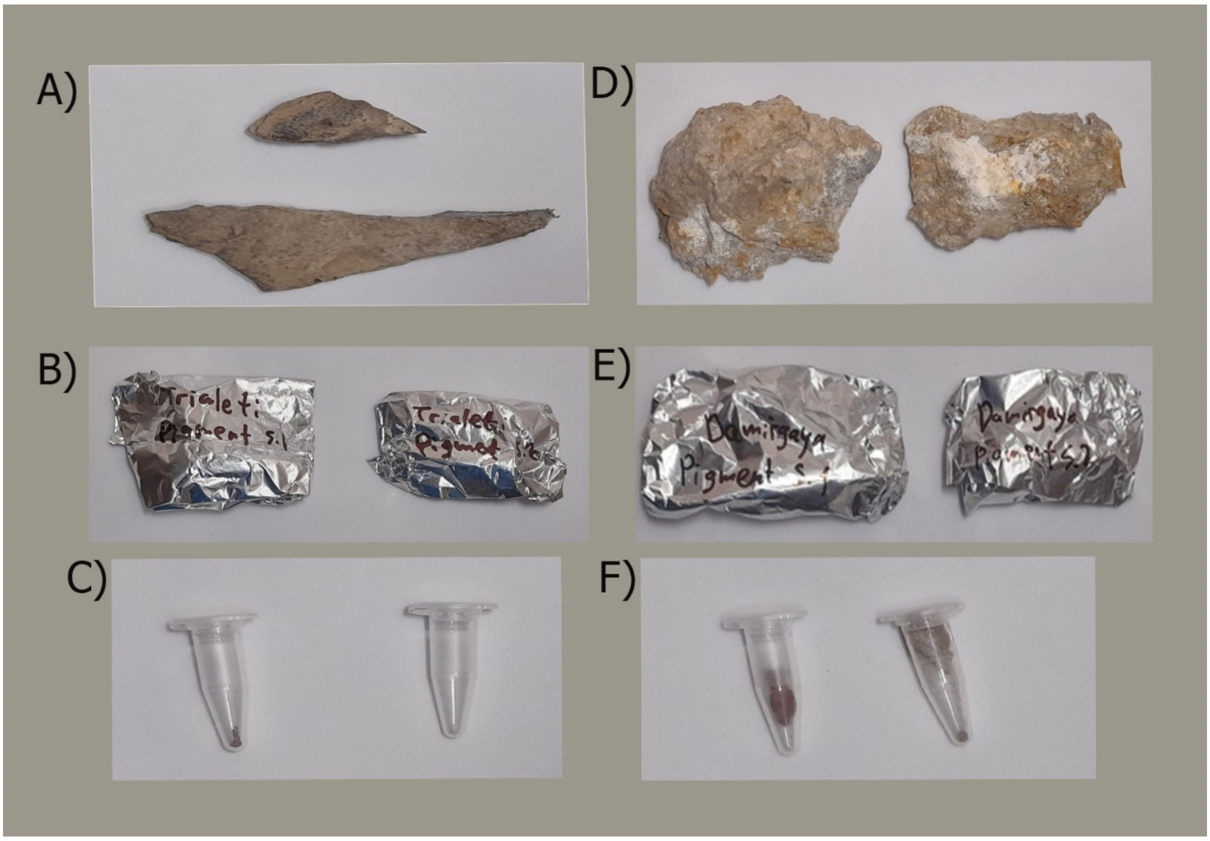

Figure 2.4 -Rock and pigment samples from Trialeti (A-C) and Damirgaya (D-F)

Pigments were collected separately into tubes with toothbrushes from the grinding tools of Khramis Didi Gora (Figure 2.5), including a grinding stone (KDG816/87), two mortars (KDG1718 and KDG884), and three pestle/handstones (KDG1149/1152, KDG1208 and KDG898).

Figure 2.5 - Grinding tools from Khramis Didi Gora

2.1.2 Sample preparation

Preparation of cross-section

Under a stereomicroscope, samples DS1 and DS2 were oriented so that their surface was parallel to a polyester resin base in dedicated plastic cups. Polyester resin and hardener were then poured into the container. The embedded samples were left to rest for about half an hour and then put in an oven for hardening, at about 70 °C for 24 hours. The section was then cut perpendicularly to the surface, after the container had been removed. Polishing was finally carried out with silicon carbide abrasive discs (up to 4000 grit). Two cross-sections were obtained from each sample, being each of them the opposite face of the same sample, halfway cut.

Preparation of the thin-sections

An adequate size slab for installation on a slide was cut from each sample, DRS1, DRS2, TRS1, and TRS2, using a diamond saw. The slab was then lapped flat and smooth. After epoxy had set on a hot plate, a glass slide was affixed to the lapping face of a slab.

A thin-section saw was used to cut the slab close to the slide. The thickness was further decreased on a thin-section grinder, up to the approximate thickness of 30 microns, being lapped by hand on a glass plate with 600 grit carborundum. A fine grinding with 1000 grit was an option prior to polishing. The slice was held in a holder and polished on a polishing machine with nylon cloth and diamond paste until a suitable finishing was achieved for microscopy or SEM investigation.

Preparation for XRPD

Correspondingly, all pigments from the grinding stones of Khramis Didi Gora (samples KDG1208; KDG1718; KDG1149; KDG898 and KDG884; KDG816) were ground by agate mortar and pestle for XRPD analysis. Likewise, Trialeti pigment samples were analyses by XRPD there were in powder, unfortunately their amount was not enough for several analyses.

2.2 Analytical Techniques

To classify and define inorganic pigments, as well as recognize technology and compatibility with local supplies, a multi-disciplinary archaeometric approach was applied using complementary techniques: XRPD, FTIR and Raman spectroscopy, SEM-EDX, and OM (Table 1).

Table 1 - The number of samples taken from rock art sites and grinding tools from Neolithic settlements, and how they were analysed.

Sample	**Sample type**			**XRPD**	**Raman**	**FTIR**	**OM**	**SEM-EDX**
	Powder	***Cross-s.***	***Thin-s.***					
DRS1			X	-	-	-	X	-
DRS2			X	-	-	-	X	X
DS1		X		-	X	X	X	X

DS2	X	-	X	X	X	X
TRS1	X	-	-	-	X	X
TRS2	X	-	-	-	X	-
TS1	X	X	-	-	-	-
TS2	X	-	-	-	-	-
KDG817/816	X	X	-		-	-
KDG884	X	X	-	X	-	-
KDG898	X	X	-	X	-	-
KGD1149	X	X	-	X	-	-
KDG1208	X	X	-	X	-	-
KDG1718	X	X	-		-	-

2.2.1 Optical Microscopy (OM)

Damirgaya loose samples were first observed under a stereomicroscope before being embedded in resin. A Leica stereomicroscope, equipped with a Leica DFC420C camera, at the Istituto Centrale per il Restauro (ICR), Rome, Italy, was used (Figure 2.6). Images of the loose fragments and cross sections were taken with the Leica Image 1000 software.

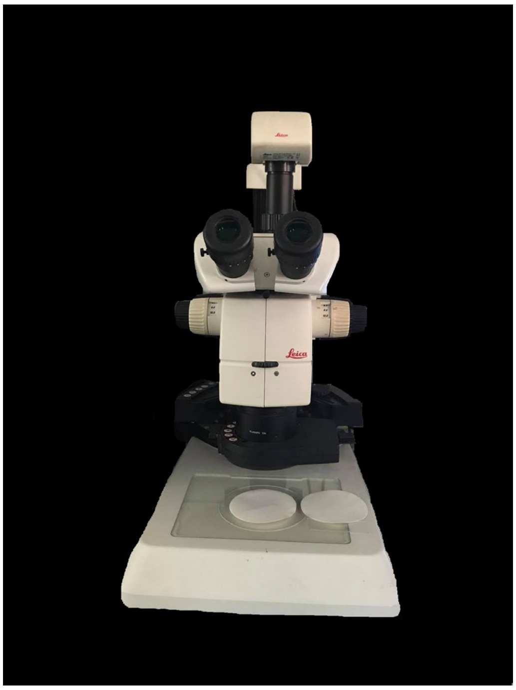

Figure 2.6 - Leica Stereomicroscope, equipped with a Leica DFC420 C camera, at ICR, Rome, Italy

A Leica DM750P polarized optical microscope equipped with a Leica MC190-HD camera (Department of Earth Sciences, Sapienza University of Rome, Italy) was used for petrographic analysis in thin section with the software LAS V4 4.12, to describe the minerals in each rock sample and identify the rock type (Figure 2.7).

Figure 2.7 - Leica DM750PZeiss D-7082 Oberkochen polarized optical microscope equipped with a Leica MC190-HD camera (Department of Earth Sciences, Sapienza University of Rome, Italy)

2.2.2 Scanning Electron Microscopy coupled with Energy Dispersive X-ray analysis (SEM-EDX)

Microstructural features and qualitative chemical composition of selected minerals in the thin sections have been investigated using a ZEISS EVO 60 SEM equipped with EDX Oxford system and INCA X-sight dispersive X-ray spectrometer (EDS Oxford Instruments Detector 7636 Energy) at ICR, Rome, Italy (Figure 2.8). The Aztec software has been used to visualize spectra, images, and elemental maps of thin sections DRS2 and TRS1, as well as cross sections DS1 and DS2.

Figure 2.8 - SEM-EDX system at ICR, Rome, Italy

2.2.3 X-Ray Powder Diffraction (XRPD)

XRPD data were collected at the Department of Earth Sciences of 'Sapienza' University of Rome, using a θ/2θ Bragg-Brentano Seifert MZ IV diffractometer. The operating conditions were 40 kV and 30 mA. Samples were analysed in the 3-60° 2θ range, with a step scan of 0.02° 2θ and a counting time of 3s. Diffraction patterns were analysed using XPowderX software and the Powder Diffraction File (PDF) database was available in order to qualitatively and semi-quantitatively characterize the mineralogical assemblage of each pigment sample (Botticelli et al., 2021) from Khramis Didi Gora. Sample from Trialeti were also analysed.

2.2.4 Fourier-transform infrared (FTIR) and Raman spectroscopy

A microscopic fragment was pressed on a diamond cell and analysed by a Thermo Scientific Nicolet iN10 MX at ICR, Rome, Italy (μ-FTIR). The instrument is equipped with an MCT/A detector cooled with liquid nitrogen. Spectral data were collected under the following conditions: 4000–400 cm^{-1} spectral range (with cooled detector) or 4000–700 cm^{-1} at room temperature, transmission mode, 16 scans, 8 cm^{-1} resolutions. The Ominic Picta and Excel softwares were alternatively used for band analysis, in order to identify inorganic and organic components in pigment samples DS1 and DS2.

Representative pigment samples from Khramis Didi Gora: KDG884; KDG898; KD1149 and KDG1208 were also analysed after being ground with potassium bromide (KBr) powder and pressed to obtain pellets.

Raman Spectroscopy was utilized to complement FTIR results and evaluate the key minerals, namely hematite for the red hue, as well as possible organic materials. The instrument provided by Madatec at ICR, Rome, Italy is equipped with a Lab Grade (BAC100) laser probe with 85 μm spot-size, an i-Raman 785-nm laser and a thermoelectrically cooled (TEC) linear array detector (2048 pixels, 14x200 μm). A digital camera and LED illuminator allowed precision targeting and focusing of the laser spot, by means of a 20x objective.

Spectra were collected in the 175-3200 cm^{-1} range with resolution of 5 cm^{-1}. The following operative conditions were chosen: laser power of 30 mW; acquisition time of 2 seconds; average on 5 repetitions. Spectra were then analysed alternatively by the software BWSpec™ or in Excel.

The IRUG and RRUFF databases (available online at www.irug.org and http://rruff.info/, respectively) were used to identify the peaks in FTIR and Raman spectra. Reference spectra from scientific papers were also taken as references for band assignment and compound identification.

3. Results

3.1 FTIR spectroscopy

On Damirgaya samples, µ-FTIR analysis revealed that sample DS1 contains clay minerals, low calcite $CaCO_3$, and quartz, SiO_2, while sample DS2 contains gypsum $CaSO_4$, calcite, and quartz, and the main colouring agent is hematite.

Specifically, DS1 and DS2 Damirgaya samples have different bands, which were attributed to several minerals, as specified in Table 2.

Table 2 - FTIR results for Damirgaya

FTIR bands (cm^{-1})				
Reference	**Present work**		**Attribution**	**Reference list**
	DS1	***DS2***		
470, 535 and 548	477, 532	548	Hematite	Rosina et al., 2019
418, 455, 470, 535, 670, 3140	456, 3332, 3335	670, 671	Goethite	Salama, 2015 Darchuk, 2010
465, 779, 780, 797, 799, 1080, 1087, 1091, 1148	778, 797, 1069, 1135, 1176	466, 1095, 1099	Quartz	Dumoulin, 2020 Moyo, 2016 Hussein, 2020 Lofrumento et al., 2012 Hernanz et al., 2014
662, 779, 712, 713, 784, 1311-1326, 1414, 1433, 1616,	719, 722, 724, 1331, 1432, 1634,	670, 1331, 1432	Ca-Oxalate	Lofrumento et al., 2012 Prinsloo, 2008 Brecoulaki, 2006

FTIR bands (cm^{-1})				
Reference	**Present work**		**Attribution**	**Reference list**
	DS1	***DS2***		
1619, 1623, 3342, 422, 457, 668, 1007, 1111, 1112, 1619, 1620, 3403, 3405, 3406, 3456.	422, 456, 1001, 1620, 1621	1620, 1621, 3400, 3408, 3473	Gypsum	Poliszuk & Ybarra, 2014 Moyo, 2016 Hernanz, 2014 Doménech-Carbó et al., 2020 Alemayehu et al., 2013 Brecoulaki, 2006 Hernanz, 2014 Hussein, 2020 Poliszuk & Ybarra, 2014
695, 779, 797, 1034, 3416, 3620, 3630, 3654, 3683, 3696	797, 3630, 3694	686, 780, 795	Kaolinite	Vahur, 2010 Moyo, 2016 Chukanov & Chervonnyi, 2016

Calcium carbonate was also identified in Khramis Didi Gora samples KDG884, KDG898, KDG1149 and KDG1208. The typical spectral features of calcite are associated to weak signals due to the Si-O stretching band (in the 1100–1000 cm^{-1} range) attributable to silicates, which correspond to the mineralogical assemblage commonly composing red ochres. The complete list of bands and compounds documented for the samples from Khramis Didi Gora is in Table 3:

Table 3 - FTIR results for Khramis Didi Gora

FTIR bandas (cm^{-1})			
References	**Present work**	**Attribution**	**References**
470, 485, 498, 535, 540, 548, 580, 616	482, 504, 530, 533, 619	Hematite	Vargas et al., 2019 Hussein, 2020 Rosina et al., 2019 Salama, 2015
418, 455, 670	427, 442	Goethite	Salama et al., 2015
669, 679, 1007, 1111, 1118, 1619, 3405, 3456	645, 1004, 1625, 1626, 3475	Gypsum	Brecoulaki et al., 2006 Hussein, 2020
695, 779, 797, 914, 1010, 1032, 1034, 1035, 3416, 3610, 3619, 3620, 3650, 3654, 3696	778, 1026, 1029, 1032, 1040, 3620	Kaolinite	Moyo, 2016 Dumoulin, 2020 Alemayehu et al., 2013 Salama, 2015 Guglielmi et al., 2020
514, 695, 696, 779, 780, 798, 799, 1080, 1082, 1084, 1085, 1150, 1163, 3433, 3434	514, 697, 779, 780, 796, 1080, 3442	Quartz	Moyo, 2016 Hussein et al., 2020 Doménech-Carbó, 2020 Salama, 2015
710-715, 779, 1311, 1315, 1322, 1323, 1324, 1326, 1328, 1398, 1410, 1421, 1430, 1433, 1610, 1617, 3425	712, 1384, 1426, 1433, 3329, 1369, 1314, 779	Ca-oxalate	Doménech-Carbó, 2020 Dumoulin, 2020 Moyo et al., 2016 Guglielmi, 2020 Solla et al., 2015 Alemayehu et al., 2013

The FTIR examination revealed that there is no organic binder present, or at least that it is below the detection limit of the instrument, because there was no band attributable to organic molecules, such as an animal protein, in the FTIR spectra in case of Damirgaya and Khramis Didi Gora samples.

3.2 Raman spectroscopy

The main Raman bands such as hematite, goethite, quartz, and anatase found for the samples from Damirgaya are reported in Table 4. Likewise, we attempted to detect organic compounds using Raman Spectroscopy, but due to the presence of intense fluorescence, no organic substance could be identified.

Table 4 - Raman results for Damirgaya

Raman bands (cm^{-1})				
	Present work			
References	***Sample DS1***	***Sample DS2***	**Attribution**	**References**
216, 218, 226, 230, 240, 283, 289, 291, 294, 295, 403, 405, 410, 411	224, 226, 288, 410	272	Hematite	Darchuk et al., 2010 Rosina et al., 2019 Rousaki et al., 2017 Needham et al., 2018 Haaland et al., 2020 Erdogu & Ulubey, 2011 Lofrumento et al., 2012 Guglielmi, 2020
299, 304, 380, 391	366, 375		Goethite	Darchuck, 2016 Guglielmi, 2020 Westlake et al., 2012
126, 203, 462	130, 466-480	127	Quartz	Wojcieszak & Wadley, 2019 Prinsloo, 2008

142, 143, 511		146	Anatase	Rousaki, 2017 Prinsloo, 2008

3.3 Optical microscopy and scanning electron microscopy on thin sections

Damirgaya rock samples

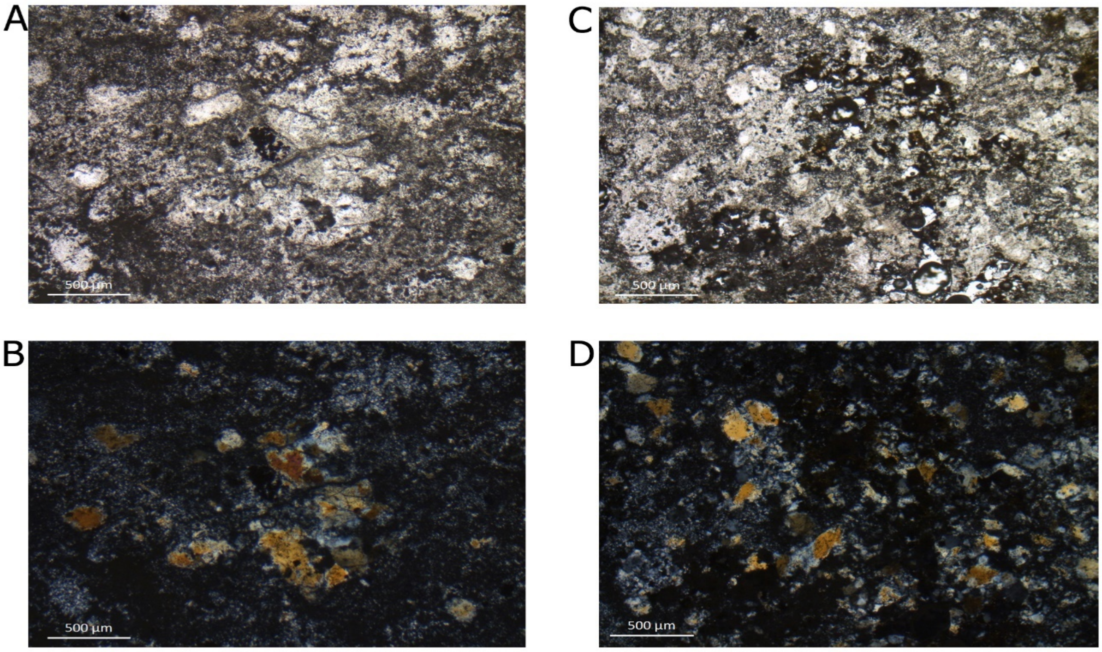

Figure 3.1 - Optical microscopy images (4x magnification) of: A) DRS1, PPL; B) DRS1 in XPL; C) DRS2 in PPL; D) DRS2 in XPL

With the use of an optical microscope, it was possible to identify that rock samples of Damirgaya composed of quartz, but it is also characterized by other minerals. Iron oxides are likely present, as well as phyllosilicates (Figure 3.1).

The following elements were found in the thin section of DRS2: Si, Al, Cl, S, Na, Ca, Ti, Fe, Mg, P, K (Figure 3.2). Accordingly, the rock mineralogical compositions were similar in DRS2 cross and thin section observations. In terms of cross-section analysis results, DRS2 has the following major elements: Si, Al, Cl and Fe, with minor S, Ca, Na and Ti (Fig. 3.2).

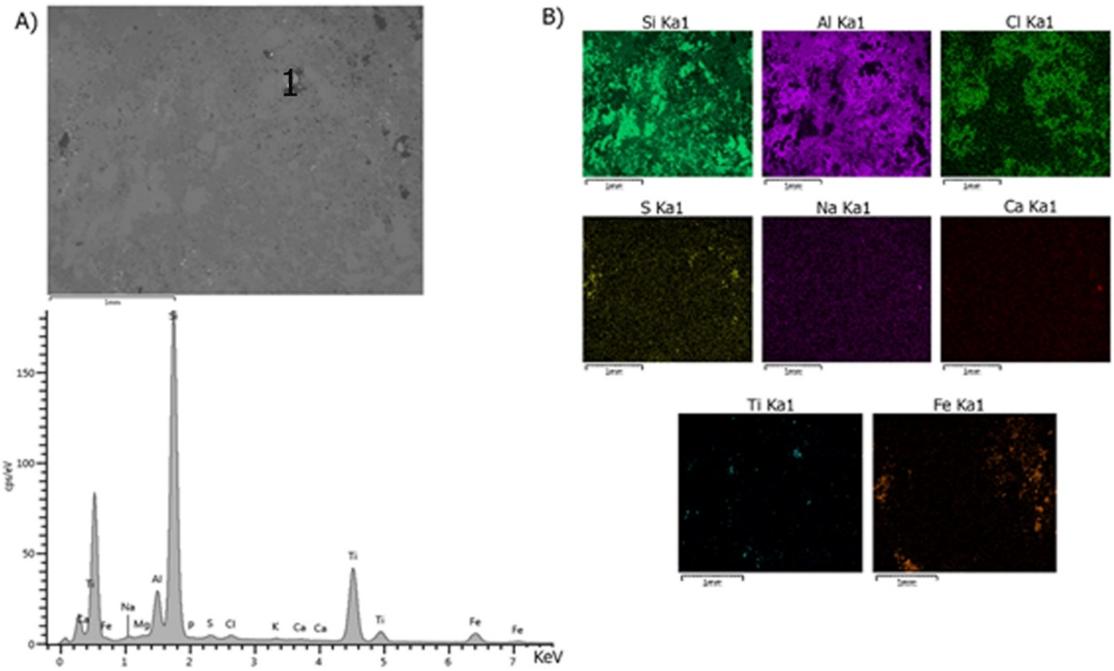

Figure 3.2 - A) SEM-EDX spectrum of point 1, and BSE image of DRS2; B) EDX elemental map of DRS2 specimen

Trialeti rock sample

On the Trialeti rock samples, it was possible to identify the rock type as dacite, which is primarily linked with andesite and trachyte volcanic rocks. Specifically, it is a felsic extrusive igneous rock intermediate in composition between andesite and rhyolite (Figure 3.3).

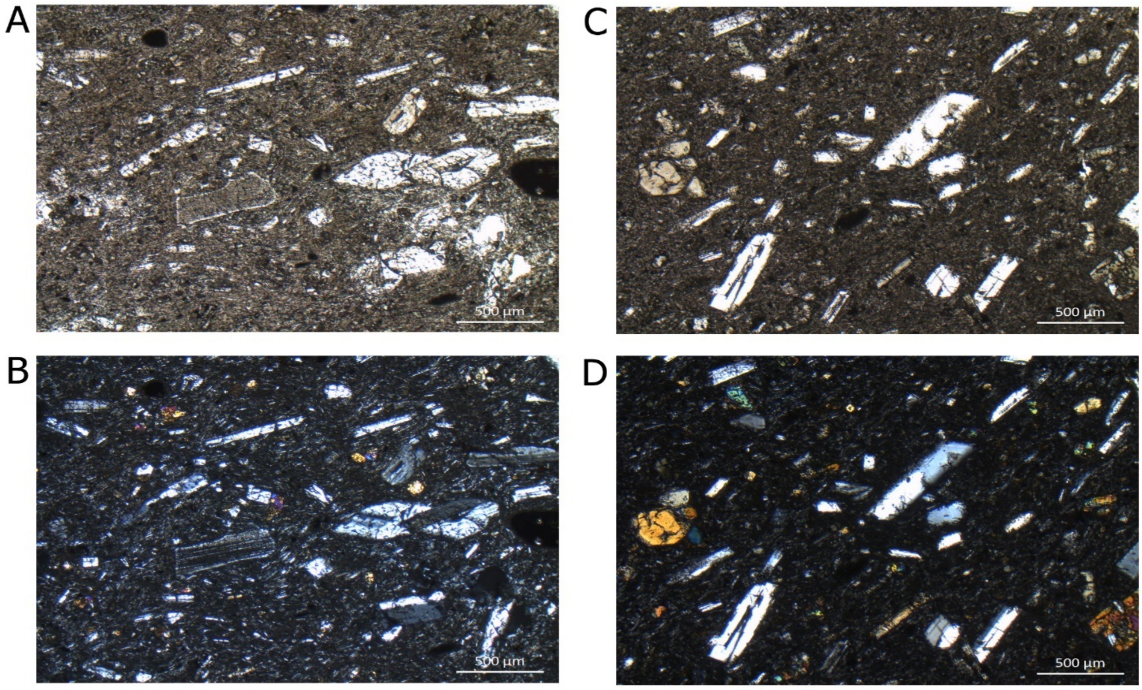

Figure 3.3 - Optical microscopy images (4x magnification) of: A) TRS1 in PPL; B) TRS1 in XPL; C) TRS2 in PPL; D) TRS2 in XPL

In the thin sections TRS1 and TRS2, dacite shows a porphyritic texture, with quartz, hornblende, biotite, pyrite, and feldspar.

The following major elements were detected by SEM-EDX: Si, Al, Ca, Na, K, Mg, Fe, Ti, and Mn (Figure 3.4). Minor amounts of additional elements were discovered in this thin section from Trialeti: Mn, Zn and Cr.

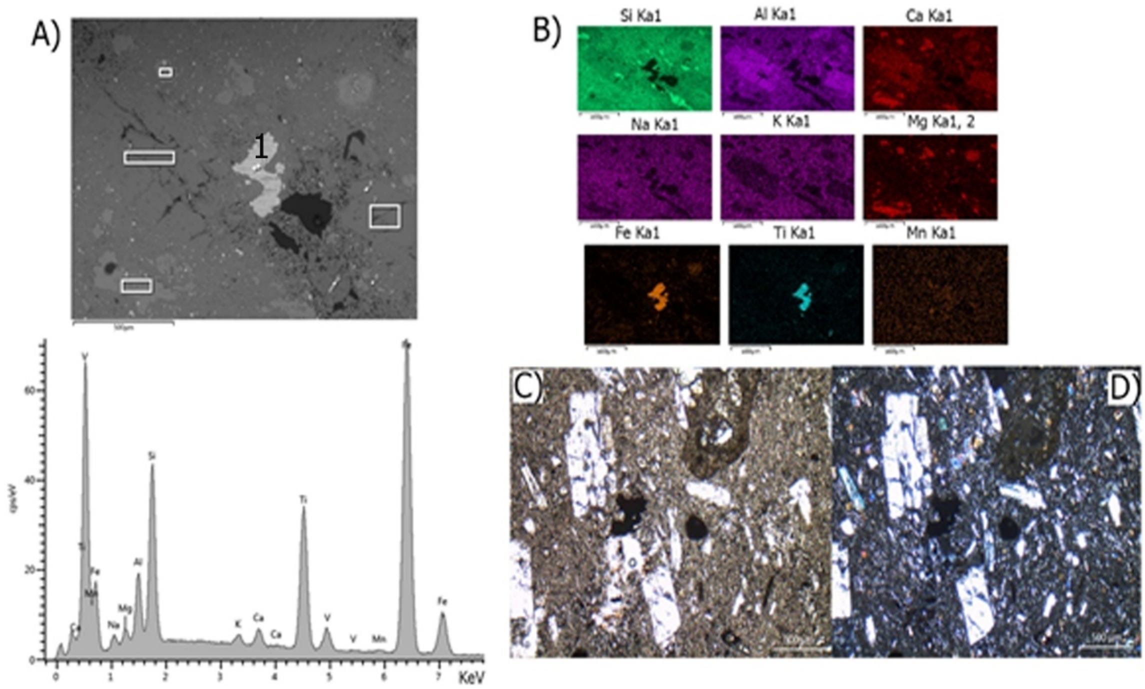

Figure 3.4 - TRS1 thin section in OM, transmitted visible light, in PPL (C) and XPL (D); A) BSE-image of the same area in TRS1 and EDX spectrum of point 1, of rock sample; B) EDX maps of (from left to right, top to bottom): Si, Al, Ca, Na. K, Mg, Fe, Ti, Mn

Among the detected elements there is also titanium (Ti), which may come from the rock or from partially altered minerals in a microcrystalline Si-Al-K-Na based matrix.

OM results are represented in Table 5.

Table 5 - Results of the OM analysis performed at the Earth Science Department, 'Sapienza' University, Rome, Italy

Sample	**Identified minerals**
TRS1	Quartz, hornblende, biotite, pyrite, feldspar
TRS2	Quartz, hornblende, biotite, pyrite, feldspar
DRS1	Quartz
DRS2	Quartz

3.4 Optical microscopy and scanning electron microscopy on cross-sections

Damirgaya pigment samples

Figure 3.5 - Specimen DS1 before embedding, picture taken by Stereo microscope

The surface of sample DS1, once observed under a stereomicroscope before embedding (Figure 3.5), appeared darker in hue than DS2, and it had a reddish tone in comparison to DS2, which had a brownish tone, and less thickness than DS2.

By SEM-EDS, it was possible to find the following elements in the pigment layer of DS1: Si, P, K, Ca, Fe, V, Mg, S, Na (Figure 3.6).

It should be emphasized that the mineralogical composition of DS1 and DS2 observed by SEM-EDX investigation is identical; for instance common elements which were revealed on both samples are: Si, Al, S, P, Na, P, Cl, V, Fe, Ca, Mg, and K.

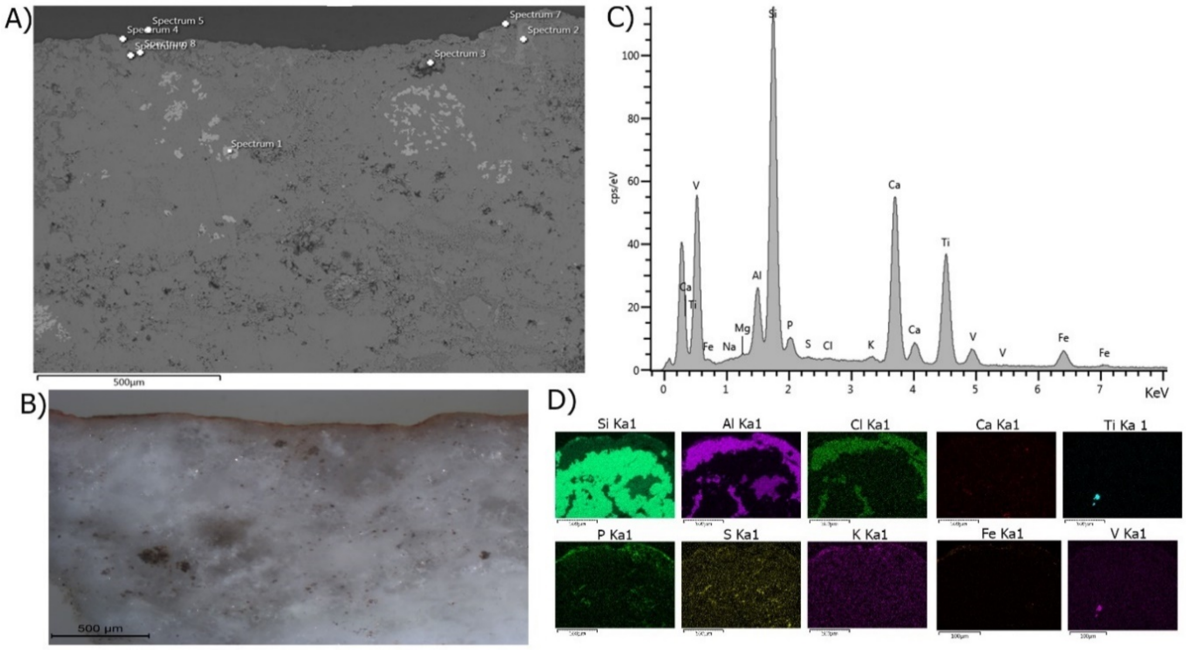

Figure 3.6 - A) SEM-EDX, BSE image of DS1 cross-section; B) OM, image of DS1 cross-section; C) EDX spectrum of DS1, point four, from the pigment layer (A); D) EDX, elemental maps of DS1 cross-section: (from left to right, top to bottom) Si, Al, Ti, Ca, V, Cl, P, K, Fe and S.

On the contrary, in sample DS2 the pigment layer, once observed under a stereomicroscope before embedding, appeared more fragile when it was sampled and brownish in colour (Figure 3.7).

Figure 3.7 - Specimen DS2 before embedding, picture taken by Stereo microscope

SEM-EDX (point 2 of the BSE image, Figure 3.8) indicates that the following elements were identified in the pigment layer of DS2 cross-section: Si, Al, S, Mg, P, Na, Ti, Ca, Fe, Cl, K, V, and as previously indicated, in terms of mineralogy, it bears a lot of similarities with DS1.

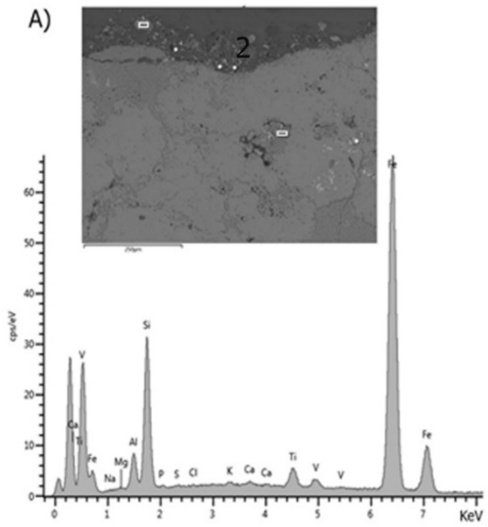

Figure 3.8 - A) BSE image of DS2 and SEM-EDX spectrum of point 2 and B) EDX elemental maps of Al, Si, Cl, P, S, K, Ca, V, Fe, Ti

The microscope inspection of the cross section followed, under UV light. It was used on DS1 and DS2 in order to detect the presence of any organic substance, but no fluorescence was recorded (Figure 3.9).

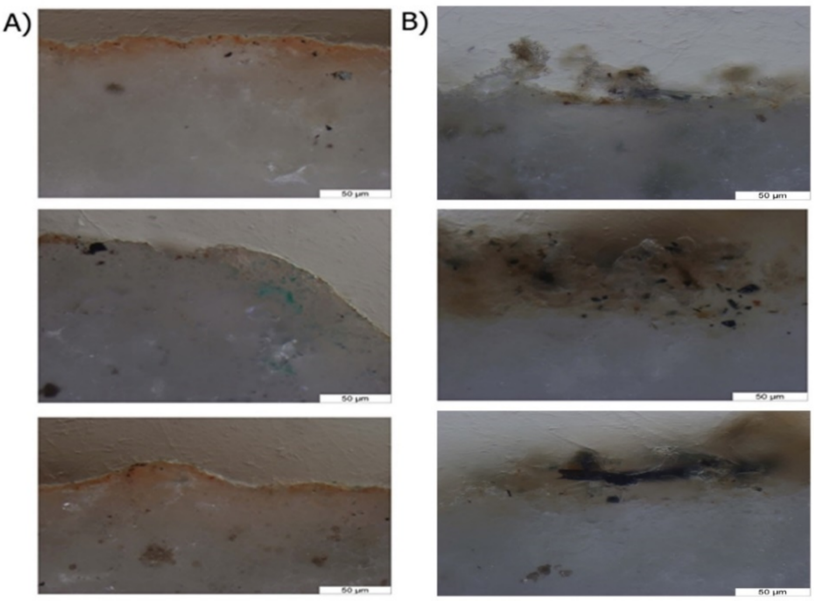

Figure 3.9 – Visible light OM images taken on (A) DS1 and (B) DS2 cross sections

3.5 XRPD on pigment samples

Powdered samples were produced to identify the minerals in each pigment sample using X-ray diffraction. The mineral phases and their abundance in the collected samples are summarized in Table 6.

Table 6 - XRPD results: identified minerals and their abundances in each sample (++++ = very abundant, +++ = abundant, ++ = present, + = scarce, and tr = trace); legend: ++++ = very abundant; +++ = abundant; ++ = present; + = scarce, tr = trace; mineral abbreviations are as follows:Qtz = quartz, Cal = calcite, Dol=dolomite, Hem=hematite, Gth=goethite, Gyp=gypsum, Pl=plagioclase, K-fds=K-feldspar, Ms=muscovite, Cpx=clinopyroxene, Hbl=hornblende, Ol=olivine, We=whewellite

	Qtz	***Cal***	***Dol***	***Hem***	***Gth***	***Gyp***	***Pl***	***K-fds***	***Ms***	***Clays***	***Cpx***	***Hbl***	***Ol***	***We***
KDG 816 817	++	++	-	-	-	+	+++	+	-	-	-	-	-	-
KDG 884	++	+	-	*tr*	-	-	++	-	++	+	-	-	-	-
KDG 898	*tr*	*tr*	-	*tr*	-	*tr*	++++	-	-	+	+	-	-	-
KDG 1149	+	*tr*	-	+	+	-	+++	-	-	+	-	+	-	-
KDG 1208	++	-	-	*tr*	-	-	++++	-	-	*tr*	-	-	+	-
KDG 1718	++	*tr*	+	*tr*	-	*tr*	++++	-	-	-	-	-	+	-
T S1	*tr*	-	-	*tr*	-	+	-	+	-	-	-	-	-	++++

Quartz, sanidine, hematite, and whewellite were all found in TS1.

Because of the small sample amount, the diffractogram of TS2 could not be interpreted.

Quartz, calcite, gypsum, albite, and sanidine were found in KDG816/817.

Quartz, muscovite, montmorillonite, albite, calcite, and hematite were in KDG884.

Quartz, albite, gypsum, hematite, augite, montmorillonite, and calcite were described in KDG898.

Goethite, anorthite, calcite, chlorite, quartz, hornblende, and hematite were all found in KDG1149.

Quartz, albite, illite, hematite, and olivine were documented in KDG1208.

Albite, quartz, fayalite, gypsum, hematite, calcite, and dolomite were all found in KDG1718.

Sanidine was only found on the grinding stone pigment KDG816/817 and rock art specimen TS1. Muscovite was only found on KDG884 mortar, while montmorillonite was found on both KDG884 and the pestle/handstone KDG898. Augite was discovered on KDG898 specimen. On the pestle/handstone KDG1149, goethite, anorthite, chlorite, and hornblende were also identified. Olivine was described on the pestle/handstone KDG1208 and the mortar KDG1718. On KDG1208, an illite-type clay mineral was identified. On the sample KDG1718, dolomite was also observed.

Here follows a summary of all results, which are then considered in the discussion (Table 7):

Table 7 - Summary of analytical results

Sample	**SEM-EDX** **main elements**	**OM (thin sect.)** **minerals**	**Raman/FTIR** **compounds**	**XRPD** **minerals**
DS1 Bis	Major: Ti, Si, Al, Ca Minor: Cl, S, P Trace: Fe, V, Mg, Zn, Cr, Cu, Sb, As			
DS2 Bis	Major: Ti, Si, Al, Fe Minor: Ca, P, S, Na, Cl, K, Ba Trace: V, Mg, Sr, Co			-
DS1			Hematite, goethite, quartz, Ca-Oxalate, gypsum, kaolinite	
DS2			Hematite, quartz, anatase, Ca-Oxalate, gypsum, kaolinite	
DRS1		Quartz		

DRS2	Major: Si, Ti, Al, Ca, Fe Minor: Na, P, S, Cl, K, Mg	Quartz		-
TRS1	Major: Ti, Si, Fe, Al Minor: Ca, Na, P, K, Cl, V, Mg, Mn, Zn, Cr	Quartz, hornblende, biotite, pyrite, feldspar		-
TRS2		Quartz, hornblende, biotite, pyrite, feldspar		
TS1				Quartz, sanidine, gypsum, hematite, whewellite
TS2	-	-	-	-
KDG816/817				Quartz, calcite, gypsum, albite, sanidine
KDG884			Kaolinite, quartz, gypsum, Ca-Oxalate	Quartz, muscovite, montmorillonite, albite, calcite, hematite
KDG898			Kaolinite, quartz, gypsum, Ca-Oxalate	Quartz, albite, gypsum, hematite, augite, montmorillonite, calcite
KDG1149			Goethite, quartz, kaolinite, gypsum,	Goethite, anorthite, calcite, chlorite,

			Ca-Oxalate	quartz, hornblende, hematite
KDG1208			Hematite, goethite, quartz, kaolinite, gypsum, Ca-Oxalate	Quartz, albite, illite, hematite, fayalite
KDG1718				Albite, quartz, fayalite, gypsum, hematite, calcite, dolomite

4. Discussion

4.1 Chemical and Mineralogical composition of Rock and Pigment Samples

Mineralogical, geochemical, and geochronological data from rock paintings can greatly enhance our understanding of human behaviour and interaction with the natural environment (Pecchioni et al., 2019).

For what concerns the rock samples investigated in the present work, optical microscopy on thin sections from Damirgaya revealed the presence of quartz, and iron oxide particles. During SEM-EDX analysis, the presence of these minerals was confirmed. Concerning Trialeti TRS1 and TRS2 the mineralogical assemblage was more complex such as: quartz, hornblende, biotite, pyrite, and feldspar This composition, as determined for Trialeti rock samples, is consistent with geological references from Gabunia's investigation (Gabunia, 1980) and the Georgian geological map (Adamia, 2004). Despite the fact that little is known about the geology of the Marneuli region, we used Adamia's geological map (Adamia, 2004) to determine that the Marneuli region of Damirgaya is formed of conventional sedimentary strata, as indicated by our examination of thin sections of DRS1 and DRS2.

Concerning the pigment samples, the major elements in the ochraceous layers were found to be Si, Al, Ti, and Fe. Other minor elements like P, Na, Cl, or Ca were also detected by SEM-EDX and effectively are in the same red/brown layer. Hematite was identified as the predominant mineral phase of the red particles in samples DS1 and DS2 by Raman spectroscopy, which revealed typical bands at 226, 292, and 410 cm^{-1}. Hematite is a naturally occurring pigment, but it can be synthesized using thermal and mechanical processes that convert hydrated Fe-oxides such as goethite - FeOOH (or a goethite-containing substance such as a yellow ochre) to its anhydrous form - Fe_2O_3. Hematite is made by heating goethite to temperatures above 250–300°C, so that it undergoes dehydration (Sanz et al., 2021). Likewise, the presence of hematite was confirmed in three of the samples from grinding tools and rock art sites, based for instance on the presence of the Raman bands of haematite at 226, 292, and 410 cm^{-1}, which were detected in the samples from Damirgaya and Khamis Didi Gora. Its presence was also confirmed by XRPD in case of Khramis Didi Gora Samples and TS1, and FTIR spectroscopy for Damirgaya samples.

Crystals of goethite were indeed linked with clay minerals and quartz. Goethite was confirmed in the sample DS1 by Raman spectroscopy. The chemical composition of this red layer was determined by SEM-EDS as including Fe and minor Al, Mg, Si, and Ti. Red ochre was also associated with vanadium. The lack of Mn in its chemical analysis by SEM-EDX excludes the possibility of yellowish-brown earth pigment sienna, which contains at least some manganese oxides (Piovesan, 2016). Further observed minerals, such as quartz and titanium oxide, are most likely the result of detrital material being transported by water run-off or aeolian transport of dust. Analogously, quartz grains are interpreted as part of the ochre residue since such grains are rare. They could come from the processed ochre fragments or represent an additive intentionally mixed to the ochre powder (Rosso, 2016).

In case of DS2 the earthy yellow ochre showed to be associated with clay minerals and to be dark yellow.

Hematite and goethite were also detected on the Trialeti rock art pigment sample TS1.

Moreover, in the case of Damirgaya, Trialeti - as pigment or rock sample, and on Khamis Didi Gora pigments, the presence of gypsum and calcite was documented on some samples by either SEM-EDX, FTIR, or XRPD. Particularly, gypsum was documented by the contemporary presence of Ca and S by SEM-EDX in samples DS1, DS2, DRS2 and TRS1. It was also confirmed by XRPD and FTIR in samples KDG816/817, KDG898, KDG1718 and TS1, DS1, DS2 and Khramis Didi Gora grinding tools as well. Calcium sulphates dehydrate, namely gypsum, is an eminent outcome from environmental impact (Gliozzo, 2014). The production of gypsum on stone is a well-known process that affects historical monuments in polluted and urban settings. The formation of a calcium sulfate crust occurs when atmospheric sulfur dioxide reacts with calcium from the stone substratum. Flowing groundwater, rather than building materials, is the most commonly postulated source for gypsum deposition in the context of rock art (Lebon, 2019). Also, bird and bat droppings are particularly high in phosphate, and the contemporary presence of calcium and phosphate observed by SEM-EDX could be explained as a biodeterioration product.

The typical bands from calcium oxalates were discovered by FTIR analysis in the pigment specimens from Damirgaya and Khramis Didi Gora: at about 1320, 768 e 663 cm^{-1}. The presence of whewellite was seldom confirmed on TS1 by XRPD. Calcium oxalates are generated by a variety of processes, the most common of which being lichen and bacteria action on the rock, which produces calcium oxalates, after secreting acids that dissolve calcium carbonates. The presence of Ca-oxalate in pigments is remarkable and described in several previous case studies of rock art in South Africa, and other examples in Australia, Argentina, North America, Spain, and France. The majority of previous findings suggests that Ca-oxalates may form during the erosion of painting layers resulting from biological activities of algae, fungi, or lichens (Gheco, 2019). Also, Ca-oxalate/whewellite was identified by XRPD in rock art sample TS1, unfortunately TS2 interpretation was not possible due to the small sample size.

Minor elements were also discovered during SEM-EDX investigation, including Sr, Cr, Zn, Cu, and As. During the 1970s, for example, the Marneuli region where the site of Damirgaya is located underwent deforestation and chemicals were used on neighbouring lands: Cl and Na may have come from there, while phosphorus may derive from animal faeces. Indeed, Cl was detected by SEM-EDS in inclusions in the rock, so it might alternatively come from the rock itself.

Identification of elements such as vanadium (V), copper (Cu), or zinc (Zn), which is specific to DS1 and only the presence of V for DS2 and Zn and V for TRS1 may be useful for future provenance investigations, to better understand the source of the ochre found in the Marneuli and Trialeti region. Particularly, vanadium (V) in Roman ochre has been told to serve as a provenance marker. Vanadinite is in fact a typical secondary product of the oxidation zone of lead deposits developing in arid climates and is associated in nature with galena and goethite. Therefore, although the association of this phase with other minerals characteristic of iron-rich soils was not unexpected, especially with yellow ochre, its occurrence in the pigments analysed here might indicate the provenance of these materials (Piovesan, 2016). The presence of Cr, Cu and As in the samples DS1 is characteristic for green earth (Roldan, 2016), which corresponds to the minerals celadonite or glauconite.

Barium has been detected in sample DS2 and it might be ascribed to contamination due to the burial environment.

Also, the presence of Mg, Sr, Cr, K, and Cu could possibly indicate impurities in the colouring compounds or the pigment layer, or even outsider dirt that defiled the painting over time (Elsayed, 2019).

These findings showed that chemical-mineralogical data from selected sampled pigments can provide critical information for understanding the pigment utilization process, specifically the process of mixing and binding certain elements to produce functional pigments.

Specifically, red pigments in Khamis Didi Gora suggest two separate recipes: one with red ochre, apparently found nearby, producing a brown red, as in sample KDG884 and another with a blend of this red ochre and clays. In the instance of Khramis Didi Gora samples, some of the minerals identified by XRPD may have come from the grinding tool, while others, such as hematite and goethite, are due to the pigment itself, red or yellow ochre respectively.

4.2 Technology and compatibility with local supplies

As anthropologists, archaeologists, and sociologists have pointed out, technology is emphasized as a cultural option that is influenced by economic, social, and ideological factors. In order to fully comprehend past technical decisions, we must consider the entire course of the *chaine operatoire* for objects development within their total life cycle or behavioural chain. This involves a thorough examination of how the object properties (such as colour, mechanical strength, and chemical composition) are affected by its manufacture, use, reuse, discard, and burial, as well as how natural and social production processes influence the entire assemblage. However, beyond individual artefacts, it is also necessary to understand the broader natural, technical, economic, social, and ideological context in which technological decisions were made (Sillar et al., 2000).

One of the goals of the present research was to figure out the technological ability of the people who produced such unique rock art paintings and left traces of their activities on grinding tools. On account of that, and in parallel with the empirical analysis, archaeometric sources and archaeological samples were used.

When discussing rock art technology, as in this case, we must consider pigment preparation methods such as grinding, mixing, or heating (processes may be used to alter optical properties such as colour, but they may also be used to facilitate grinding or improve adhesion to the wall) as well as paint application modes on the rock. As a result, pigments may be combined with extenders (clay, calcite, quartz, bone, talc, and so on) and binders (water, vegetable oil or animal fat). Such preparation improves paint adhesion, adjusts texture and consistency, and provides better coverage and possibly even better preservation. Clays seem to have been applied to red pigments on purpose, most of the time. References have shown that water is the most functional and common binder (Chalmin, 2003). In case of pigments, archaeological evidence suggests that Palaeolithic artists sometimes rendered red pigment from the colour changes caused by the temperature transition of yellow goethite (FeOOH) into hematite (Fe_2O_3) (Hovers, 2003).

If there is the possibility to use local resources, we can identify the elemental and structural compositions of ancient paints, as well as their probable geographic origin, thanks to a thorough physicochemical analysis. The oxygen-isotope ratios of fine-grained quartz extracted from ochre samples may provide an indication of ochre provenance, for example. Multiproxy archaeometric investigation helps to be aware of geological provenance (Smith & Pell, 1997), and ochre provenance is usually determined through material examination (Montalto, 2010). Concerning the sites of interest of the present research, there is currently a short note about an ochre mine in south Caucasian Georgia, thanks to a geological survey mission conducted in 1930, with the aim of discovering mineralogical pigments in West Georgia. During this geological examination, geologists discovered the following outcrops: Shemokmedi (Ozurgeti region), Nagomari, Tsiteli Mta (Makharadze district), and Meskhisouli, Ubisa – Shrosha – Tseva (Zestaponi region). Furthermore, ochre outcrops have been confirmed in most western Georgia, including Gagra, Kobuleti, Batumi, Kutaisi, Khashuri, and a few in the east, including Tetritskaro (Vachnadze, 1958), which is crucial for the present research because archaeological materials come from this area. Scrutinized mines are recorded in (Montseladze, 1930). In terms of mineralogy, Tsiteli Mta shares certain similarities with Trialeti, for instance, during a geological inquiry, geologists uncovered the following minerals: andesite, dacite, plagioclase, biotite, quartz, and yellow and red hue clays.

Table 8 - Chemical data of scrutinized ochre mines from West Georgia (Montselidze, 1930)

Sample	H_2O at 105-110°C	LOI	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	$Cu(OH)_2$ in HCl	Approx
Tsiteli Mta #2B #1	11.92 5.5	8.03 12.59	48.51 46.02	21.18 34.4	15.18 6.33	0.14	3.74 0.17	3.22 Trace	71 76.97	
Shemoq-medi #2 #7 #3 #4 #1 #22	3.5 3.0 4.86 4.73 2. 4 3.8	13. 67 8.4 10.14 14. 3	39.03 23.69 45.05 49.41 40.72	34.74 8.6 28.24 38.16	12.41 57.62 7.96 22.97 7.36 6.43	20.12 0.05	0.57 0.51 1.28 1.81	Trace 0.41 0.37 0.09	67.46 32.16 82.82 75.70	Lead Part of Analyse/ Red Clay
Meskhisouli #3	10.68	6.90		28.28	10.71		0. 52	Trace	54.72	

#1	9.98			4.05	74.32		0.31	Trace	10. 70	
#22	5.77	11.25		32.27	8.75		0. 45	Trace	53. 51	
#2		14. 76	40. 99	35.38	7.00		0.63	0, 3	67.81	

There is a chance that more mines in the East and other parts of Georgia must be explored, and present findings would be useful to other scholars in the field of material science and geology.

Furthermore, since archaeometry investigation of pigments in Georgia has not yet been established, there is no data that will be relevant during for comparison.

Anthropological data should also be considered, while trying to identify ochre sources for the samples hereby analysed. It is worth considering the etymology of Damirgaya, which comes from the Azeri culture, who named the rock area "Iron Rock". It might have analogies with Geghamavan I, which was dubbed "Iron Cave" by Armenians because of a source of iron oxides in proximity of the site. We may apply the same reasoning to Damirgaya and hypothesize that the people who made these pictographs most likely obtained ochre pigment near the rock shelter. However, in order to have a strong claim, geological and potential rock art surveys near the sites must be conducted in the near future, and raw geological materials must be analysed with several analytical techniques in order to understand pigment origin.

In terms of the analytical results, it was feasible to detect the presence of various chemical elements on thin and cross sections of rock art pigments and rock specimens from Damirgaya and Trialeti. For what concerns the finding of Trialeti plato, its rocks belong to Upper Pliocene calc-alcaline basaltic continental lavas, as documented by the geological map of Georgia (Adamia, 2003) and in agreement with archaeometric data hereby collected during thin and cross-section study. On the contrary, Marneuli has andesite-basaltic rocks as well as sedimentary carbonaceous rocks, which are well depicted in the Damirgaya thin- and cross-section data. Additionally, minerals found in both rock and pigment samples are compatible.

Because the SEM-EDX study is usually semi-quantitative (due to the lack of a precise calibration method prior to the analysis), it was not possible to estimate the real abundance of specific chemical elements.

The presence of vanadium in DS1 and DS2 is homogeneous in all the points analysed on the painted areas, and it is lower in DS2, but there is no presence of vanadium in the rock specimen DRS2. On the contrary, there is vanadium in the rock sample TRS1, which hypothetically could mean that the source of the ochre could be in the proximity of Trialeti or in the midst of both rock art sites.

4. 3 Dating Issue

Dating is the necessary information without which we cannot even start to reconstruct history. Dating allows us to contextualise the site we are studying and explain it within the frame of its period and contemporary events/sites. Additionally, dating an archaeological site provides useful hints to reconstruct the migration patterns of pre-historic populations. In the specific case of rock art, it might also give relevant information on the materials used to produce the artwork, where human beings, animals, symbols, and other unanimated objects were portrayed (Pecchioni et al., 2019).

The most frequently utilized analytical methods for dating are relative and absolute dating.

Dating rock paintings is a key tool for archaeological studies to better understand the relative chronology between different human occupations of the sites, and how these prehistoric groups used to communicate. Rock paintings, on the other hand, are difficult to date due to the complexity of their composition, which includes the use of a wide range of organic and inorganic elements, as well as a mix of both. Charcoals, plant fibres, and binders such as vegetable or animal glue, blood, or honey, as well as eggs, which were utilized in the creation of rock paintings, are among the datable organic components. When the carbon content of the paint layers gets too low or perhaps non-existent, however, dating the paintings becomes an issue. Because colours were obtained from minerals like iron oxides or aluminium silicates, most rock paintings do not have any organic carbon. Other paintings include carbon, but in amounts too small to be detected using Accelerator Mass Spectrometry (AMS) dating, which uses a gas ion source to analyse micrograms of carbon. This is frequently the case with open-air rock paintings, which are subjected to a variety of environmental factors that might cause the colour to deteriorate. A further issue is that, due to the destructive nature of the techniques, acquiring pigment samples from rock art motifs is sometimes restricted. These cultural sites are vulnerable and might be regarded as part of humanity's essential legacy. As a result, in order to date such significant archaeological sites, scientists must devise new, less harmful methods (Dumoulin et al., 2020).

Furthermore, relative dating can be conducted by a comparison of the techniques and styles of various rock art sites, for instance the relative stylistic chronology has been widely utilized on Gobustan rock art sites (Farajova, 2011).

As to what concerns absolute dating, several scientific methods are involved, such as U-Th isotopes, as well as AMS and the most routinely used ^{14}C. Radiocarbon dating can be in fact applied on binders, patina, Ca-oxalate and crusts, lichens (Pecchioni, 2019). Recently, AMS has been utilized on calcium oxalates recovered on the rock art of Namibia (Dumoulin, 2020). Analogously, dating of rock art by U-Th isotopes was performed on Huashan rock panel in southern China, results implying that the rock painting practices at Mt. Huashan probably lasted more than a century (Shao et al., 2017). Another example where a multi-disciplinary approach, involving mineralogy, geochemistry, stable isotopes, and ^{14}C dating, was carried out, deals with red and white pigments of Nyero (Upper Lake Victoria Region, Uganda) rock drawings.

In my research case, I utilized relative chronology, more precisely gained technological awareness of pigment preparation from prehistoric people who carried out astonishing rock art sites in Damirgaya and Trialeti and inhabited the Neolithic settlement of Khramis Didi Gora, who thought up on various tools which they used for pigment production. To acknowledge pigment preparation, which encompasses the *entire chaine operatoire* process and includes obtaining raw materials, such as ochre in our case, transporting them to the site, grinding them, and then utilizing them on rock art sites, material science was utilized as a combination of specific analytical techniques.

Figure 4.1 - Depiction of Anatolian rock art sites: The Hakkari, Tirsin, Cildir, and Deraser Cave (Arcgis)

Furthermore, stylistic comparisons with other rock art sites from nearby and distant regions were useful, with the following results: in the case of Damirgaya, stylistic parallels such as animal motifs, site etymology, and archaeological material recovered during both sites' excavations indicate a linkage between Damirgaya and the Armenian Neolithic rock art of Geghamavan-1. Furthermore, Damirgaya has several aspects in common with the Anatolian Neolithic rock art sites listed below, in terms of stylistic motifs and limited spatial distribution: The Hakkari, Tirsin, Cildir, and Deraser Cave (Figure 4.1).

Rock art patterns similar to those represented on Damirgaya and Trialeti were depicted on Gobustan rock art sites, and on ceramic fragments from Neolithic settlements of Georgia.

5. Conclusions

By using complementary analytical techniques this study has helped to give a better knowledge of Damirgaya, Trialeti rock art and Khamis Didi Gora pigment traces.

Prehistoric rock art site Damirgaya and Neolithic settlement grinding tools from Khramis Didi Gora revealed common minerals such as hematite, quartz, gypsum, calcite, and in certain cases goethite, by FTIR analysis. However, it was not possible to identify organic binders, possibly because of their absence or their content being below the detection limit. UV light observation of the cross sections in fact did not show any fluorescence attributable to organic substances. Compatibility between Damirgaya pigment and rock specimens was also documented during EDX mapping. Hematite, quartz, gypsum, and calcite were the most documented minerals, both by XRPD and FTIR data from Khramis Didi Gora. Although calcite was found in practically all pigment samples, which might be due to biological activity, gypsum was found on Damirgaya and Khramis Didi Gora. Since gypsum could be due to environmental deterioration processes and it might have great impact on culture heritage sites, it will be beneficial to carry out further conservation observation for future preservation.

SEM-EDX was used to determine the composition of the pigments used at Damirgaya and of the rocks from both Trialeti and Damirgaya. According to semi-quantitative chemical analysis, they contain high percentage of Ti, Si-rich (quartz) and Al–Si-rich inclusions, most likely as alumino-silicates. Additionally, there are Ca, P, S, Na, and Cl, with V as minor element. Other minor elements are Zn, Cr, Mn, Cu, Sr, Co, Ba, As, Sb. Specifically, the content of vanadium in the Damirgaya cross-section and the Trialeti thin section might correspond to an ochre source in the vicinity of these two locations. However, a detailed geological examination near these archaeological sites is advisable in order to strengthen this hypothesis.

When it comes to dating, there are a few things to keep in mind. Even though Khramis Didi Gora has absolute dating and has a lot in common with Damirgaya and Trialeti rock art sites in terms of technology of pigment preparation, it is still difficult to say that the latter two sites are dated to the Neolithic. However, based on stylistic observation, which is one of the most important methods during relative dating, we may say that Damirgaya shares many similarities with Anatolian Neolithic sites.

As a result of the lack of a usable database during our study, we conducted preliminary research that will serve as a foundation for future pigment investigations in Georgia, namely in the Trialeti and Marneuli regions, as well as a preliminary geological survey that will strengthen future research.

Problem Statement

Several cultural problems are related with the main subject of this thesis:
• Lack of reference materials on the rock art sites, due to limited bibliography, scarce evidence of painted rock art sites in Georgia and ignorance of rock value;
• Contemporary decorations due to human impact on the surface/graffiti by shepherds in the case of Damirgaya;
• No pigment studies from archaeological findings in Georgia, in the same context with case studies using analytical techniques which are routinely applied in culture heritage.

The chances offered by the present study were also limited by the fact that rock art is a fragile cultural heritage, and it was only possible to collect a higher number of samples, having some limitations in order to obtain a full data-set.

Significance and Future Directions

Archaeometric approaches for rock art are crucial to acknowledge its conservation history. It is compulsory to design appropriate preventive protocols involving analytical chemistry, that will contribute to deepen the knowledge and hence the future preservation of this vulnerable rock art sites. In the case of Trialeti rock art, it has been included in European Rock Art Trials and the making of touristic trials will start from Summer 2022. In the frame of a correct preservation process, my data will be made available and could be utilized by conservators.

Furthermore, the database obtained as a thesis outcome could be used by anyone interested in this field or willing to pile up the investigation on red pigments eventually recovered on other artefacts at the Georgian National Museum.

Future possible studies may include geological and archaeological surveys to uncover potential ochre source locations, which are mostly found in prehistoric areas, as well as to find more rock art sites in Georgia and pursue the *chain opératoire* of ochre using experimental archaeology. Finally, for conservation purposes, the collaboration with the European Rock Art Trial is desirable.

Appendix 1: FTIR

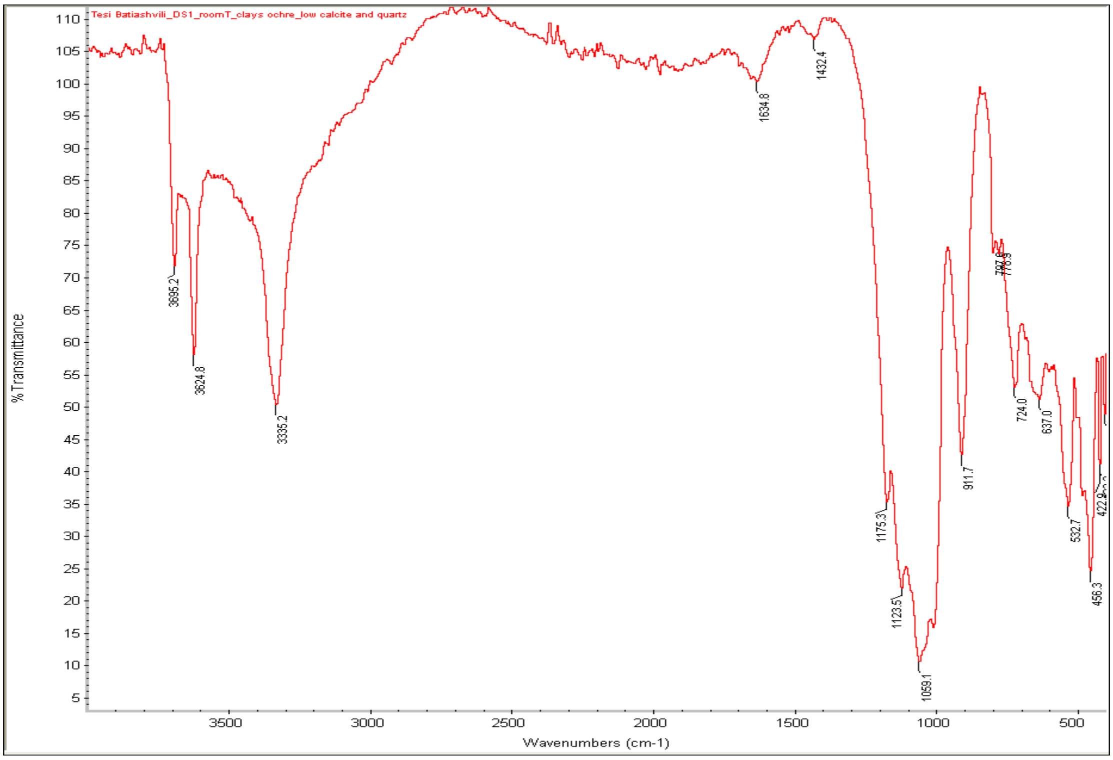

Plate I - Pigment sample DS1, spectrum collected at room temperature

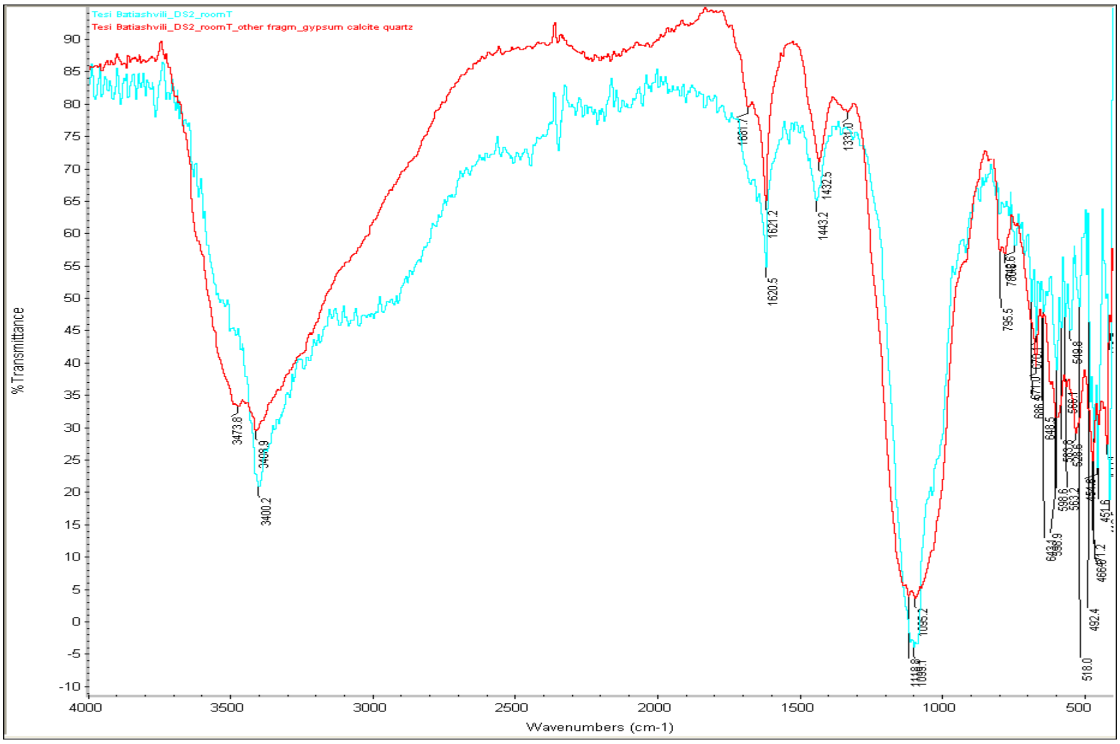

Plate II - Pigment sample DS2, spectra collected at room temperature on 2 different microfragments.

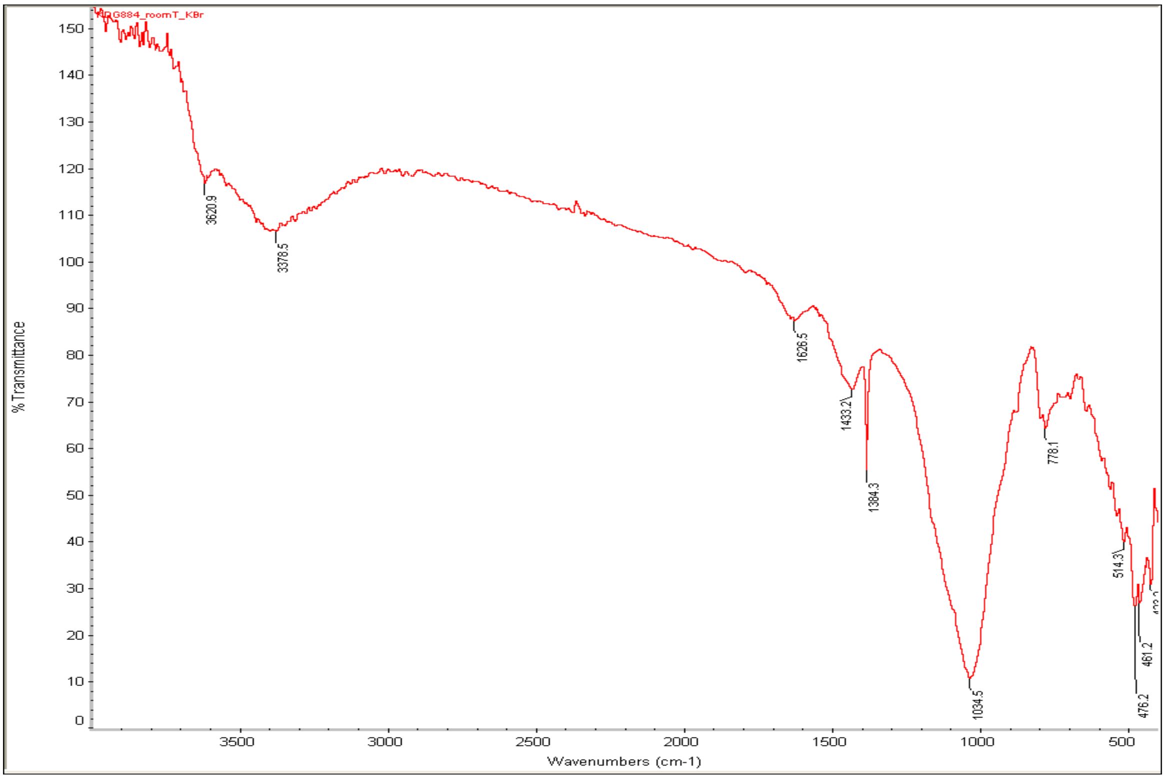

Plate III - Pigment sample KDG884, spectrum collected at room temperature

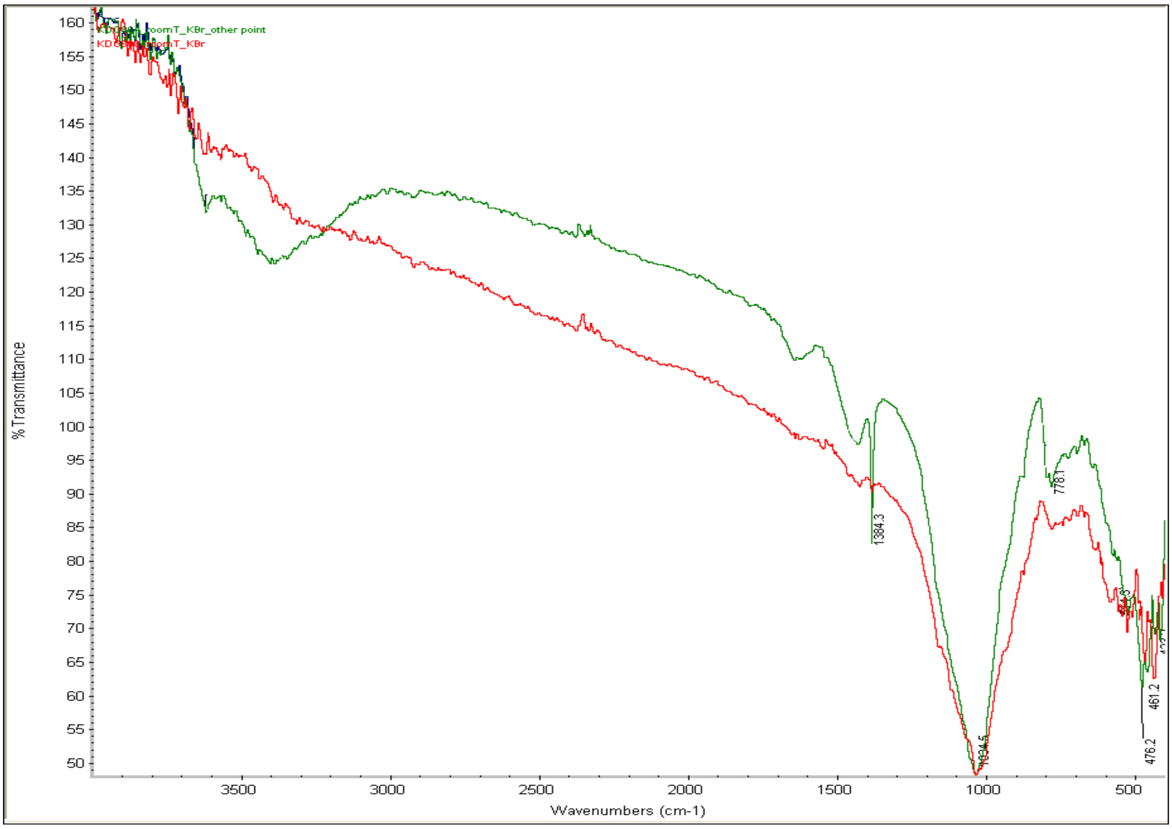

Plate IV- Pigment sample KDG898, spectrum collected at room temperature on 2 different points of the same KBr pellet

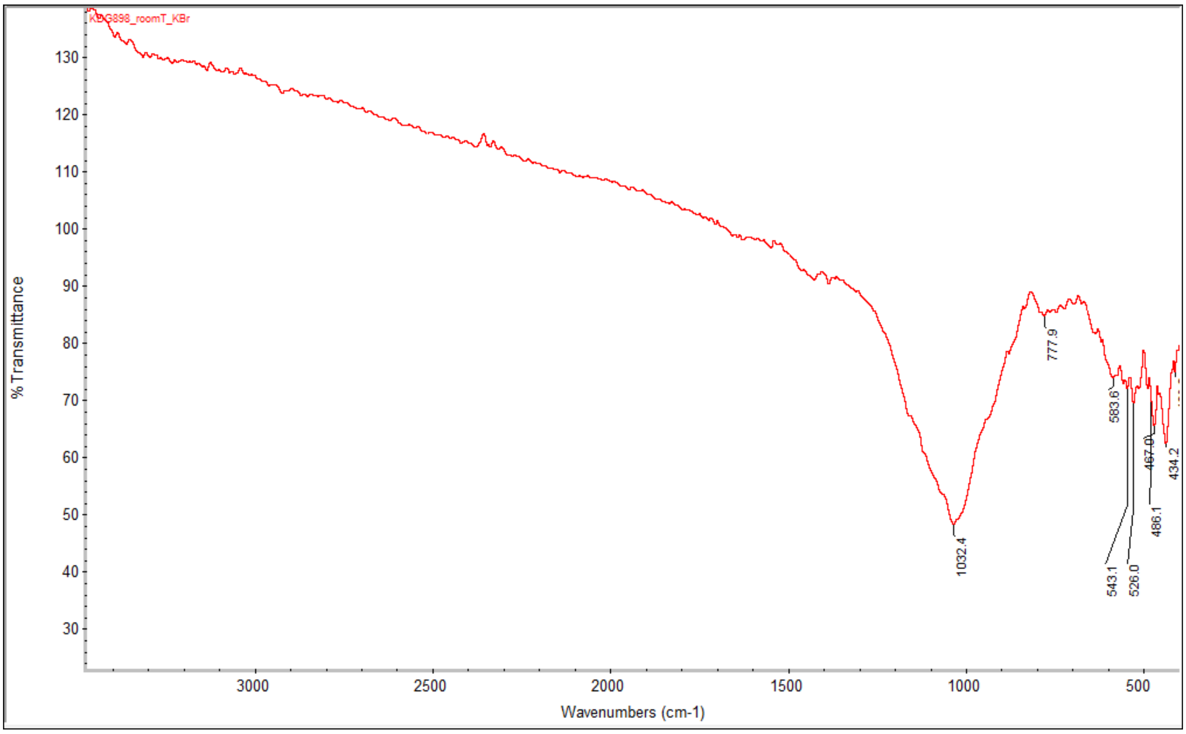

Plate V- Pigment sample KDG898, spectrum collected at room temperature.

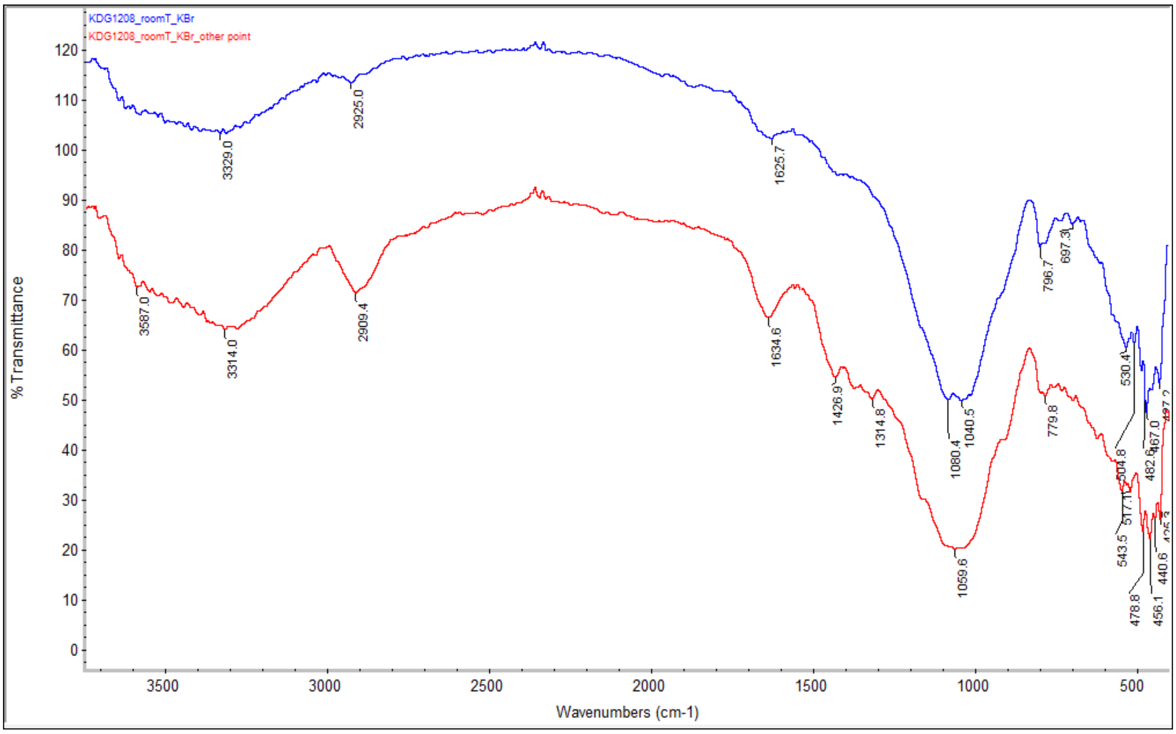

Plate VI- Pigment sample KDG1208, spectrum collected at room temperature on 2 different points of the same KBr pellet

Appendix 2: Raman Spectroscopy

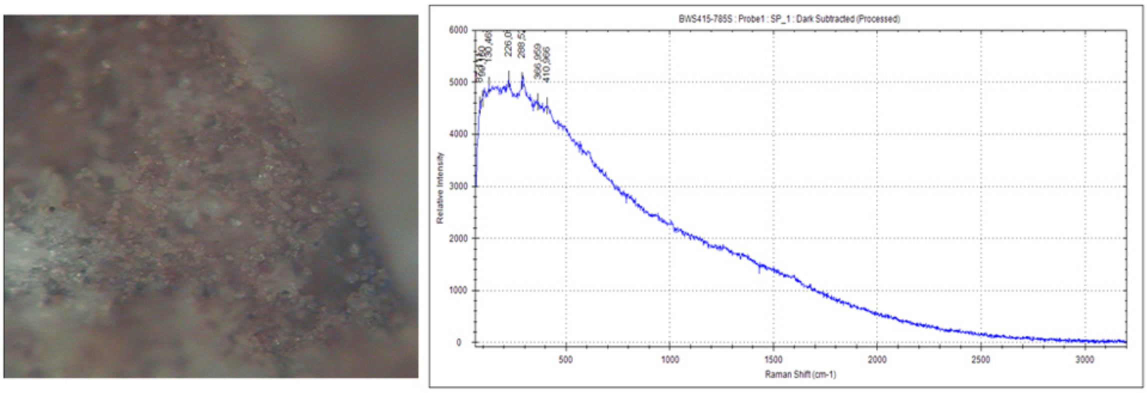

Plate VII - DS1 pigment, Raman spectrum and corresponding area under investigation

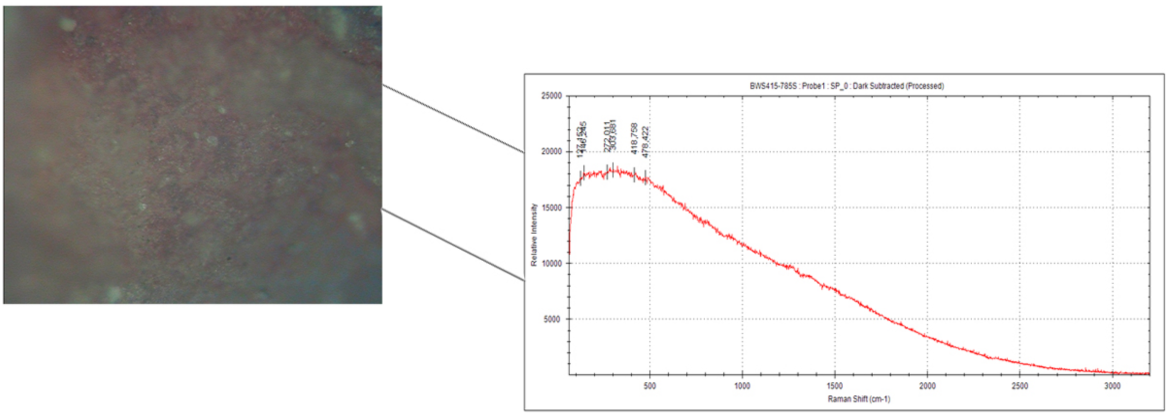

Plate VIII - DS2 pigment, Raman spectrum and corresponding area under investigation

Appendix 3: XRPD

The XRPD spectra collected for all samples are shown in this appendix. The spectrum of TS2 is not shown because it gave very low signals, possibly due to the low amount of sample.

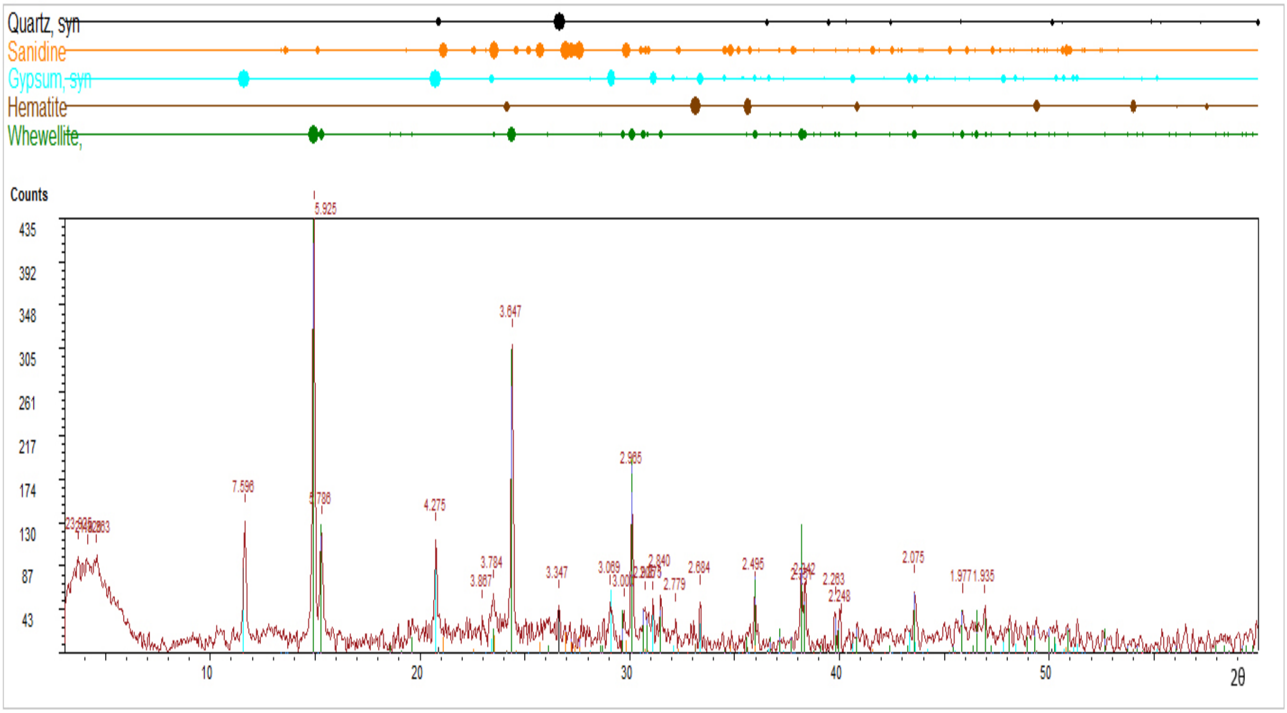

Plate IX- XRPD spectrum of TS1

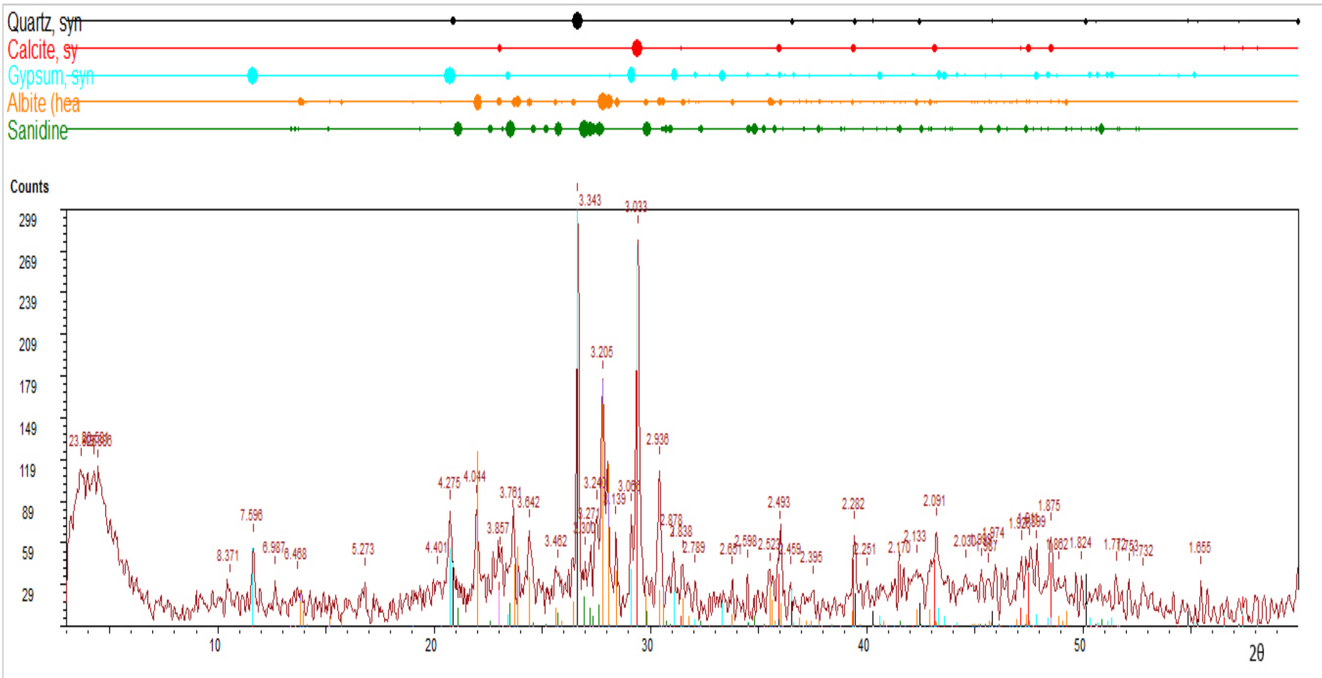

Plate X - XRPD Spectrum of KDG816/817

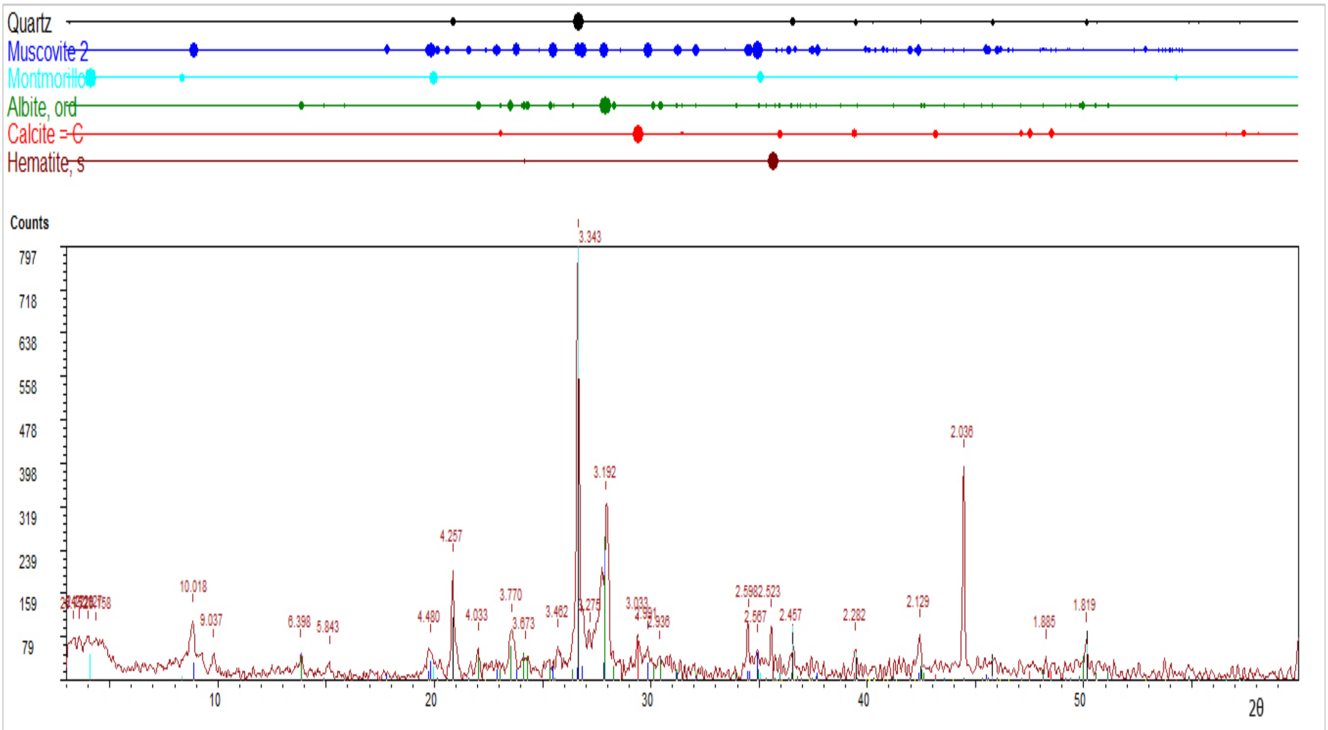

Plate XI- XRPD Spectrum of KDG884

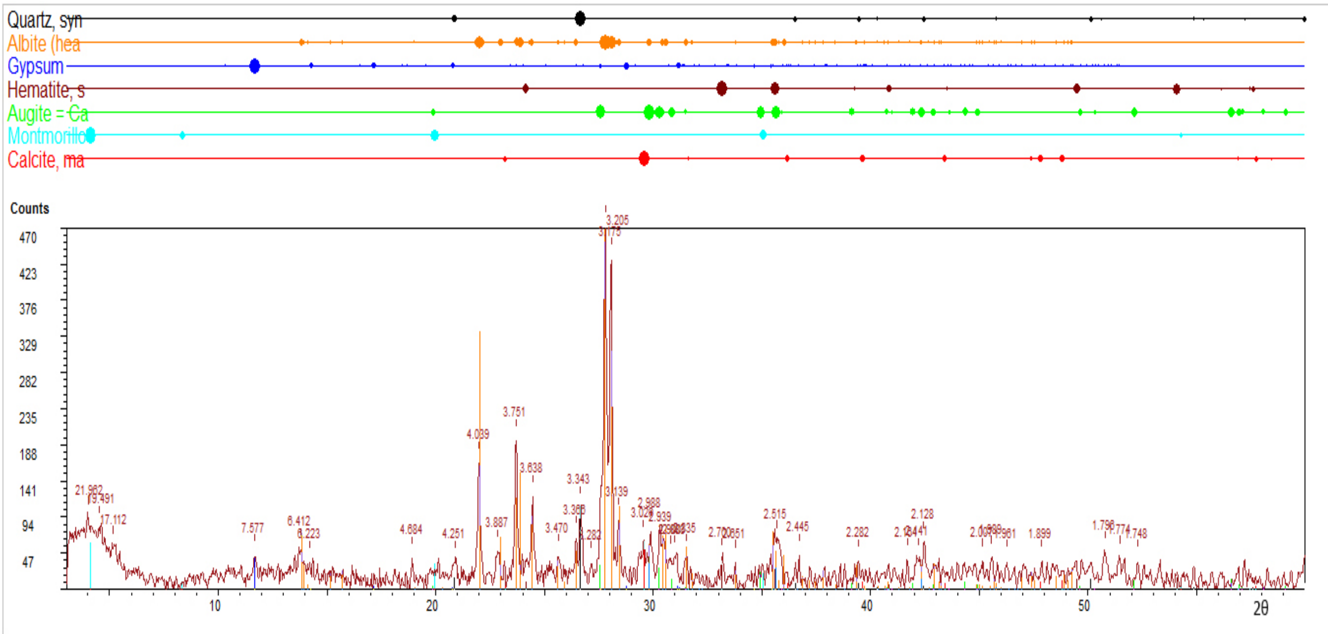

Plate XII - XRPD Spectrum of KDG898

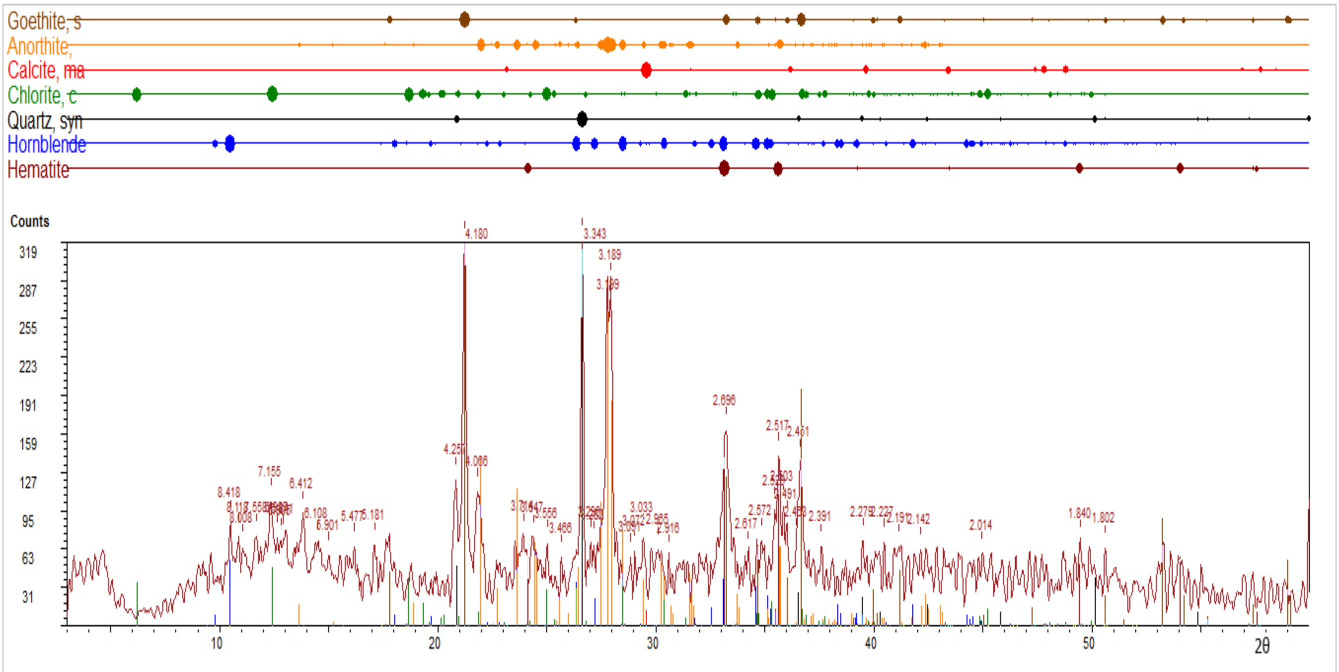

Plate XIII - XRPD Spectrum of KDG1149

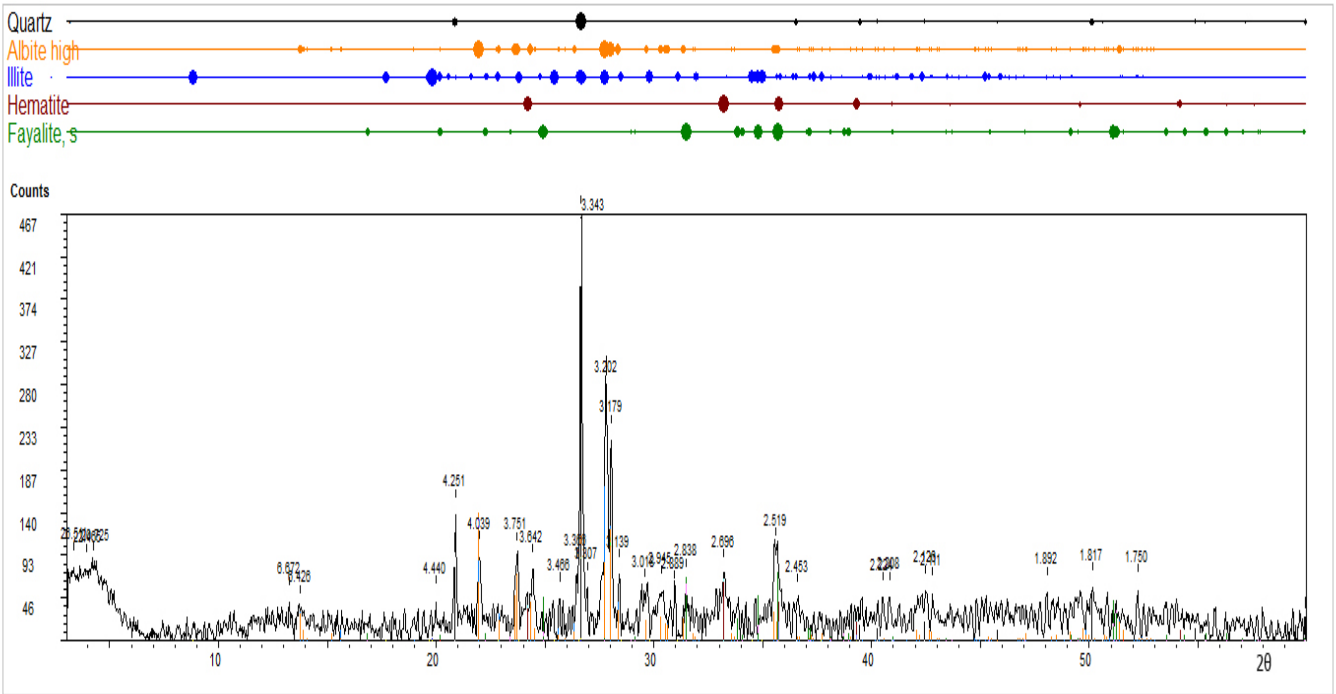

Plate XIV - XRPD Spectrum of KDG1208

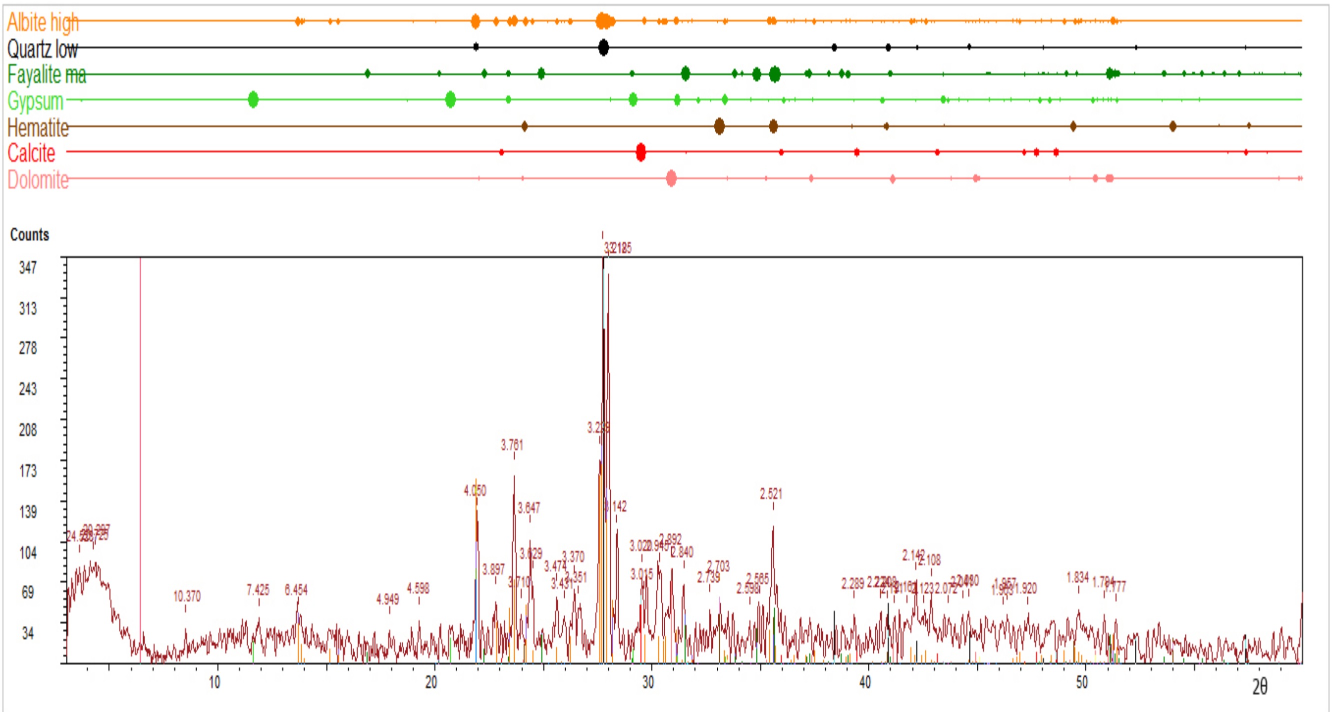

Plate XV- XRPD Spectrum of KDG1718

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