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Colour of the past in South Caucasus: The first archaeometric investigation on rock art and pigment residues from Georgia

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ABSTRACT

This research is the first archaeometric investigation of Damirgaya and Trialeti painted rock art and pigments from grinding tools from the Neolithic settlement of Khramis Didi Gora, in South Caucasus, Georgia. The aims of this research are to characterise the rocks and pigments including identification of organic binder, as well as investigate the compatibility of inorganic pigments with locally available supplies and methods of production.

Stylistic similarities and influences are compared with adjacent archaeological sites from Armenia and Azerbaijan, where traces of monochromatic red pigment were recovered in settlements, barrows and artefacts.

Optical microscopy (OM) on loose samples and thin sections, X-ray powder diffraction (XRPD), and scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) were used to determine the mineralogical and chemical composition of the samples. Employing micro-Fourier-transform infrared (μ -FTIR) and Raman spectroscopy, compounds were further characterized in both rock paintings and grinding tools.

It was not possible to identify or ascertain the presence of binders, either because of their low concentration or complete molecular breakdown deterioration. From the pigment residues on both the rock art and grinding tools, hematite was the main colouring agent, with different associated minerals. For the rock samples, it was found that the rock art at Trialeti is on a dacite, whereas the one from Damirgaya is on a rock composed of quartz, with traces of iron oxides and phyllosilicates, suggesting that the rock originated from hydrothermal activity. The research presented here is the first chemical and mineralogical characterization of pigment residues and rock art from South Caucasian prehistory.

1. Introduction

The Caucasus is characterized by vast intertwining of mountains, steppes, marshes, and valleys, surrounded on two sides by the Black and Caspian Sea (Sagona, 2017). Today, this territory includes the Republic of Georgia, Azerbaijan, and Armenia. In geographic terms, Georgia can be divided according to its main orographic units: the Greater and Lesser Caucasus mountains, the intra-Caucasus depression, and the Sioni and Kura River basins (Chataigner et al., 2014; Gamkrelidze et al., 2021).

From the archaeological point of view, the Caucasus has a significant number of prehistoric and historic archaeological sites, where material culture is well expressed in settlements, barrows, and rock art sites. However, Caucasian rock art is scarcely known. It almost exclusively

consists of petroglyphs and a few examples of pictographs. The most significant rock art sites are known in five districts of Azerbaijan: Gobustan, Shikhov, Apseron, Gemigaya (Nakhchivan), and Kelbajar (Anati et al., 2014). Gobustan rock art sites are the most important, with more than 6000 petroglyphs representing humans, animals, various symbols and inscriptions, covering the period from the Upper Palaeolithic to the Middle Ages (Sigari et al., 2020). Engravings and paintings have been discovered in Armenia since the 1970s. In the Darband river valley, anthropomorphic and zoomorphic figures have been discovered, whereas in the Gegham Range, Vardenis Range and Syunik, a more linear technique similar to petroglyphs prevails. Most of this production dates from the 4th to the 1st millennium BCE (Gasparyan and Arimura, 2014). More recent findings include the Geghamavan-1 cave, discovered

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in 2002 on a terrace of the Kasakh River gorge in Armenia, in the proximity of the newly founded village of Geghamavan at the western foot of Mt. Ara. The cave is believed to have been used continuously from the 12th to the 6th millennium BCE. The site is called “red cave” by locals, because most of the interior of the cave retains red ochre paintings on the ceiling, walls, facade and on the surfaces of broken rock slabs (Khechoyan and Gasparyan, 2014).

South Caucasus Georgia has very few known rock art sites (Fig. 1). In west Georgia, specifically in the *Apkhazeti* village of Anukhva, painted human hand contours, crosses, and circles have been found. At Mghvimevi, in the Chiatura district, art impressions belonging to the Palaeolithic period have been found (Ksica and Ksicová, 1994). Sometimes engravings are depicted in Middle Bronze Age burials 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 (Gogvadze, 2010). The most noticeable Georgian rock art examples are in the Patara Khrami/Trialeti petroglyphs (Sagona, 2017). In the Trialeti area, about 100 petroglyphs have been discovered near the gorge of river Patara Khrami, including real and ‘hybrid’ animal figures, crosses and sun depictions, as well as hunters with their arrows. Based on archaeological findings and iconographic investigation, the petroglyphs have been dated from the Mesolithic to the Bronze-Iron Age (Gabunia, 1980). As well as petroglyphs in South Caucasus, Georgia has sites of painted rock art.

The sources of potential pigments in South Caucasus archaeological sites are documented as occurring in different forms. They have been found as lumps in North-Georgia: in the Apiancha Cave, below the Apiancha mountain range (right bank of the Kodori river, near the village of Tsebelda, see Korkia, 2001) and at Khergulis Klde Cave (uncertain dating, Neolithic/Bronze Age/modern periods, in Szymczak, 2020). Ochres have been found as traces on grinding tools, in the Middle Palaeolithic layers of the Apiancha cave (Korkia, 2001) and at Imiris Didi Gora, a site belonging to the Shulaveri culture (6th-beginning of 5th millennium cal. BC) in south-east Georgia. In this case, ochres have been found in longitudinal striations and as peripheral traces on a massive ovoid cobble, described as a ‘palette’ for the soft grinding and mixing of pigments (Hamon, 2008). This is also the use suggested for the lithic tools from the Shulaveri site of Khramis Didi Gora, based on pigment residues. In other Shulaveri contexts in Georgia, ochre has been used for the decoration of surfaces in Neolithic houses (Japaridze and Javakhishvili, 1971). In the same period, burial sites have revealed the

abundant use of ochre, e.g. at Mentesh Tepe, in Azerbaijan, either on the deceased bodies or on the floor (Lyonnet et al., 2016). For the later Caucasian Eneolithic period red pigments have been found in sites such as the Arukhlo I settlement in the Kvemo Kartli region, Bolnisi Municipality. The site has significant archaeological discoveries, including a round-shaped stone depicting a human face in light red pigments, found along with numerous pottery fragments (Chikovani et al., 2015). Traces of pigments have also been discovered in some Early Bronze Age ‘Bedeni barrows’ of Georgia, along the Bedeni Plateau south of Tbilisi. Unfortunately no compositional data or supply is known for these pigments (Gobejishvili, 1981).

Re-discovered in the 2010s, the rock art sites of Damirgaya and Trialeti are among the few examples of Georgian painted rock art and the subject of the present research. The investigation was aimed at characterising their chemical and mineralogical composition and compatibility of the residues with local sources. It has also provided a characterisation of the rock type at both sites, integrating the latterly proposed geological setting for Damirgaya (Losaberidze et al., 2022) and giving the earliest description of the geology at Trialeti. For the first time, an archaeometric investigation has been applied to the pigment residues sampled from grinding tools found at the Neolithic settlement of Khramis Didi Gora, thanks to the collaboration with the Georgian National Museum. As these grinding stones have relative chronology, they can contribute to the comparison of Neolithic technological awareness at Khramis Didi Gora with rock art at nearby sites.

Micro-Fourier Transform Infrared (μ -FTIR) and Raman spectroscopy were combined with fluorescent staining for the characterisation of inorganic and organic compounds. The mineralogical composition was confirmed for pigments and rock samples coming from Trialeti and Damirgaya by X-ray Powder Diffraction analysis (XRPD). Optical microscopy (OM) and scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS) were applied on thin-sections and cross-sections for the identification of the parental rock in Trialeti and Damirgaya, additionally to establish the morphology and composition of the pigment layers in the samples from Damirgaya.

2. Geographical and geological framework

2.1. Damirgaya

Damirgaya is a rock shelter (Fig. 2a) located in southern Georgia in the northern foothills of the Lesser Caucasus, 3 km south of the village of

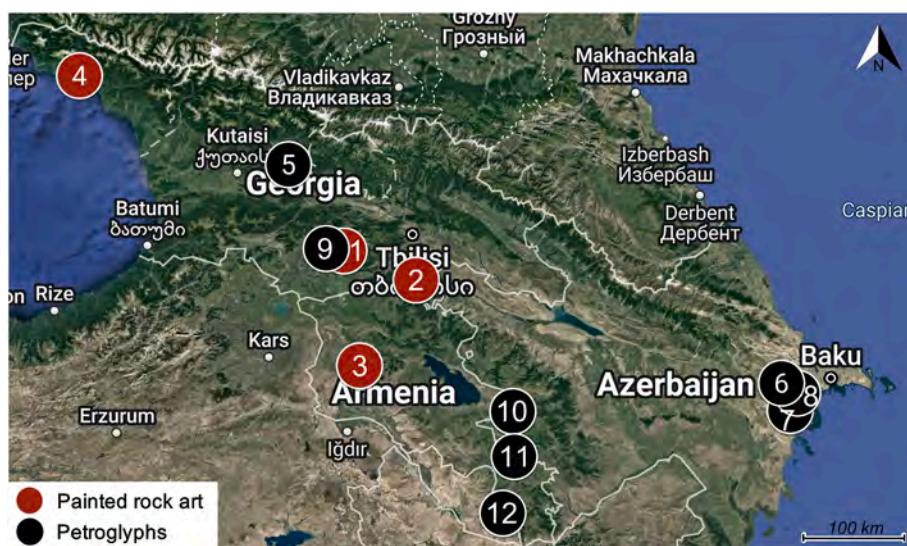


Fig. 1. Map of the Caucasus depicting the presence of prehistoric painted and engraved rock art sites discussed in the article (<https://google.com/maps>): 1) Trialeti, 2) Damirgaya, 3) Geghamavan-1, 4) Anukhva 5) Mghvimevi, 6) Apseron, 7) Gobustan, 8) Shikhov 9) Trialeti, 10) Kelbajar, 11) Ughtasar, 12) Gamigaya

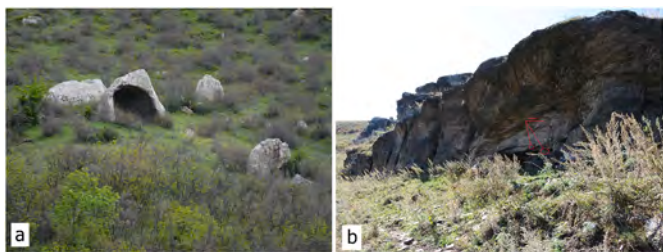


Fig. 2. a) Damirgaya and b) Trialeti rock shelters.

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 (Fig. 3), which belongs to the Kura depression, the Cenozoic foreland basin that extends toward eastern Georgia, south Azerbaijan and the Caspian Sea (Sachsenhofer et al., 2021).

The Marneuli block is structured from Pleistocene-Quaternary age terrigenous, carbonate, and volcanogenic deposits, namely lava breccia, andesite-basalts, and dacites (Mrevlishvili, 1997). Here, Cenomanian-Campanian calc-alkaline basaltic, andesitic, dacitic and rhyolitic shallow marine volcanic rocks at the southern borders with Armenia and Azerbaijan intercept the predominant Pleistocene-Quaternary formations with its river bed alluvions (Makadze, 2021; Adamia et al., 2004; Fig. 3). Several geological processes had impact on the origin of the site, notably weathering, erosion, and post-volcanic activities such as mobile hydrothermal solutions with consequent cooling of the superheated lava. Weathering and erosion have caused the detachment of boulders from the highest outcrops and additional erosion processes have finally formed two rock shelters, with heights of 5–10 m (Losaberidze et al., 2022).

Azeri people settled at Damirgaya in late medieval times and gave this site its present name, which means “iron rock”. It was surveyed in 1980 by Tamaz Kiguradze (Menabde and Kiguradze, 1986). A pilot investigation was carried out in 2017 (Losaberidze and Eloshvili, 2020),

followed by a more detailed geological and archaeological survey in 2020 (Losaberidze et al., 2022). The rock shelter where paintings have been discovered, Rock shelter 1 (5.5 m high, 7.3 m wide), opens towards the west. Red paintings are along the eastern and southeastern walls of the interior. Sixty-five motifs have been documented, including contemporary graffiti (Losaberidze et al., 2022). The images are 10–20 cm wide and are mainly divided into four groups: 1) geometric – triangles, zigzag lines and rhomboids; 2) zoomorphic – bovinds and canids; 3) anthropomorphic – a poorly preserved human figure; 4) indeterminate. The motifs have been affected by intensive damage, both natural and anthropogenic. Interpretation of the motifs has been made possible by digital enhancement of the acquired images (Losaberidze and Eloshvili, 2020).

The dating of Damirgaya has been suggested by Menabde and Kiguradze (1986) as a large span of time between the Neolithic and the Early Bronze Age. 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 the pottery fragments are likely to come from the Middle Ages. An archaeological survey carried out in the nearby area identified seven sites with materials dating to the Neolithic period (Chilingarashvili et al., 2020).

Stylistic comparisons with other rock art sites from nearby and relatively distant regions can be useful for relative dating. In the case of Damirgaya, where the motifs are still visible, stylistic parallels in terms of animal motifs, site etymology, and archaeological material recovered during excavations might suggest a link between Damirgaya and the Armenian Neolithic rock art of Geghamavan-1 (Fig. 4, IV-V). 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 recovered medieval scattered pottery fragments, faunal remains and obsidian tools (Khechoyan and Gasparyan, 2014). Furthermore, rock art patterns similar to those represented at Damirgaya were depicted in Gobustan rock art site (Fig. 4, VI).

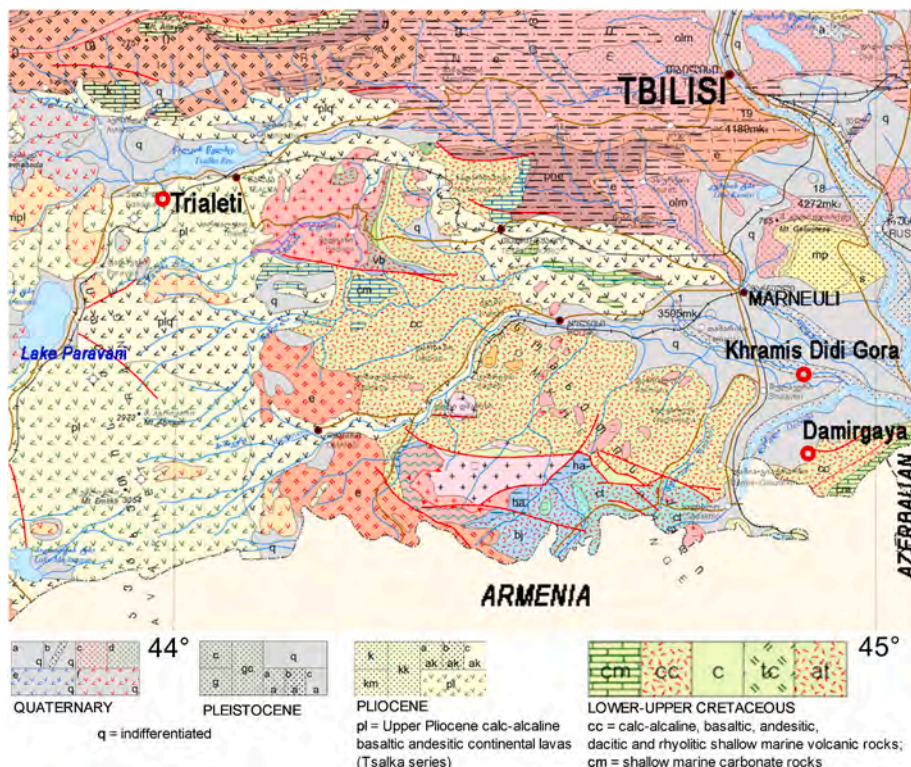


Fig. 3. Geological map, modified after Adamia et al. (2004), with location of the archaeological sites under investigation.

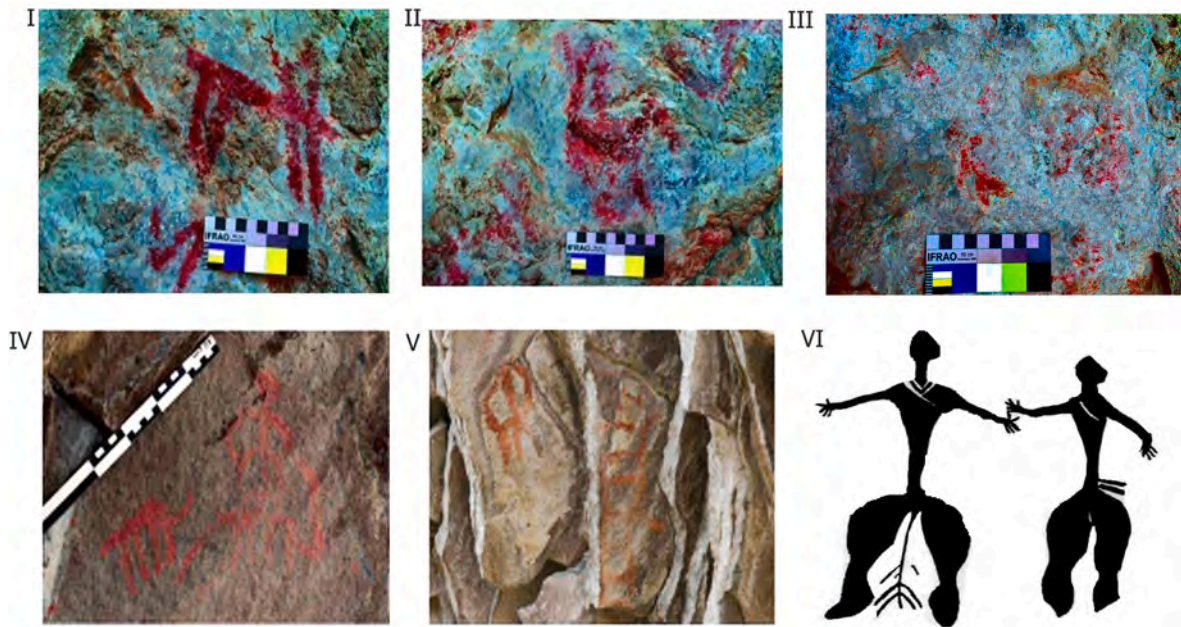


Fig. 4. I-III) animals and human motifs from Damirgaya (Photos by Losaberidze, modified with DStretch enhancement); IV-V) animal and human signs from Geghamavan-1 cave (Khechoyan and Gasparyan, 2014); VI) schematic of human motifs from Gobustan (Anati, 1999).

2.2. Trialeti

The Adjara-Trialeti zone (also mentioned as the Achara-Trialeti by [Adamia et al., 2010](#), or Adzharo-Trialet by [Eppelbaum and Khesin, 2012](#)) stands out in the northwest of the Lesser Caucasus. It is the basaltic rift that originated in the Paleocene-Eocene and divided the Transcaucasian intermontane depression into the Georgian (to the north) and Artvin-Bolnisi (to the south) massifs. The Adjara-Trialeti ridge, which has summits up to 2850 m, is made up of Albian-Lower Senonian island-arc volcanics, Upper Senonian limestone, Paleocene-Lower Eocene tuffaceous flysh, as well as Middle-Upper Eocene subalkaline and alkaline intermediate volcanics. The last Eocene folding was followed by small syenite-diorite intrusions ([Gamkrelidze et al., 2021](#)).

Trialeti pictographs are in a gorge of the river Avdriskhevi (Fig. 2b),

at the southern section of village Gantiadi (former village Tak-Kilissa), 12-km away from the small town of Tsalka, in the Kvemo Kartli region ([Regional Co-operation for Cultural Heritage Development, 2012](#)). The gorge developed within the Upper Pliocene calc-alkaline, basaltic-andesitic continental lava flow which takes the name of ‘Tsalka series’ ([Adamia et al., 2004](#); see Fig. 3), and pseudo-terraces formed by soil erosion and irregular wash away.

Several petroglyphs were discovered in Trialeti in the 1880s and rediscovered in 1976, but the painted rock art remained uncovered until 2018–2019, when a survey was conducted by the Georgian Culture Agency ([Gabunia et al., 2019](#)). Archaeologists also recovered numerous obsidian artefacts and faunal remains. Amongst the pictographs, motifs are of two kinds: three horizontal parallel lines (Fig. 5a–b) and animal-like figures (Fig. 5c–d), all in monochromatic red pigment. However, motifs in Trialeti are less visible than in Damirgaya rock art

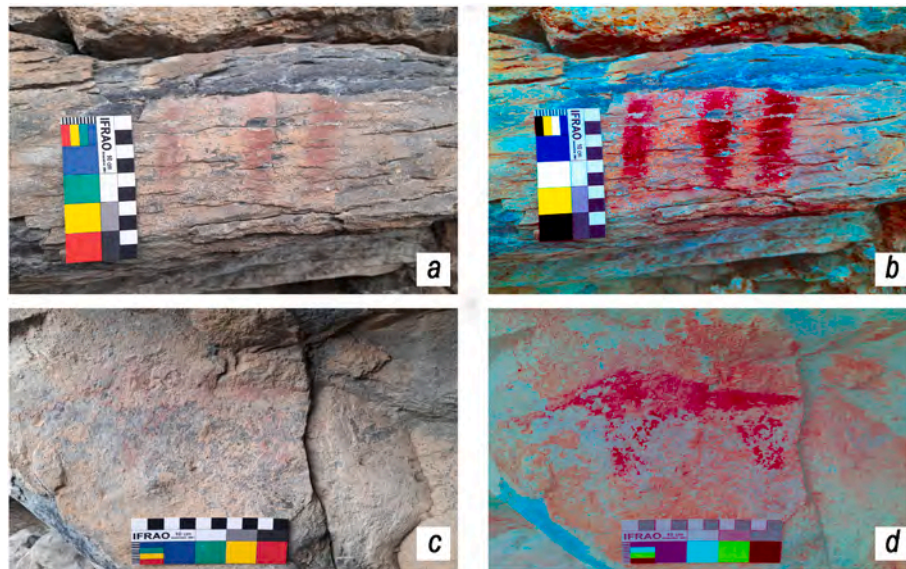


Fig. 5. Trialeti pictographs: (a) geometric figure; (b) same pictograph, digitally enhanced by DStretch plugin in ImageJ software; (c) animal-like figure; (d) same figure with DStretch enhancement (photos by L. Losaberidze).

and it is harder to reconstruct pictographs and make parallels with adjacent sites. Archaeological information on the site is still unpublished and the present research constitutes its first archaeometric study.

2.3. Khramis Didi Gora

The archaeological site of Khramis Didi Gora (Fig. 6) is in the Kura basin, between Damirgaya and the town of Marneuli, and hence shares geological features with the aforementioned site. The Neolithic of central and southern Caucasus is often referred to as the ‘Shulaveri-Shomutepe’ culture, after two key sites that 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, the ‘Shulaveri group’ is represented by several archaeological sites, Shulaveris Gora, Imiris Gora, Gadachrili Gora, Dangreuli Gora (Kushnareva, 1997), and Khramis Didi Gora (Hamon, 2008), which all developed along the Khrami River, in the Kvemo (Lower) Kartli province (McGovern et al., 2017), approximately 50 km south of the modern capital Tbilisi. The chronology of their occupation mainly extends from Neolithic to Chalcolithic, although most of them have experienced later occupation in either the Bronze Age, the Roman period or the Middle Ages. These tell (‘gora’ or ‘tepe’) settlements are typically small hamlets averaging about 1–1.5 ha in size, but Khramis Didi Gora is the largest Neolithic mound site, measuring about 4.5 ha. The architecture is of round shape structures, made with clay and mudbrick (Japaridze, 2003). The yards often contain many artefacts related with the exploitation of plants. Other activities are suggested by the scrapers and saddle querns, grinding slabs, wasted hammers and edge-ground axes, sling stones and polishing tools, bun-shaped grooved stones (possibly used as scrapers) and perforated stone weights. All these indicate a culture based on farming and agricultural practices (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 (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, 2-to-3 cm wide, occupies the ends and sides, sometimes the whole periphery, of the working surface of these grinders (Hamon, 2008). A crucial part of the present investigation is focused on the pigment residues on these grinding stone, mortars, and hand stones.



Fig. 6. The archaeological site of Khramis Didi Gora (modified after Menabde and Kiguradze, 1980).

3. Materials and methods

3.1. Sampling

Four pigment and four rock samples come from the prehistoric rock shelters of Damirgaya and Trialeti.

A few milligrams of each pigment were scraped with a plastic tool from areas where the painted surface was already disturbed (Fig. 7), while rock samples were removed from already cracked areas nearby the paintings. Sample collection was carried out with the permission of The National Agency for Cultural Heritage Preservation (“The National Agency for Cultural Heritage Preservation,” n.d.). The samples and cross-sections were labelled as follows: the two rock-painting samples from Damirgaya are DS1 (Fig. 7a) and DS2 (Fig. 7b) while those from Trialeti are TS1 (Fig. 7c) and TS2 (Fig. 7d). Rock samples and corresponding thin-sections from Damirgaya are DRS1 and DRS2 while those from Trialeti are TRS1 and TRS2. Unfortunately, the amount of sample available for TS2 was not enough for a full characterisation.

Additional sampling was carried out at the Georgian National Museum: six micro-samples of pigment residues were taken from grinding tools (pestles/hand stones, mortars and grinding stone) coming from the Neolithic settlement of Khramis Didi Gora (Fig. 8).

The pigment samples from Khramis Didi Gora are labelled according to the grinding tool from which they originated and its code in the museum catalogue. The sampled tools are: two mortars (KDG1718 and KDG884, Fig. 8a,c), a grinding stone (KDG816/87, Fig. 8b) and three pestle/handstones (KDG1149/1152, KDG1208 and KDG898, Fig. 8d–f).

3.2. Analytical techniques

To characterise inorganic and organic compounds, and understand pigment technology and compatibility with local sources, a multi-disciplinary archaeometric approach was applied using the complementary techniques of XRPD, micro-FTIR and Raman spectroscopy, SEM-EDS, OM and fluorescent staining. The list of samples and the type of analysis is given in Table 1. For some of those, the type of sample constrained the number of analyses to be performed on it. For example, the Raman spectrometer is equipped with a microscope and the analysis can be superficial. Hence, we decided to focus on the pigment samples we had as loose fragments (DS1 and DS2), for which we could visualise the spot to be analysed. Analogously, the staining protocol, which is optimised for cross-section analysis, was only tested on the cross-sections DS1 and DS2. For some samples, the analysis was constrained by the amount of sample. Because of this, and time constraints, micro-FTIR and SEM-EDS analysis were carried out on a few representative samples.

Before being embedded in resin, loose samples and cross-sections from Damirgaya were first examined and imaged under a Leica stereomicroscope, equipped with a Leica DFC420C camera (with Leica Image 1000 software), at the Istituto Centrale per il Restauro (ICR), Rome, Italy. For petrographic analysis the protocol described in Botticelli et al. (2022) was applied. The rock samples were identified according to a protocol developed by Hughes (1982).

To investigate microstructural features and qualitative chemical composition of the rock/pigment sections, SEM-EDS elemental mapping was conducted on the thin-sections DRS2 and TRS1 to characterise selected minerals, as well as on the cross-sections DS1 and DS2 to establish the stratigraphy.

To semi-quantitatively characterise minerals in the pigment residues from Khramis Didi Gora, and in the pigment/rock samples from Trialeti and Damirgaya, XRPD was conducted using the instrument, operating conditions and data processing protocol described elsewhere (Botticelli et al., 2020).

In most of the powdered pigment samples (Table 1), spectroscopic techniques were used to complement XRPD results and identify key minerals, as well as possible organic compounds. For micro-FTIR, a

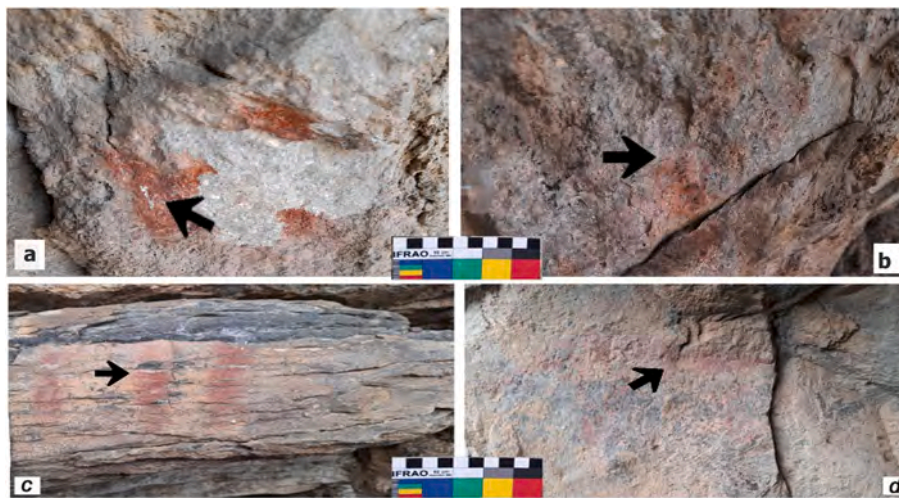


Fig. 7. Sampling areas (black arrows) at Damirgaya: a) DS1, b) DS2; at Trialeti: c) TS1, d) TS2.

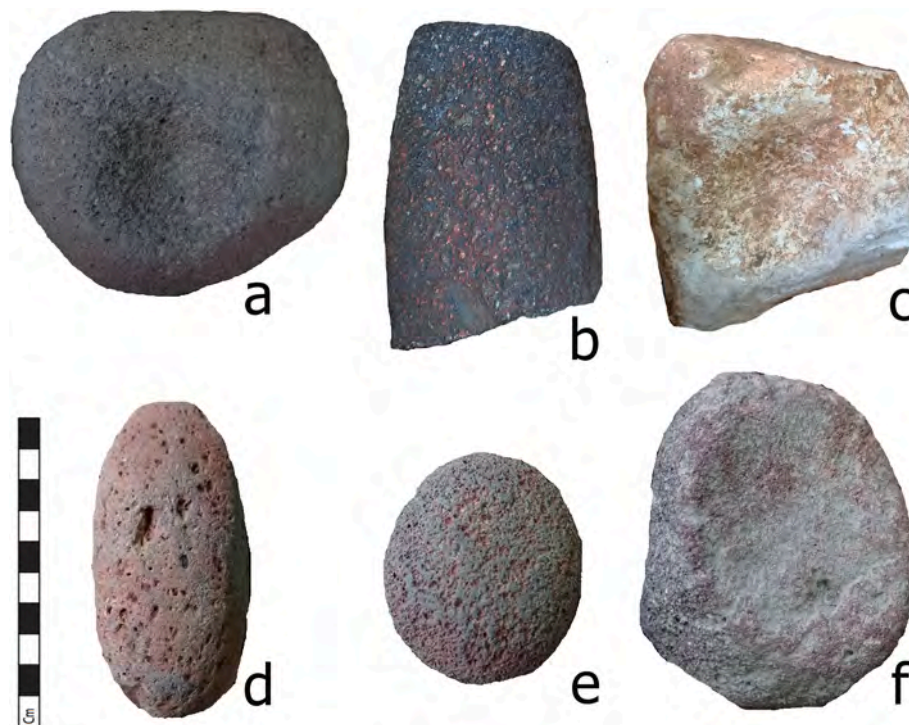


Fig. 8. Grinding tools from Khramis Didi Gora including: two mortars, a) KDG1718 and c) KDG884; one grinding stone b) KDG816/87; three pestles/handstones, d) KDG1149/1152, e) KDG1208 and f) KDG898.

microscopic fragment of the pigment samples DS1 and DS2 was pressed in a diamond cell. Representative pigment samples from Khramis Didi Gora 9KDG884; KDG898; KD1149 and KDG1208) were analysed in KBr pellets. Raman spectroscopy was conducted non-destructively on the loose fragments DS1 and DS2.

A staining procedure was applied for the identification of possible proteinaceous compounds on DS1 and DS2 cross-sections.

Analytical conditions are summarised in Table S1.

4. Results

4.1. Rock samples

Table 2 summarises the outcomes of the minero-petrographic

investigation on the rock samples from Damirgaya and Trialeti.

The rock samples from Damirgaya were found to be composed of quartz with abundant content of high-crystalline kaolinite, identified by XRPD (Fig. S2, a-b) and confirmed by SEM-EDS analysis (see Al and Si maps in Fig. 9). Minor zunyite, a sorosilicate with formula $\text{Al}_{13}\text{Si}_5\text{O}_{20}(\text{OH},\text{F})_{18}\text{Cl}$ (Berrada et al., 2009), could be identified in the XRPD patterns of DRS1 and DRS2, but also in the frequent co-occurrence of aluminium and chlorine in the elemental maps collected by SEM-EDS (Al and Cl maps in Fig. 9). Quartz is uniformly distributed in a fine-grained matrix, which also includes iron oxides. The high content of quartz was confirmed both by OM and SEM-EDS analysis (Fig. 9), along with dispersed amorphous iron oxides, small titanium-oxide crystals (Fe and Ti maps in Fig. 9) and pseudocubic alunite crystals.

Thin-sections from Trialeti revealed that the rock has a porphyritic

Table 1

Summary of samples taken from rock art and grinding tools of the prehistoric sites under study, and method of analysis (P = powder, L = loose sample, CR = cross-section, TS = thin-section, KBr = potassium bromide pellet).

| Sample | XRPD | Raman | μ -FTIR | OM | SEM-EDS | Staining |
|------------|------|-------|-------------|-------|---------|----------|
| DRS1 | P | – | – | TS | – | – |
| DRS2 | P | – | – | TS | TS | – |
| DS1 | – | L | P | L, CS | CS | CS |
| DS2 | – | L | P | L, CS | CS | CS |
| TRS1 | P | – | – | TS | TS | – |
| TRS2 | P | – | – | TS | – | – |
| TS1 | P | – | – | – | – | – |
| TS2 | P | – | – | – | – | – |
| KDG817/816 | P | – | – | L | – | – |
| KDG884 | P | – | KBr | L | – | – |
| KDG898 | P | – | KBr | L | – | – |
| KDG1149 | P | – | KBr | L | – | – |
| KDG1208 | P | – | KBr | L | – | – |
| KDG1718 | P | – | – | L | – | – |

Table 2

Summary of mineral phases identified for each prehistoric rock art site; minerals are listed in order of abundance.

| Damirgaya | Trialeti |
|--|--|
| quartz, SiO_2 | plagioclase, labradorite $(Ca,Na)(Si,Al)_4O_8$ |
| kaolinite, $Al_2Si_2O_5(OH)_4$ | hornblende, $(Ca,Na)_{2-3}(Mg,Fe,Al)_5Si_6(Si,Al)_2O_{22}(OH)_2$ |
| zunyite, $Al_{13}Si_5O_{20}(OH, F)_{18}Cl$ | biotite, $K(Mg,Fe^{++})_3[AlSi_3O_{10}(OH,F)_2]$ |
| alunite, $KAl_3(SO_4)_2(OH)_6$ | clinopyroxene, augite $(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)_2O_6$ |
| iron and titanium oxides | quartz, SiO_2 |
| | iron and titanium oxides |

texture, with occurrence of bimodally distributed phenocrysts in a fine-grained, partially-vitrified matrix. Phenocrysts mainly include big grains of partially-altered plagioclase (likely labradorite, Fig. 10a), with small prismatic hornblende, tabular biotite and clinopyroxene, possibly augite (Fig. 10b). The high plagioclase and medium clinopyroxene content was further confirmed by XRPD (Fig. S1, c-d). This mineralogical assemblage (Table 2), along with minor quartz in corroded and rounded phenocrysts, support the classification of both TRS1 and TRS2 as dacite. Iron-based minerals were frequently observed in both thin-sections. They are dark-brown in both PPL and XPL observations, round or elongated in shape, with irregular edges, rarely showing intergrowth. SEM-EDS analysis showed that they contain Fe and Ti as major elements (Fig. 10c).

4.2. Rock art samples

Table 3 summarises the main inorganic compounds identified in the pigment samples from Damirgaya.

The surface of sample DS1 from Damirgaya (Fig. 11a), observed with a stereomicroscope, appeared darker in hue than DS2, with a reddish tone, while DS2 showed a brownish tone. OM and SEM-EDS analysis of the cross-sections from Damirgaya confirmed the elemental composition defined for the rock samples, showing areas with Si only, some with Cl and Al (Fig. 11b), and small Ti-based crystals (Fig. 11c). Predominant signals of hematite (Froment et al., 2008) were identified by Raman spectroscopy at the surface of the fragment DS1 with minor goethite (Fig. S3). Other mineral phases typical in red ochres, such as quartz or calcite, were not detected, possibly saturated by the high background fluorescence. OM and SEM-EDS analysis identified a very thin pigment layer in DS1 (less than 10 μ m), with sub-micrometric particle of bright red (Fig. 11a), possibly a red ochre with pedogenic origin (Hradil et al., 2003; Popelka-Filcoff and Zipkin, 2022). EDS showed that the layer contains iron, as the main element, along with potassium, aluminium and phosphorus.

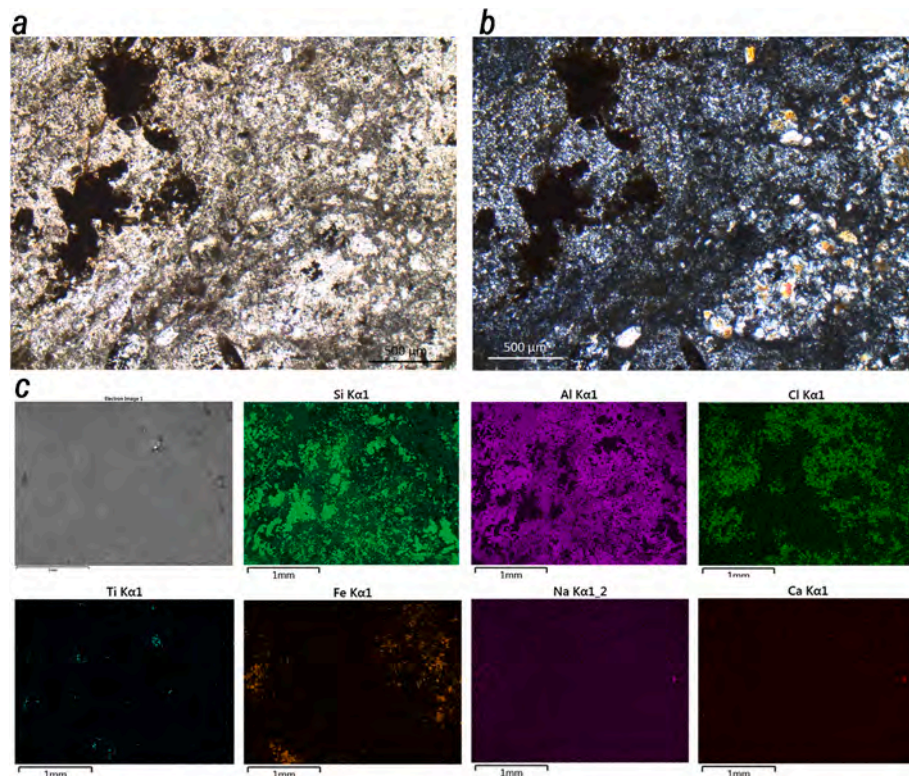


Fig. 9. OM images of a representative area in the thin-section DRS2, under visible light, a) PPL, b) XPL, with SEM-BSE image of a different area of the same thin-section, and corresponding chemical maps of silicon (Si), aluminium (Al), chlorine (Cl), titanium (Ti), iron (Fe), sodium (Na) and calcium (Ca).

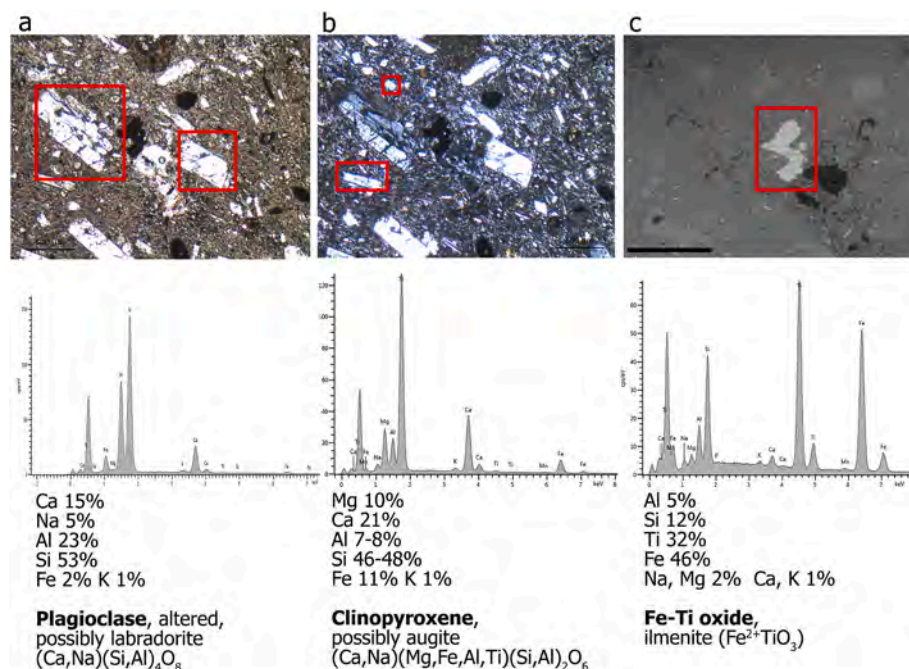


Fig. 10. Main mineralogical and chemical features of cross-sections TRS1 and TRS2 from Trialeti, as found by OM (visible light, scale bar = 500 μm , a = PPL; b = XPL) and SEM-EDS semi-quantitative analysis (c = SEM-BSE image).

Table 3

Summary of mineral phases identified for each cross-section from Damirgaya; minerals in the same class (main pigment, associated minerals, secondary products) are listed in order of abundance.

| | DS1 | DS2 |
|---------------------|---|---|
| Main pigment | Hematite, Fe_2O_3 | Goethite, $\text{FeO}(\text{OH})$ |
| Associated minerals | Goethite, $\text{FeO}(\text{OH})$ Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ Quartz, SiO_2 | Hematite, Fe_2O_3 Lepidocrocite, $\text{FeO}(\text{OH})$ |
| Secondary products | Phosphate-based 'cave' mineral | Gypsum, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ Oxalates, $\text{CaC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$ Phosphate-based 'cave' mineral |

Mineralogical and chemical features of this sample vary remarkably from those of DS2 (Table 3). The latter displays a light-to-dark brown pigmented surface, when observed as loose fragment under the stereomicroscope (Fig. S3). The pigment layer appears thicker ($\sim 100 \mu\text{m}$) than in DS1 (Fig. 12a). There are white irregularly-shaped particles surrounded by fine black and orange grains in a homogeneous matrix, possibly of organic nature (see the darkest areas around the particles in the SEM micrograph, Fig. 12b).

The Raman spectrum of DS2 was strongly affected by noise and background fluorescence. The most intense bands were tentatively attributed to goethite (Cornell and Schwertmann, 2003), with minor contribution from hematite (Fig. S3).

For both samples, μ -FTIR spectroscopy provided a further characterization of the mineral assemblage: either quartz, calcite, gypsum or kaolinite were identified as accessory minerals (band assignment in Table S4). Hematite as the main pigment was confirmed when the analysis was performed at room temperature, although its typical signals showed a slight shift in band position between DS1 and DS2. The presence of goethite was also found, showing bands constant in position for both samples but more intense in DS2, which explains the difference in colour between the painted fragments from Damirgaya. Also contributing to the different hue between DS1 and DS2 is the more abundant gypsum in the latter, in combination with traces of oxalates (Table S4), which might correspond to natroxalate, a sodium-based oxalate (Frost

et al., 2003).

Further IR bands in the samples from Damirgaya could be attributed to a phosphate-based 'cave mineral', justifying the homogeneous distribution of phosphorous in the EDS maps, more evident in DS1 than in DS2 (Fig. 11). It is worth noting that there is no correlation between Ca and P at the surface in the EDS maps (Figs. 11c and 12b).

The sole organic compound detected by fluorescence staining is protein-based, in sample DS1 only. Interestingly, the orange fluorescence is slightly visible at the pigment level, but it is mainly present in the porous areas of the rock, where SEM-BSE images had shown recrystallizations (Fig. 13).

Secondary products were also found to predominate in the pigment samples from Trialeti. As the latter was in a powder form and in very small amounts, only XRPD analysis was carried out, with meaningful results for TS1 only. Here, the colouring agent, hematite, was found in trace, whewellite was the most abundant phase, gypsum and K-feldspar were scarce.

4.3. Ochre residues from the grinding tools

In the ochre residues from the grinding stones hematite was in trace (for most of the samples) or scarce (KDG1149) amount by XRPD (Table S5). For KDG816/817, it was not possible to identify it at all. Gypsum was detected in samples KDG816/817, KDG898, KDG1718. FTIR analysis showed good agreement with the diffractometric results, but proved to be more sensitive in the discrimination of iron oxides and hydroxides (Table S4). Goethite was confirmed by both FTIR and XRPD in KDG1149. Accessory minerals were found to be quartz and calcite, as already identified by XRPD, the first being in all samples and the latter absent in KDG898. The typical IR bands from Ca-oxalates were identified on the pestle KDG1208. Interestingly, a small but sharp IR feature at 1384 cm^{-1} (higher intensity in KDG884, lower intensity in KDG898 and KDG1149) was tentatively assigned to nitrates (Painter et al., 1980) and linked to ferrihydrite (Cornell and Schwertmann, 2003). From XRPD data, the pigments with nitrates all show clay minerals within their mineralogical assemblage.

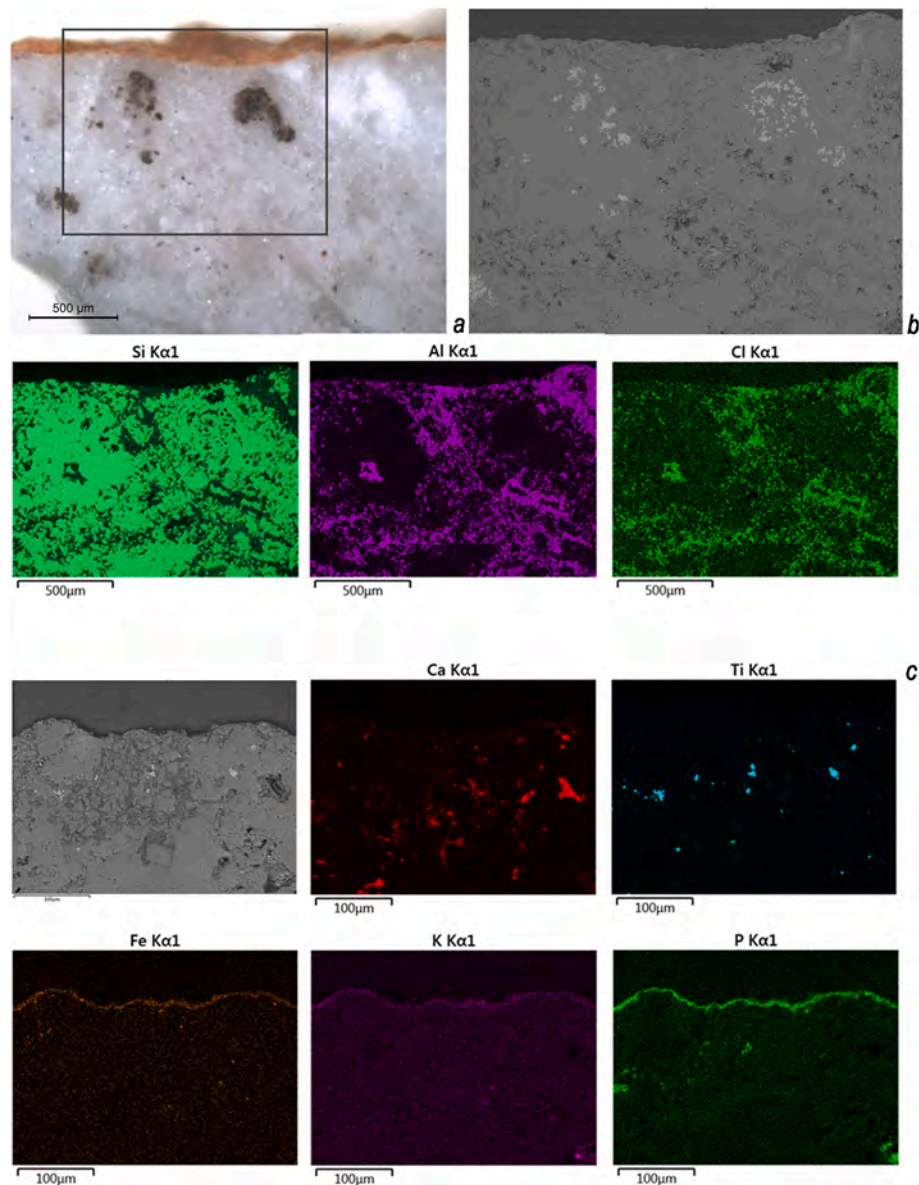


Fig. 11. a) OM image under visible light of the cross-section DS1 (scale bar = 500 μm); b) SEM image of the area in the grey rectangle of a, with chemical maps of silicon, aluminium, and chlorine; c) highly-magnified SEM-BSE image of the surface (scale bar = 100 μm), with maps of calcium, titanium, iron, potassium (K) and phosphorus (P).

5. Discussion

5.1. Rock type

The Damirgaya rock samples are likely to belong to a lithocap made of secondary quartzite formed after hydrothermal alteration. The alteration may have occurred at the level of the Cenomanian – Campanian shallow marine or Quaternary volcanic rocks present at the site (Fig. 3). The presence of highly crystalline kaolinite suggests an intermediate-to-advanced argillic acid-type alteration zone around areas of silicification (Swindale and Hughes, 1968; Inoue, 1995; Galán and Ferrell, 2013). The co-occurrence of zunyite, a very rare mineral for hypogene advanced argillic alteration zones, and traces of pyrophyllite, might reflect a specific temperature of the hydrothermal mineralized systems, just above 200 $^{\circ}\text{C}$ (Inoue, 1995).

Common textural and mineralogical features suggest a replacement of primary minerals due to hydrothermal alteration.

Trialeti rock samples belong to dacite. This type of rock is consistent

with the geology of site, which includes the Neogene–Quaternary volcanic formations of Pleistocene–Holocene basaltic andesite, dacite and rhyolite (Gabunia, 1980; Adamia et al., 2004; Adamia et al., 2010). The iron-based minerals frequently observed in thin-section are possibly due to the interaction between juvenile hydrothermal solutions and the igneous rock body during its cooling stage. Their chemical composition suggests a solid solution between ilmenite (FeTiO_3) and hematite (Fe_2O_3), namely titanohematite (Saito et al., 2007). Titanohematite lamellae seem to be exsolved within host titanomagnetite, as the content of Fe decreases while Ti decreases in these lamellae. This process possibly belongs to a C3 stage, according to the oxide classification scheme of Haggerty (1991). Evidence might indicate an intermediate stage of oxidation, where titanomagnetite is oxidized to Ti-poor titanomagnetite with titanohematite lamellae, meaning that TRS samples belong to an endogenous lava dome sampled in an area partially exposed to air, i.e. not from the surface or inner side of the dome.

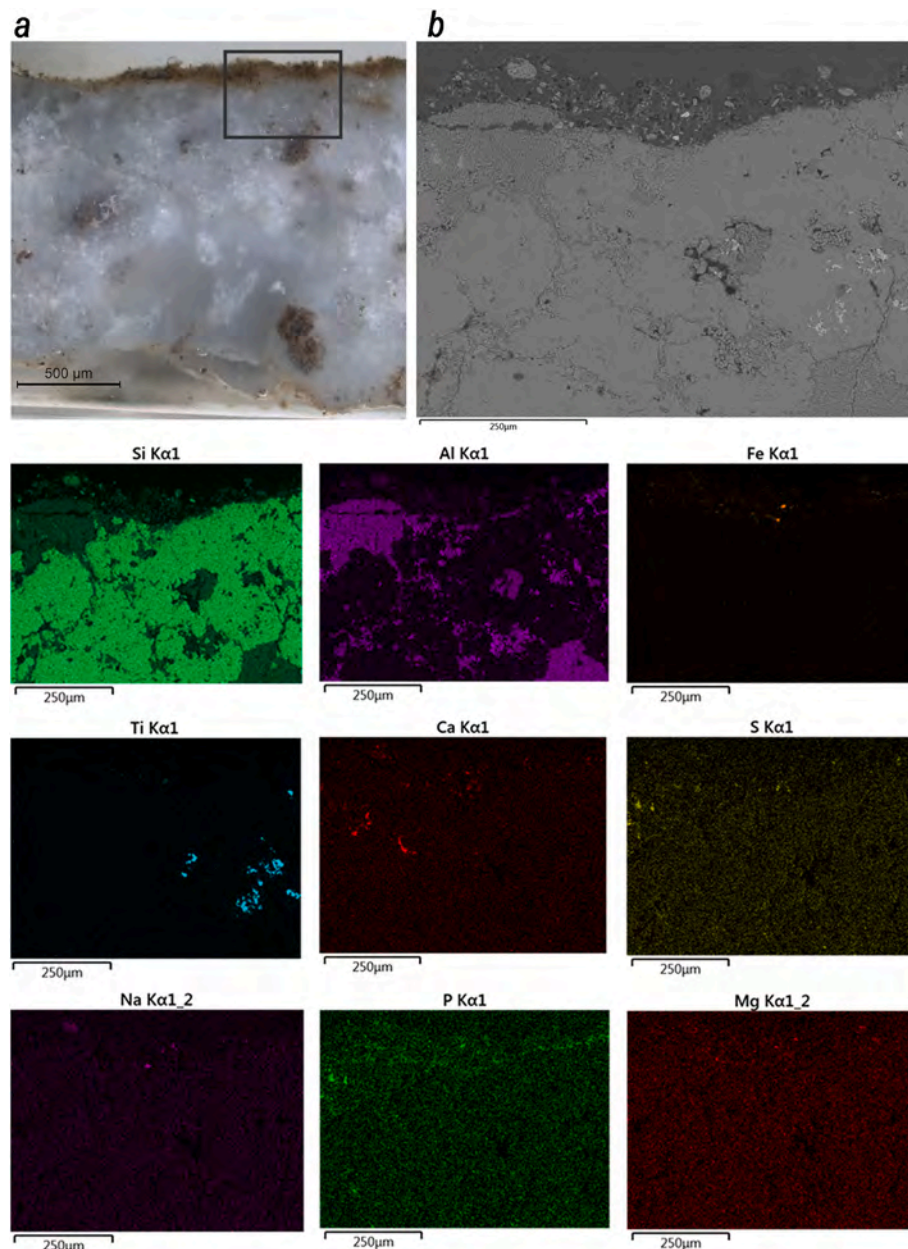


Fig. 12. a) OM image under visible light of the cross-section DS2 (scale bar = 500 µm); b) SEM-BSE image of the area in the grey rectangle of a (scale bar = 250 µm), with chemical maps of Si, Al, Fe, Ti, Ca, S, Na, P and Mg.

5.2. Pigment composition and provenance

The mineral composition of the samples from Trialeti and Damirgaya indicates that the pigments are ochres, where different proportions of the main colouring agent, i.e. hematite and goethite, determine a variation in hue.

For Damirgaya, a different position of the bands attributed to hematite in the FTIR results might indicate the local substitution of Al for Fe in the hematite of DS1 (Salama et al., 2015; Cornell and Schwertmann, 2003), and possibly a different ochre source. Current data is insufficient to confirm provenance, but it can be inferred that the nature of the red and brown pigment used in Damirgaya rock art is different, especially in terms of morphology and predominant colouring agent. However, their accessory minerals are similar, with kaolinite and quartz representing a natural component of the pigment source. Little can be said about ochre supplies in the surroundings of the sites. However, a short note about ochre mines in south Caucasian Georgia (Montseladze,

1930), recorded several ochre outcrops, most of them in western Georgia, at Gagra, Kobuleti, Batumi, Kutaisi, Khashuri, and a few in the east, including Tetrtskaro Vachnadze and Teryan, 1958). The latter is crucial for the present research because archaeological materials come from this area. More recently, oxidised zones have been identified for the hydrothermal alteration area of the nearby district of Bolnisi municipality (coordinates 44.1–45.3, 45.8–45.9, see Makadze, 2021). Here, hematite and goethite have been documented by remote sensing as a result of propylitic, argillic and phyllitic alterations, in an environment similar to the one described for Damirgaya rock samples. Alternatively, the comparable mineralogical assemblage might be due to the occurrence of the same alteration factors, as the samples come from the same environment.

The analytical investigation on the ochre residues from the grinding tools of Khramis Didi Gora showed that they include several Fe-based minerals: hematite, goethite and possibly lepidocrocite. It is likely that the majority of the accessory minerals identified in these samples come

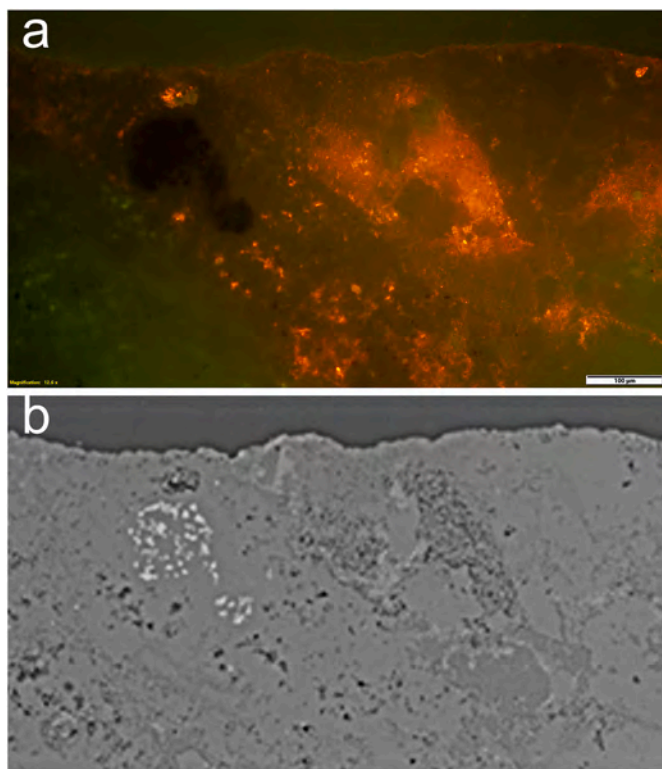


Fig. 13. a) OM image of the cross-section DS1 under visible light and specific filter-set after SYPRO Ruby staining (scale bar = 100 µm); b) SEM-BSE image of the same area.

from the grinding tools, making it difficult to assess the composition of a single pigment. For example, quartz and hornblende had been already identified in the basaltic rock from which the grinding stones are made (Hamon, 2008). Minor nitrates were also detected. Salama et al. (2015) have associated nitrates to iron ores, specifically linked to a shallow marine environment, while they were found absent in their subaerial weathering product, e.g. lateritic (pedogenic) ore. This might represent a different pigment source for KDG1208, which did not show any nitrate. For the mortar KDG884 and the pestles/handstones KDG898 and KDG1149 this interpretation seems also consistent with a sedimentary-marine ochre source (Popelka-Filcoff and Zipkin, 2022) in the proximity of the site, where a shallow marine environment is documented (Adamia et al., 2004; Fig. 3). However, the lack of IR data for some of the pigment samples from Khramis Didi Gora prevented a more accurate provenance attribution. This could be investigated in the future, together with reference samples from iron sources in the surrounding areas.

The exploitation of the nearby Akhalkalaki series (calc-alkaline basaltic continental lavas) for the grinding stones is possible, as it is a close source for this rock, North-West of the site, in the Tetrtskaro municipality. The same series has been recently described to include 'baked' interflow horizons within the Toloshi and Khertvisi lava successions, which could be interpreted as bole beds and a source of ochre in the region (Kavsadze et al., 2018). However, the mineralogical assemblage of these red beds has not been fully characterised. Further studies may focus on the documentation of interflow horizons in the vicinity of Khramis Didi Gora and their characterization for comparison with the red ochres described in the present work.

5.3. Rock art deterioration

A further factor to the difference in hue among the pigments from Damirgaya is the presence of gypsum. The production of gypsum on

stone is a well-known process that affects historical monuments in polluted and urban settings (Frost, 2004), where the formation of a calcium sulfate crust occurs when atmospheric sulfur dioxide reacts with calcium from the stone substratum. Flowing groundwater, rather than the support materials, is mostly responsible for gypsum deposition in the context of rock art. In this environment, the deposition might be favoured by the low pH due to bird and bat droppings, which generate different salts, including gypsum and oxalates (Lebon et al., 2019). However, the infrequent correlation between Ca and S in DS1 and DS2 (the first being found within the porosities of the rock) suggests that gypsum is at the surface while Ca-oxalates have penetrated beneath it. Hence, they might be an earlier source of Ca for the formation of gypsum. Even though oxalates are more frequently found on stone artworks (Rampazzi, 2019), several occurrences have been documented on ancient rock paintings, occasionally in association with gypsum (Russ et al., 1999). It has been suggested that Ca-oxalates – the monohydrate whewellite, $\text{Ca}(\text{C}_2\text{O}_4)\cdot\text{H}_2\text{O}$, and the dihydrate weddellite, $\text{Ca}(\text{C}_2\text{O}_4)\cdot(2.5-x)\text{H}_2\text{O}$ – may form during the erosion of paint layers resulting from the biological activity of algae, fungi or lichens, in areas not exposed to rain or runoff (Gallinaro and Zerboni, 2021; Gheco et al., 2019). A similar process is consistent with the identification of gypsum and its localisation in the samples from Damirgaya (Lebon et al., 2019). The observation of Ca-containing recrystallisations in the porosities of the rock suggests the penetration of both crust and water in the substrate even before the rock surface was painted. This is consistent with the mechanism proposed by Russ et al. (1999), which favours the dissolution and reprecipitation of oxalates in its inner structure. It has been also proposed that oxalates may come from urine of rock hyrax (Prinsloo, 2007) or pigeon colonies (Cuccuru et al., 2019).

Phosphate species found in the samples from Damirgaya are likely to occur within this environment and can be explained as the result of the decomposition of organic faeces from bats (Audra et al., 2019) or pigeons (Cuccuru et al., 2019) and their interaction with the minerals already present on the rock art surface. Dejections provide a source of phosphate and eventually ammonium ions, while the clay minerals naturally present in the red pigment or the substrate are the source of Al^{3+} ions. Alternatively, phosphorous in crusts on rock art has been considered evidence of a different biological activity, specifically epilithic lichen species known to concentrate phosphorus (Russ et al., 1999).

The fact that Ca-oxalate and phosphate species do not occur in the same layer excludes the use of a medium containing phosphorous, such as casein, milk, or egg (Domingo and Chieli, 2021; Rampazzi, 2019). The staining result corroborates the hypothesis of advanced biological activity. The fluorescence can be related to amide functional groups in the proteinaceous compounds synthesized by once-living organisms.

6. Conclusions

Technology can be interpreted as a cultural choice that is influenced by economic, social, ideological factors, as well as technical abilities. In order to fully understand choices in the methods of production of pre-historic art, we must consider the entire course of the *chaîne opératoire*, from object development to its discard. This involves a thorough examination of the object properties (such as colour, morphology, mechanical strength, and chemical composition), that are affected by manufacture, use, reuse, discarding, and burial. One of the goals of the present research was to describe the technological choices of the people who produced such unique rock art paintings and left traces of their activities on rock walls and on grinding tools. This final objective was accomplished by stylistic comparisons combined with archaeometric tools.

Based on stylistic observation Damirgaya shares evident similarities with the Armenian Geghamavan-1 cave and with the Azerbaijan Gobustan site, as all present features of the so-called 'Schematic rock art'. Because of these parallels and in agreement with the stylistic dating

proposed by Losaberidze et al. (2022), we suggest the Late Neolithic-Chalcolithic (6th-5th millennium BCE) as the most consistent period of production of Damirgaya motifs. However, the low number of known rock art sites leaves the dating issue open. In the case of Trialeti, the dating is even more difficult, because it was not possible to identify any specific typology of depiction and hence attempt a stylistic and chronological attribution.

For the first time the complementary analytical techniques of the present work have contributed to a better knowledge of Damirgaya, Trialeti rock art and the ochre residues on grinding tools from Khramis Didi Gora. The pigments from the prehistoric rock art sites of Damirgaya and Trialeti revealed common minerals such as hematite, quartz, gypsum, calcite, and in certain cases goethite. A similar mineralogical assemblage was documented for the grinding tools of Khramis Didi Gora. For the lithic tools it was hard to ascertain whether the identified minerals characterise the pigment or the stone. Further investigation might focus on non-destructive analysis on painted and unpainted areas of the tools at the Georgian National Museum.

The analysis of the two pigment samples from Damirgaya revealed that they have different morphological and compositional features, possibly representing different ochre sources; a sedimentary-marine ochre source was hypothesised for most of the samples from Khramis Didi Gora. The mineralogy of these pigments might be consistent with the geology of the sites. Ochre formations are often delocalised and undocumented, and it is difficult to determine their provenance. A detailed geological examination near these archaeological sites could provide further insight in order to fully prove their specific local origin.

Phosphates and oxalates were documented as secondary products, and are likely to come from a biological alteration, typical of semi-confined environments where animal faeces or lichens easily occur. Inorganic products found on the surface and within the pores of the rock at Damirgaya, as well as the evidence of protein beneath the red pigment layer, support this hypothesis. The staining provided no evidence of protein-based binders, because of their absence or low quantity (below the detection limit) after the occurrence of biodeterioration.

This research is the first review of international and Georgian published literature on prehistoric rock art in South Caucasus, but also a preliminary step in building a database of pigment and rock samples for this context. The present study serves as a foundation for future archaeometric investigations in Georgian rock art sites, namely in the Trialeti and Marneuli regions, as well as a preliminary geological survey that will strengthen future research.

Author contributions

M.B.: investigation, data processing, writing - original draft; M.G.: conceptualization, supervision, writing - review and editing, F.B.R.: conceptualization, supervision, writing - review and editing; L.M.: conceptualization, methodology, writing - review and editing; C.Y.: methodology, writing - review and editing; M.B.: methodology, investigation, supervision, validation, formal analysis, funding acquisition, writing - original draft.

Data availability

The data that support the findings of this study are available from the corresponding author, M.B., upon reasonable request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.quaint.2023.03.019>.

References

- Adamia, S., 2004. Scale 1:500000. 2004. Editor: Compiled by Sh. Adamia and G. Gujabadze. In: G. Abesadze, Sh. Adamia, R. Beradze, S. Bukia, M., Gamkrelidze, G., Gujabadze, Sh., Geguchadze, E., Devdariani, I., Vashakidze, V., Edilashvili, R., Torozov, N., Kandelaki, Dj., Kandelaki, I., Metreveli, D., Papava, O., Sepashvili, M., Pruidze, Y., Kipiani, G., Chichua, O., Shiriasvili, D. Jigauri (Eds.), *Geological Map of Georgia*. Georgian State Department of Geology/International science and technology center (ISTC).
- Adamia, S., Alania, V., Chabukiani, A., Chichua, G., Enukidze, O., Sadradze, N., 2010. Evolution of the late Cenozoic basins of Georgia (SW Caucasus): a review. *Geol. Soc. London, Spec. Publ.* 340 (1), 239–259. <https://doi.org/10.1144/sp340.11>.
- Anati, E., 1999. The art of beginnings. *Diogenes* 47 (185), 5–15.
- Anati, E., Rustamov, J.N., Muradov, F., Faradjeva, M.N., 2014. *Rock Art, Azerbaijan. Atelier monographs*.
- Audra, P., De Waele, J., Bentaleb, I., Chronáková, A., Kristúfek, V., D'Angeli, I.M., Carbone, C., Madonia, G., Vattano, M., Scopelliti, G., Cailhol, D., Vanara, N., Temovski, M., Bigot, J.Y., Nobécourt, J.C., Galli, E., Rull, F., Sanz-Arranz, A., 2019. Guano-related phosphate-rich minerals in European caves. *Int. J. Speleol.* 48, 75–105. <https://doi.org/10.5038/1827-806X.48.1.2252>.
- Berrada, S.H., Belkabar, A., Marcoux, E., 2009. Pyrophyllite - zunyite - diasporite mineralization at Chouichiat, Anti-atlas, Morocco. *Can. Mineral.* 47 (2), 441–456. <https://doi.org/10.3749/canmin.47.2.441>.
- Botticelli, M., Mignardi, S., De Vito, C., Liao, Y., Montanari, D., Shakarna, M., Nigro, L., Medeghini, L., 2020. Variability in pottery production at Khalet al-Jam'a necropolis, Bethlehem (west bank): from the early-middle Bronze to the iron age. *Ceram. Int.* 46 (10), 16405–16415. <https://doi.org/10.1016/j.ceramint.2020.03.200>. Part B.
- Botticelli, M., Mignardi, S., De Vito, C., Sala, M., Mazzotta, G., Da Silva Gondim, L., Medeghini, L., 2022. The 'metallic ware' from Tell el Far'ah North (West Bank): petrography, technology, and provenance of a hidden ceramic industry. *Ceram. Int.* 48 (1), 1366–1374. <https://doi.org/10.1016/j.ceramint.2021.09.222>.
- Chataigner, C., Badalyan, R., Arimura, M., 2014. *The Neolithic of the Caucasus*. Oxford University Press, Oxford. <https://doi.org/10.1093/oxfordhb/9780199935413.013.13>.
- Chikovani, G., Abuladze, J., Zhvania, D., 2015. *Settlements of the Early Farming Period Culture Explored by Kvemo Kartli (Aruchlo) Archaeological Expedition (1966-1988)*. Georgian National Museum, Otari Lordkipanidze Centre of Archaeology, Tbilisi, pp. 43–62.
- Chilingarashvili, G., Losaberidze, L., Eloshvili, M., 2020. *Municipality of Marneuli, Village Kasumlo, Damirgaya Archaeological Excavation Report*. Georgian National Museum, Tbilisi.
- Cornell, R.M., Schwertmann, U., 2003. *The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses*, second ed. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Cuccuru, S., Mameli, P., Mariani, A., Meloni, P., Oggiano, G., 2019. Contrasting decay of historical building stone: relationships between petrophysical features and frontal polymerization treatment suitability on medieval buildings of north Sardinia, Italy. *Bull. Eng. Geol. Environ.* 78, 1669–1682. <https://doi.org/10.1007/s10064-018-1242-5>.
- Domingo, I., Chieli, A., 2021. Characterizing the pigments and paints of prehistoric artists. *Archaeol. Anthropol. Sci.* 13, 196. <https://doi.org/10.1007/s12520-021-01397-y>.

- Eppelbaum, L., Khesin, B., 2012. Geophysical Studies in the Caucasus. Lecture Notes in Earth System Sciences. Springer, Berlin, Heidelberg, pp. 5–16. <https://doi.org/10.1007/978-3-540-76619-3>.
- Froment, F., Tournié, A., Colomban, P., 2008. Raman identification of natural red to yellow pigments: ochre and iron-containing ores. *J. Raman Spectrosc.* 39 (5), 560–568. <https://doi.org/10.1002/jrs.1858>.
- Frost, R.L., 2004. Raman spectroscopy of natural oxalates. *Anal. Chim. Acta* 517 (1–2), 207–214. <https://doi.org/10.1016/j.aca.2004.04.036>.
- Frost, R.L., Jing, Y., Ding, Z., 2003. Raman and FTIR spectroscopy of natural oxalates: implications for the evidence of life on Mars. *Chin. Sci. Bull.* 48 (1), 1844–1852. <https://doi.org/10.1007/BF03184066>.
- Gabunia, M.K., 1980. Petroglify Patara Khrami. Mefšniereba.
- Gabunia, M., Jakeli, N., Agapishvili, T., 2019. Prehistory rock art from Trialeti. *Bulletin of the Georgian national museum. Series Soc. Sci. IX (54-B)*, 13–23.
- Galán, E., Ferrell, R.E., 2013. Chapter 3 - genesis of clay minerals. In: Bergaya, F., Lagaly, G. (Eds.), *Developments in Clay Science*, ume 5. Elsevier, pp. 83–126. <https://doi.org/10.1016/B978-0-08-098258-8.00003-1>.
- Gallinaro, M., Zerboni, A., 2021. Rock, pigments, and weathering. A preliminary assessment of the challenges and potential of physical and biochemical studies on rock art from southern Ethiopia. *Quat. Int.* 572, 41–51. <https://doi.org/10.1016/j.quaint.2020.05.056>.
- Gamkrelidze, I., Okrostsvardize, A., Koiava, K., Maisadze, F., 2021. Geological structure of Georgia. In: *Geotourism Potential of Georgia, the Caucasus. Geoheritage, Geoparks and Geotourism*. Springer, Cham. https://doi.org/10.1007/978-3-030-62965-3_2.
- Gasparyan, B., Arimura, M., 2014. Study of the stone age in the Republic of Armenia. Achievements and perspectives. In: Gasparyan, B., Arimura, M. (Eds.), *Stone Age of Armenia*. Center for Cultural Resource Studies, Kanazawa University, Japan, pp. 13–33.
- Gheco, L., Tascon, M., Gastaldi, M., Ahets Etcheberry, E., Pereda, S., Mastrangelo, N., Quesada, M., Marte, F., 2019. Hidden paintings, forgotten histories: a micro-stratigraphic approach to study coated rock art. *Archaeol. Anthropol. Sci.* 11, 5037–5052. <https://doi.org/10.1007/s12520-019-00854-z>.
- Gobejishvili, G., 1981. The Culture of Bedeni Barrows. *Metsniereba*, Tbilisi, p. 144.
- Gogvadze, D., 2010. Big Catalogue of Georgia Petroglyphs. Shota Rustaveli National Science Foundation.
- Haggerty, S.E., 1991. Chapter 5. Oxide textures - a mini-atlas. In: Lindsley, D.H. (Ed.), *Oxide Minerals: Petrologic and Magnetic Significance*. De Gruyter, Berlin, Boston, pp. 129–220. <https://doi.org/10.1515/9781501508684-008>.
- Hamon, C., 2008. From neolithic to Chalcolithic in the southern Caucasus: economy and macrolithic implements from Shulaveri-Shomu sites of Kwemo-Kartli (Georgia). *Paleorient* 34, 85–135. <https://doi.org/10.3406/paleo.2008.5258>.
- Hradil, D., Grygar, T., Hradilová, J., Bezdíčka, P., 2003. Clay and iron oxide pigments in the history of painting. *Appl. Clay Sci.* 22 (5), 223–236. [https://doi.org/10.1016/S0169-1317\(03\)00076-0](https://doi.org/10.1016/S0169-1317(03)00076-0).
- Hughes, C.J., 1982. Petrography of igneous rocks. In: Hughes, C.J. (Ed.), *Developments in Petrology*, ume 7. Elsevier Scientific Publishing Co., Amsterdam and New York, pp. 125–146. <https://doi.org/10.1016/B978-0-444-42011-4.50010-5>.
- Inoue, A., 1995. formation of clay minerals in hydrothermal environments. In: Velde, B. (Ed.), *Origin and Mineralogy of Clays*. Springer, Berlin, Heidelberg. https://doi.org/10.1007/978-3-662-12648-6_7.
- Japaridze, O., 2003. *At the Origins of Georgian History*. Tbilisi State University, Tbilisi, p. 417.
- Japaridze, O., Javakishvili, A., 1971. Culture of the Ancient Farming Population of the Territory of Georgia. Issued by Soviet Georgia, Tbilisi, p. 114.
- Kavsadze, M., Beridze, T., Gabarashvili, K., Lobzhanidze, K., Vashakidze, G., Tognidze, M., 2018. Are the reddened weathering horizons between the Khertvisi and Toloshi basalt flows (Akhalkalaki volcanic plateau, Georgia) bole beds?. In: *Mineralogical Society of Georgia, Georgian Technical University. Power of geology is the precondition for regeneration of economics [Proceedings of the 4th International Scientific-Practical Conference on Up-to-date Problems of Geology, 29-30 May 2018]*, Tbilisi, pp. 49–51.
- Khechoyan, A., Gasparyan, B., 2014. Rock-painting phenomenon in the Republic of Armenia. In: Gasparyan, B., Arimura, M. (Eds.), *Stone Age of Armenia*. Center for Cultural Resource Studies, Kanazawa University, Japan, pp. 315–337.
- Korkia, L., 2001. The use of mineral dyes by palaeolithic man in his daily activities (according to Apiancha finds). *Dziebani: J. Centre Archaeol. Stud. Georgian Acad. Sci.* 8, 12–15.
- Ksica, M., Ksicová, O., 1994. *Felsbilder zwischen Schwarzem Meer und Beringstraße*. Preh-Art-Expo, Brno.
- Kushnareva, K.K., 1997. The Southern Caucasus in Prehistory: Stages of Cultural and Socioeconomic Development from the Eighth to the Second Millennium BC. *University Museum Monograph 99*, Trans Michael HN. Univ. of Pennsylvania Museum of Archaeology and Anthropology, Philadelphia).
- Lebon, M., Galletta, X., Bondetti, M., Pont, S., Mauran, G., Walter, P., Bellot-Gurlet, L., Puaud, S., Zazzo, A., Forestier, H., Auetrakulvit, P., Zeitounj, V., 2019. Characterization of painting pigments and ochres associated with the Hoabinhian archaeological context at the rock-shelter site of Doi Pha Kan (Thailand). *J. Archaeol. Sci. Rep.* 26, 101855 <https://doi.org/10.1016/j.jasrep.2019.05.020>.
- Losaberidze, L., Eloskvili, M., 2020. Preliminary report of newly rediscovered rock art site Damirgaya, Southern Georgia. *Rock Art Res* 37, 99–102.
- Losaberidze, L., Chilingarashvili, G., Eloskvili, M., Datunashvili, G., Chilingarashvili, Z., Kirkitadze, G., Abaishvili, L., Aghapishvili, T., 2022. New prehistoric rock art from the Caucasus? Results of the study of the Damirgaya rock shelter in Georgia. *J. Archaeol. Sci. Rep.* 44, 103548 <https://doi.org/10.1016/j.jasrep.2022.103548>.
- Lyonnet, B., Guliyev, F., Bouquet, L., Bruley-Chabot, G., Samzun, A., Pecqueur, L., Jovenet, E., Baudouin, E., Fontugne, R., Raymond, P., Degorre, E., Astruc, A., Guilbeau, D., le Dosseur, G., Benecke, N., Hamon, C., Poullmarc'h, M., Courcier, A., 2016. Mentesh tepe, an early settlement of the Shomu-Shulaveri culture in Azerbaijan. *Quat. Int.* 395, 170–183. <https://doi.org/10.1016/j.quaint.2015.02.038>.
- Makadze, D., 2021. Identification of hydrothermally altered zones in the area of Bertakari and Bneli Khevi deposits (Bolnisi ore district, south Georgia) with remote sensing method. *Bull. Georgian Natl. Acad. Sci.* 15 (3), 53–58.
- McGovern, P., Jalabadze, M., Batiuk, S., Callahan, M.P., Smith, K.E., Hall, G.R., Kvavadze, E., Maghradze, D., Rusishvili, N., Bouby, L., Failla, O., Cola, G., Mariani, E., Boaretto, E., Bacilieri, R., This, P., Wales, N., Lordkipanidze, N., 2017. Early neolithic wine of Georgia in the south Caucasus. *Proc. Natl. Acad. Sci. USA* 114 (48), 201714728. <https://doi.org/10.1073/pnas.1714728114>.
- Menabde, M., Kiguradze, T., 1986. The results of Kwemo Kartli archaeological excavations in 1980–1981. In: *Archaeological Expeditions of State Museum of Georgia. Metsniereba*, Tbilisi, pp. 17–28.
- Menabde, M., Kiguradze, T., Gotsadze, K., 1980. Kwemo-Kartli Excavation Reports 1978–1979. *Georgian National Museum, Archaeological Excavations. VII*.
- Montseladze, I.S., 1930. Report on the Work of the Geological Exploration Party for the Exploration of Mineral Paints in Western Georgia, pp. 1–10. Tbilisi, Gruzgeofond.
- Mrevlishvili, N., 1997. *Geology of Georgia*. Tbilisi State University Press, Tbilisi.
- Painter, P.C., Youtcheff, J., Given, P.H., 1980. Concerning the putative presence of nitrate in lignites. *Fuel* 59 (7), 523–526. [https://doi.org/10.1016/0016-2361\(80\)90183-0](https://doi.org/10.1016/0016-2361(80)90183-0).
- Popelka-Filcoff, R.S., Zipkin, A.M., 2022. The archaeometry of ochre sensu lato: a review. *J. Archaeol. Sci.* 137, 105530 <https://doi.org/10.1016/j.jas.2021.105530>.
- Prinsloo, L.C., 2007. Rock hyraces: a cause of San rock art deterioration? *J. Raman Spectrosc.* 38 (5), 496–503. <https://doi.org/10.1002/jrs.1671>.
- Rampazzi, L., 2019. Calcium oxalate films on works of art: a review. *J. Cult. Herit.* 40, 195–214. <https://doi.org/10.1016/j.culher.2019.03.002>.
- Regional Co-operation for Cultural Heritage Development, 2012. <http://www.rcchd.icomos.org/>. (Accessed 10 December 2022).
- Russ, J., Kalluarachi, W.D., Drummond, L., Edwards, H.G.M., 1999. The nature of a whewellite-rich rock crust associated with pictographs in Southwestern Texas. *Stud. Conserv.* 44 (2), 91–103. <https://doi.org/10.1179/sic.1999.44.2.91>.
- Sachsenhofer, R.F., Bechtel, A., Gratzner, R., Enukidze, O., Janiashvili, A., Nachtmann, W., Sanishvili, A., Tevzadze, N., Yukler, M.A., 2021. Petroleum systems in the Rioni and Kura basins of Georgia. *J. Petrol. Geol.* 44, 287–316. <https://doi.org/10.1111/jpg.12794>.
- Sagona, A., 2017. *The Archaeology of the Caucasus*. Cambridge University Press. <https://doi.org/10.1017/9781139061254>.
- Saito, T., Ishikawa, N., Kamata, H., 2007. Magnetic petrology of the 1991–1995 dacite lava of Unzen volcano, Japan: degree of oxidation and implications for the growth of lava domes. *J. Volcanol. Geoth. Res.* 164 (4), 268–283. <https://doi.org/10.1016/j.jvolgeores.2007.05.015>.
- Salama, W., El Aref, M., Gaupp, R., 2015. Spectroscopic characterization of iron ores formed in different geological environments using FTIR, XPS, Mössbauer spectroscopy and thermoanalyses. *Spectrochim. Acta-A: Mol. Biomol. Spectrosc.* 136, 1816–1826. <https://doi.org/10.1016/j.saa.2014.10.090>.
- Sigari, D., Shirinli, S., Abdullayev, R., 2020. Gobustan rock art cultural landscape (Azerbaijan). In: Smith, C. (Ed.), *Encyclopedia of Global Archaeology*. Springer International Publishing, Cham. <https://doi.org/10.1007/978-3-030-30018-0>.
- Swindale, L.D., Hughes, I.R., 1968. Hydrothermal association of pyrophyllite, kaolinite, diaspore, dickite, and quartz in the Coromandel Area, New Zealand. *N. Z. J. Geol. Geophys.* 11 (5), 1163–1183. <https://doi.org/10.1080/00288306.1968.10420245>.
- Szymczak, K., 2020. Archaeological materials from caves in the south Caucasus recovered by Stefan Krukowski during his stay in Georgia 1916–1918. *Folia Quat.* 88, 5–16. <https://doi.org/10.4467/2195923fq.20.001.13190>.
- The National Agency for Cultural Heritage Preservation. n.d. <https://heritagesites.ge/en?lang=en>. (Accessed 10 December 2022).
- Vachnadze, N.D., Teryan, A.N., 1958. Mineral paints. natural resources of the Georgian SSR, Vol. I. Metallic minerals, pp. 284–294.