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In situ Raman characterization of minerals and degradation processes in a variety of cultural and geological heritage sites

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ABSTRACT

We test the capabilities of *in situ* Raman spectroscopy for non-destructive analysis of degradation processes in invaluable masterpieces, as well as for the characterization of minerals and prehistoric rock-art in caves. To this end, we have studied the mechanism of decay suffered by the 15th-century limestone sculptures that decorate the retro-choir of Burgos Cathedral (N Spain). *In situ* Raman probe detected hydrated sulfate and nitrate minerals on the sculptures, which are responsible for the decay of the original limestone. In addition, *in situ* Raman analyses were performed on unique speleothems in El Soplao Cave (Cantabria, N Spain) and in the Gruta de las Maravillas (Aracena, SW Spain). Unusual cave minerals were detected in El Soplao Cave, such as hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$), as well as ferromanganese oxides in the black biogenic speleothems recently discovered in this cavern. In the Gruta de las Maravillas, gypsum ($CaSO_4 \cdot 2H_2O$) was identified for the first time, as part of the oldest cave materials, so providing additional evidence of hypogenic mechanisms that occurred in this cave during earlier stages of its formation. Finally, we present preliminary analyses of several cave paintings in the renowned "Polychrome Hall" of Altamira Cave (Cantabria, N. Spain). Hematite (Fe_2O_3) is the most abundant mineral phase, which provides the characteristic ochre-reddish color to the Altamira bison and deer paintings. Thus, portable Raman spectroscopy is demonstrated to be an analytical technique compatible with preserving our cultural and natural heritage, since the analysis does not require physical contact between the Raman head and the analyzed items.

1. Introduction

In most cases, mineralogical investigations of cultural and geological items require an initial phase of mineral sampling, which may sometimes pose a threat to the preservation status of a protected heritage site. For instance, detailed mineralogical characterization of building materials has enabled the detection of the source of stone pathologies in a variety of historical buildings and masterpieces [1–6, among others]; however, the need for material sampling (in the order of grams) for subsequent destructive analysis in the laboratory can damage the masterpieces or other elements of interest.

Another example of potentially destructive sampling is given by mineralogical studies in protected caves, which are usually sites of significant aesthetic, geological and touristic relevance [7]. Oversampling and bad practice on the part of researchers during field work might produce severe damage in the caverns [8,9], in particular, to speleothems [10]. Remarkably, some caves host both relevant geological and archeological features that lead cave managers and authorities to maximize preservation measures. The restrictive policies for material sampling and the impossibility of remaining for long periods in these subterranean environments, due to visitor perturbations on microclimate [11], are in direct contrast with the need to characterize the composition and origin of the elements that are subject to protection.

In this context, portable, and non-invasive analytical techniques provide new opportunities for studying the mineralogical composition of delicate and precious materials, without the need for sample preparation. In the present study, we test the capabilities of a miniaturized Raman spectrometer for *in situ* non-destructive analysis of minerals in

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degraded limestone sculptures in Burgos Cathedral (N Spain) and in three Spanish caves that accommodate valuable speleothems and prehistoric rock-art. Raman analyses were utilized in each case to shed light on particular mineralogical issues and unanswered questions.

2. Study sites

2.1. The retro-choir of Burgos Cathedral

In situ Raman spectroscopy was used to perform a preliminary screening of the type of materials responsible for the decay of the 15th-century sculptures that decorate the retro-choir of Burgos Cathedral (N Spain). The retro-choir comprises five retables carved in limestone by the French sculptor and architect, Felipe Vigarny. Among them, the ones representing the *Crucifixion of Christ* and the *Descent from the Cross* are affected intensively by degradation mechanisms, including limestone disaggregation, flaking, peeling, and stone cracking (Fig. 1).

Burgos Cathedral was declared a World Heritage Site by UNESCO in 1984 (http://whc.unesco.org/en/list/316) and represents the top tourist attraction of the city of Burgos and of the Castile and Leon region, welcoming up to 350,000 visitors each year. In this case, preliminary *in situ* Raman analyses allowed for the selection of representative areas for subsequent sampling and further detailed laboratory analysis using other mineralogical techniques [6].

2.2. El Soplao Cave

El Soplao Cave was opened as a show cave in 2005 and receives up to 200,000 visitors each year. Spectacular helictites and huge speleothems are the most relevant aesthetic features of this mining show-cave [12]. Other unusual speleothems have also been described, including amberine stalactites [13], flowstones containing layers of cemented detrital materials [14], black ferromanganese crusts and stromatolites [15,16], frostwork-type speleothems and moonmilk deposits [17], some of which were studied in our *in situ* survey.

2.3. Gruta de las Maravillas

The Gruta de las Maravillas (Cave of Wonders), located in the village of Aracena (Huelva, SW Spain) has been open to the public since 1914, and currently welcomes about 150,000 visitors every year. This cavern boasts a wide variety of speleothem types, including anthodites, subaqueous and subaerial flowstones and coralloids, cave raft cones and huge columns. In this study, we analyzed the mineralogical characteristics of rare bluish helictites in the Palmatoria sector of the cave. The presence of subaqueous speleothemic calcite crusts and erosive forms, such as cupolas and scallops (usually related to phreatic mechanisms)

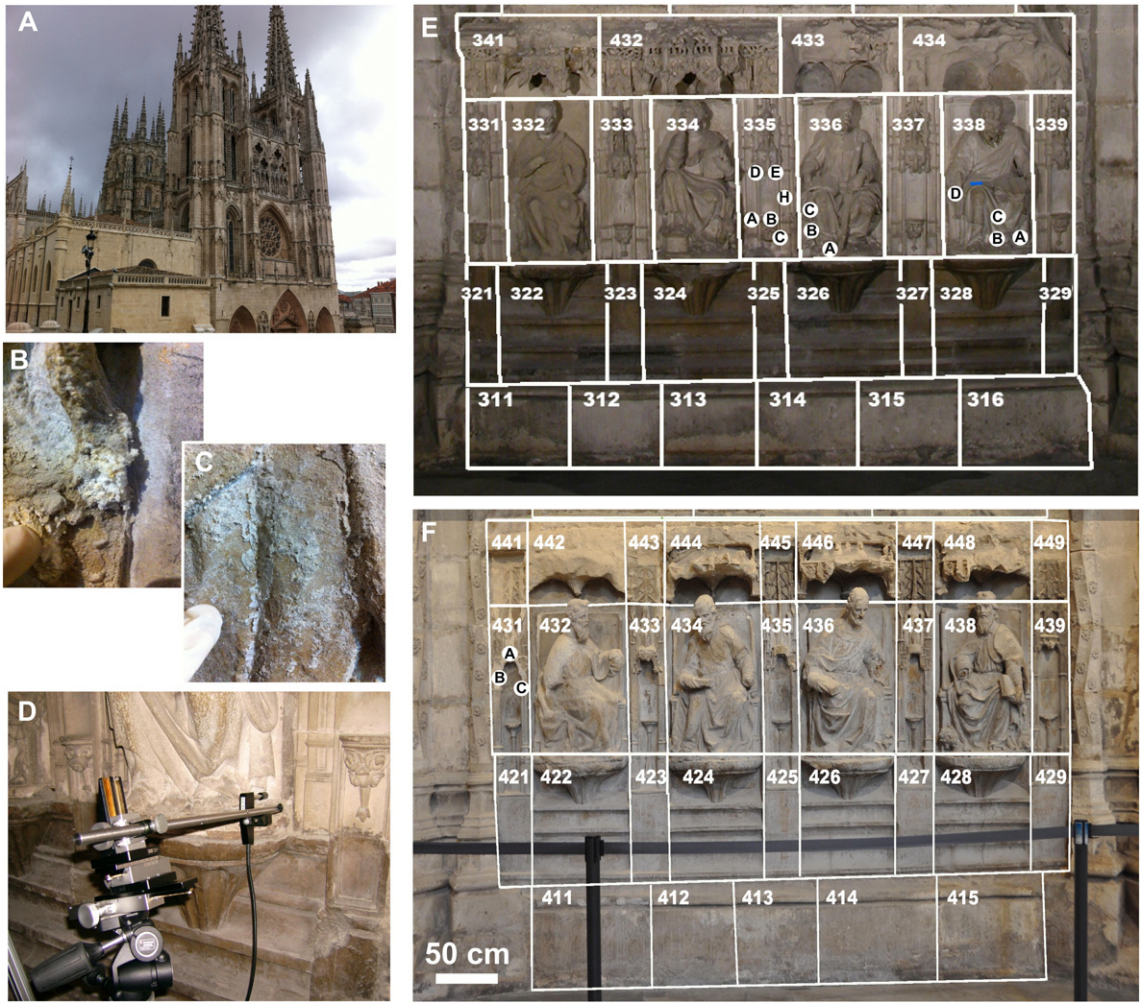

Fig. 1. A. General view of Burgos Cathedral; B, C. Efflorescences and flaky mineral patina on the retro-choir surface; D. *In situ* Raman analysis on the retro-choir; E. Position of the analyses performed on the *Crucifixion of Christ panel*; F. Position of the analyses performed on the *Descent from the Cross* (see Table 1 and main text for details; the sketch of the retro-choir is courtesy of Carlos Sanz).

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