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Marking petroglyphs with calcite and gypsum-based chalks: Interaction with granite under different simulated conditions and the effectiveness and harmfulness of cleaning methods

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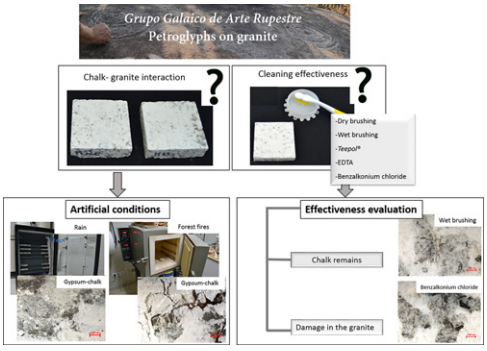
HIGHLIGHTS

- Interaction of granite with commonly used chalks to mark engravings under simulated conditions.
- Effectiveness of chalk cleaning on granite with different products was evaluated.
- Persistence of chalks after artificial rain events and simulated fires was detected.
- *Teepol* left cleaner residues on the sample.
- Benzalkonium chloride achieved the best results to extract both chalks.

GRAPHICAL ABSTRACT



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ABSTRACT

Marking petroglyphs with chalk is a common practice to enhance them for documentation and reproduction. Although this procedure has started to be less frequently used, there is no knowledge about the interaction between the rock engravings nor about the effectiveness achieved by the common cleaning procedures of such markers considering the chalk extraction and the induced damage to the rock.

This study evaluates the interaction between two chalks of different composition (calcite and gypsum) and a granite on which the majority of NW Iberian Peninsula-petroglyphs are carved. Granitic samples marked with these chalks were subjected to artificial rain events and high temperatures (700 °C) related to fires. After each aging test, chemical and physical modifications on the rock were analysed by means of stereomicroscopy, x-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and colour spectrophotometry. Moreover, the evaluation of the effectiveness and harmfulness of several mechanical and chemical cleaning procedures commonly used in the field of cultural heritage conservation was carried out.

Both chalks remained at different extent on the surface after the artificial rain events. Water would promote a different penetration-depth of the chalks into the stone, depending on their solubility. High temperatures led to mineral phase transformations of the chalks influencing the interaction with the rock.

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Regarding cleaning effectiveness, despite a few chalk remains were found in all the cleanings, chemical methods showed higher effectiveness than mechanical procedures even though some of them leave chemical contamination. Benzalkonium chloride can be considered as the cleaner with the best results to extract both types of chalk on granite.

1. Introduction

The importance of the petroglyph sites in the Atlantic coastal area led to the recognition of these monuments as the *Grupo Galaico de Arte Rupestre*, archaeological site of special protection in NW Iberian Peninsula (Vázquez, 1983; de la Peña, 1995; Whitley, 2011; Carrera et al., 2002). This rock art site mainly on granitic outcrops is a fragile archaeological heritage, subjected to two main groups of deterioration agents (de la Peña, 1995; Carrera et al., 2002). The first deterioration agent is composed of the natural agents such as rain, biological colonization, wind and soluble salts from marine aerosol. Water and biological colonization metabolites can cause hydrolysis on silicate minerals, leading to kaolinization or mica transformation into vermiculite (Stoch and Sikora, 1976). Soluble salts favour the development of sand disaggregation (Silva et al., 2003), a process that is intensified by the scourge of the wind. Biological colonization can also led to physical weathering of the rock, by means of the growth of the rhizina of fungi or the roots of vascular plants. All these processes contribute to the natural weathering of the rock in the outcrop. The second deterioration agent of petroglyphs is the human activity: ornamental rock extractive activities, forest exploitation with inadequate forest species, mountain clearing techniques, vandalism, etc. All these activities, which affect those rock art sites lacking of protection measures, are considered the most aggressive deterioration factors of petroglyphs on NW Iberian Peninsula (Carrera, 1997, 2002). One of the anthropic deterioration factors are the forest fires, either accidental or deliberate, that possess a risk of physico-chemical alterations of the rock by the exposure to high temperatures (Gomez-Heras et al., 2009).

Among the anthropic deterioration agents, the methods used to document the engravings that involve direct contact with the rock can also be considered. Recently, Vazquez et al. published a review (in Galician) about the evolution of the techniques employed in the NW Iberian Peninsula in order to document petroglyphs (Vázquez et al., 2015). Chalk, made of calcium carbonate (calcite, $CaCO_3$) or calcium sulphate (gypsum, $CaSO_4.2H_2O$), has been frequently used to enhance engravings (Fig. 1A), facilitating the subsequent free-hand drawing or the copy directly on a plastic placed on the marked petroglyph by using a pen. The marker's fidelity is, nevertheless, affected by worker's subjectivity and then, different alternative procedures like frottage began to appear, although it was barely used due to its aggressiveness (Vázquez et al., 2015). Nowadays, non-invasive and digital methods, e.g. photogrammetry or laser scanning start to be used as complementary techniques since they allow to achieve very accurate 3D reproductions (Malzbender et al., 2001; Seoane, 2005; Mudge et al., 2006; Arcà et al., 2008; Ortiz Sanz et al., 2010; Martínez Rodríguez et al., 2012; Nieves and Echevarría López, 2012; Westoby et al., 2012; Pires et al., 2014; Vilas Estévez et al., 2015). Despite the appearance of these new non-destructive techniques of documentation, the use of chalk to mark petroglyphs is still frequent, usually by unskilled people; Fig. 1B shows chalk remains in engravings sited in Santa María de Oia (Spain). The marketed chalk may be calcite or gypsum; in general, there is no information on the commercial product related to the composition, so calcite and gypsum-based chalks are indistinctly used as markers. Scientific publications about the interaction between the chalk and the rock substrate with petroglyphs are scarce (Bednarik, 1990; Tratebas et al., 2004; Fernández, 2015; Pozo-Antonio et al., 2015). Bednarik (1990) pointed the risk of physicochemical damage on the granite caused by chalk, although any empirical data were provided. Recently, Fernández (2015) and Pozo-Antonio et al. (2015) studied the interaction between calcite-chalk and granite after simulating artificial rain events and high temperatures, detecting a low penetration due to the low solubility of the calcite. However, due to the indistinctly use of gypsum and calcite-based chalks to mark engravings, a more complete study in order to find the most damaging chalk is required.

As a deterioration agent of engravings, forest fire has been considered due to the ascertained colour changes of the granitic surfaces (Gomez-Heras et al., 2009). However, only one article is focused on the behaviour of the chalk on petroglyphs subjected to high temperatures (Tratebas et al., 2004) concluding that the fire does not influence on the chalk penetration in a sandstone. These results matched with those registered for granitic substrates in laboratory experiences (Fernández, 2015; Pozo-Antonio et al., 2015). However, they were performed only with calcite-chalk.

Considering all mentioned before, and in the specific case of petroglyphs on granite on the NW Iberian Peninsula, it is clear that the application of chalk either of calcite or gypsum on granite can be considered as a chemical contamination. So, its interaction with the rock deserves a specific study whose results could lead to conservation recommendations to archaeological heritage managers. Once the granite-chalk interaction is faced, it would be also important to evaluate the cleaning

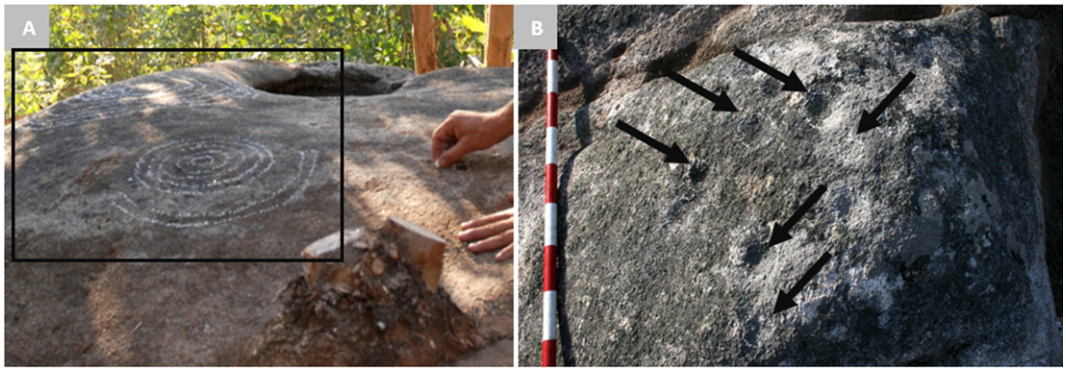

Fig. 1. Engravings marked with chalk in Santa María de Oia (Pontevedra, Spain). A: Marking process. B: Chalk remains found in the engravings. Images are reproduced by courtesy of Carmen Gómez Feito.