carbonate and other bio-mineral features like the phosphate bands of apatite, which are main indicators of bone or dentine. The ability to distinguish between the different carbonate phases by Raman spectroscopy is another advantage of this method, since most mollusks and stony corals are of aragonite, while Corallium rubrum always consists of calcite. Unfortunately, some shells like Spondylus show the same Raman features (pigments plus calcite) as C. rubrum. This is why an additional microscopic investigation of the surface structures is important, e.g. to search for the very unique verrucae structures of red corals. After this first step, a success rate of already 90 % of identified materials can be reached only using microscopic and Raman spectroscopic analyses.

For the remaining "critical cases" we suggest a complementary examination using XRF and XRD to distinguish between coral and mollusks, which is the most difficult case together with the differentiation between bone and ivory. This multi-stage approach enables a fast identification of bio-minerals with a success rate of almost 98 %. We analyzed numerous fibulae, helmets, daggers or necklaces from Celtic tombs and several princely seats.

101. Soft X-ray Absorption Spectroscopy of Sulfur in Lapis Lazuli

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Since antiquity, lapis lazuli has been highly valued across many cultures for its bright blue color. While the most well-known source of lapis lazuli is Afghanistan, there are other sources, including sites in Tajikistan, Russia, Canada, and Chile. Because of the significance of lapis lazuli, there has long been interest in understanding the color variations of the material and determining the geographic origin of lapis lazuli, whether used as the processed pigment ultramarine in painted works of art (e.g., paintings and manuscripts) or the raw stone in cultural heritage objects (e.g., jewelry and inlaid decorations). Naturally occurring lapis lazuli contains the blue mineral lazurite along with other minerals, such as calcite, pyrite, diopside, and sodalite, among others. Work in our laboratory identified characteristic fluorescence from the minerals associated with lazurite that showed a distinct variability with geographic origin.1 Expanding on our previous work, this study focuses on the lazurite component of lapis lazuli. Lazurite has been broadly defined as (Na,Ca)8Al6Si6O24(SO4,S,Cl)2, a member of a larger aluminosilicate-sodalite group of minerals in which the sulfur species are trapped in an aluminosilicate cage.2 We are investigating the sulfur speciation within the aluminosilicate cage of lazurite—using a diverse sample set of both lapis lazuli and ultramarine pigments from many origins including Afghanistan, Russia, and Chile—as a potential means for identifying a geological fingerprint. Sulfur x-ray absorption near edge structure (XANES) spectroscopy was performed on the samples using the newly developed soft X-ray Beamline (14-3) at the Stanford Synchrotron Radiation Lightsource (SSRL). The data gathered allow sulfate, polysulfide, and thiosulfate species, and their distributions within a sample, to be characterized, which facilitates comparisons of these species between geologically diverse sources. As a whole, our work not only contributes to a deeper understanding of lapis lazuli but also illustrates the potential of soft X-ray analysis for cultural heritage research.

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102. Identification of provenance markers in Lapis Lazuli: a study on rocks and artworks

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Lapis lazuli is a blue semi-precious stone used for more than 7000 years for carving decorative objects and jewels. The value and rareness of this gem was related to the very few quarries in which it can be found. Despite the Afghan mines are nowadays widely considered the only quarries in ancient times, some archaeologists report that the exploitation of other quarries could have been equally well-founded [1]. An exhaustive provenance study on lapis lazuli is still lacking and it could shed light to many questions regarding the old trade routes. This ongoing research is based on a multi-technique approach and divided in two phases. The first phase consisted of an extensive minero-chemical characterization of rocks from known provenances to identify peculiar markers of the various quarries. We studied a total of 46 rocks samples coming from different sources: 19 from Afghanistan (Badakhshan), 4 from Tajikistan, 13 from Lake Baikal area, and 10 from Chile (Ovalle). Markers were searched by means of microscopic techniques[2,3], such as optical microscope, Cathodoluminescence, Raman spectroscopy, Scanning Electron Microscopy (SEM-EDX), Ion Beam Analysis (IBA) and µXray-Fluorescence. We looked for the presence/absence of mineral phases, peculiar luminescence features and trace elements composition of minerals themselves[5]. The second phase of the work was the development of a non-invasive protocol based exclusively on IBA techniques (mainly micro-PIXE: Proton Induced X-ray Emission and micro-IL: IonoLuminescence)[4] and µXray-Fluorescence that are techniques suitable on artworks. In this way we was able to carry out some preliminary measurements on valuable pieces of collections belonging to different museums: the Museum of Natural History of Firenze ("Collezione Medicea di pietre lavorate") [4], the Egyptian Museum of Firenze (New Kingdom amulets and pendants) and the Regional Museum of Natural Science of Torino (some polished items of the 19th century "Collezioni Sabaude"). The first results demonstrated the applicability of our approach, and allowed to suggest the origin of the raw material used for precious objects or archaeological findings. These achievements encourage to increase the experiments on artworks and also to improve the statistics on rocks samples.

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103. Towards portable X-ray spectroscopic imaging of Palaeolithic cave art. Insights into used pigments and wall taphonomy at three Palaeolithic key cave sites

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Palaeolithic cave art has taken a more and more important place in our cultural heritage. Its preservation is one of the major issues and involves necessarily a better understanding of the cave environments and of their evolution over time. However, the on-site geo-physico-chemical study of archaeological record stays difficult and the conservation of its integrity imposes restrictions. Taking benefit of recent analytical developments in the X-ray field, new perspectives of acquiring statistically relevant data for archaeological interpretation directly in the field are provided by the implementation of portable and non-invasive characterization methods. It allows the improvement of archaeological and physico-chemical knowledge about the pigments used, the evaluation of the state of wall decorated surfaces over time and a better assessment of the relationship between pigment and wall

support.
For these purposes, complementary self-built portable spectrometers (X-ray fluorescence in one and two dimensional mode, X-ray diffraction) are combined to perform qualitative and quantitative characterization of the pigments and cave walls as well as for chemical imaging on a decimetre scale. By using this combination of portable instruments the feasibility of analysis under very difficult conditions specific to the cave environments (humidity, temperature, difficult access to the caves and to the decorated panels) was shown. Special spectrum evaluation procedures have been developed to take into account the heterogeneity of the cave walls in order to gain reliable data for chemical characterisation. The efficiency of the analytical procedure has been demonstrated for three major cave sites featuring Palaeolithic art: Font-de-Gaume and Rouffignac cave in Dordogne (France) and La Garma in Cantabria (Spain).
A large assortment of colours can be observed in these caves (red, black, yellow and purple), associated to different mineral phases (iron and/or manganese oxides, charcoal and mixtures). Their detailed characterization provides an improved comprehension of the pictorial techniques used. Furthermore, it allows a better comparison between representations in a same cave, giving more detailed insights into its pictorial homogeneity and the different execution phases of its figures. As an example, the results obtained at Rouffignac cave showed that heterogeneous mixtures of manganese oxides have been employed to design the 65 Great Ceiling figures whereas a unique pigment mixture has been used for the drawing of the Ten Mammoths Frieze. Further information has been obtained on the taphonomic wall processes.
The spectroscopic study of these cave art illustrate the strong potential of such combined in situ and non-invasive analyses to better characterize the prehistoric figures in their cave environment and in a wider perspective to better understand the symbolic practices of past societies, appreciate possible cultural changes and relationships within the Franco-Cantabrian region.

104. Biodegradation of frescoes in the “Beata Vergine del Pilone” Sanctuary, Polonghera (Italy)

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When Conservation scientists casted a glance at the frescoes decorating the cupola of the ‘Beata Vergine del Pilone’ Sanctuary in Polonghera, near Cuneo (Italy), they scarcely could believe their eyes. Those paintings, dating back to the 18th Century, looked as if an unknown vandal purposely covered the skin of most religious characters with brown paint. A couple of cherubs even reminded of the exhortation in the famous “Angelitos Negros” song: “Painter, born in my land… though the Virgin may be white, paint me some little black angels, for they go to heaven too, as all good black people do.”
This transfiguring effect was the result of a bio-chemical deterioration due to the growth of a viscous, brownish biofilm selectively covering those frescoes areas painted in pink. To study this phenomenon, a multi-disciplinary approach was adopted including both minero-chemical methods and DNA-sequencing techniques. The former allowed to characterize those materials used by the original artist(s) as well as the components responsible for their chemical deterioration, together with the by-products of microbial activity; the latter brought to identify those microbial species responsible for the sequential colonization steps.
Water played a key-role in both chemical and biological aspects. Dampness percolating from outside, due to cracks in the cupola walls or capillarity, brought pollutants such as H2S and SO2 on the frescoes surface thus triggering formation of gypsum-sulphurous crusts. This fact, coupled to the particular composition of these frescoes pinkish pigments – a mixture of Cinnabar (HgS) and Zinc White (ZnO2) – caused significant S concentrations to occur in selected areas which, in presence of catalysts (i.e. Zn and other metals), favoured colonization of a first-generation sulphate-cycling bacteria. The dead bodies of these bacteria and abundant moisture, in turn, supplied those nutrients necessary to allow the settlement of a second-generation microbial community, represented by scavenger bacteria and saprophyte fungi. These late colonizers were responsible for the biofilm development,

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selectively covering the flesh-coloured areas.
These frescoes suffered therefore both an aesthetic and a structural damage, the first related to the biofilm growth and the second to pigments alteration caused by mobilization of certain elements recycled in the by-products of microbial activity (i.e. sulphates).
The performed survey paved way for a restoration intervention, achieved by delicately dry-cleaning the frescoes surface and applying a proper biocide which allowed the effective biofilm extirpation while possibly preserving the vividness of the residual pigmented layers

105. New Evidence About the Use of Ophiolites in the Minoan Architecture. The Investigation of the Excavated Duct in the “High Priest’s House”, a Peripheral Monument of the Palace of Knossos.

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During the course of research project “Conservation and Restoration of the peripheral monuments of the archaeological site of Knossos (“High Priest’s House”, “Royal Villa”, “Royal Tomb”)”, funded by the European Union, implemented from June 2011 to date and carried out by 23rd Ephorate of Prehistoric and Classical Antiquities, conservation applications are taking place on the “High Priest’s House”, which is located south of the Palace of Knossos. The restoration took place during the winter period of 2012 – 2013 and the need for collocation of the route of the rain water became compelling. This need became a necessity since the state of preservation of gypsum (selenite) elements in the west part of the monument was critical. As a result of the restoration applications, a part of the stone drain covered by the first of the three steps leading to the adyton came to light. The position of this stone drain was designated by Sir Arthur Evans excavation of the monument in 1931. The preliminary results of the investigation for the determination of the material of the drain revealed the presence of Chrisotile a characteristic mineral of the family of Ophiolites. Although the use of this type of stone is limited in Minoan architecture, this is the only case where it is used for making a drain. The analytical techniques used in order to specify the mineralogical phases of the stone were X-Ray Diffraction (XRD), Differential Thermal Analysis (DTA), Thermogravimetric analysis (TGA) and Scanning Electron Microscopy (SEM-EDS). The combination of the results from the analytical methods with the archaeological and geological bibliography in regards to the Minoan quaries as well as the ophiolite – bearing mélange on the Island of Crete, excluded several outcrops. Further analysis of samples from most of the ophiolite outcrops that are related to Minoan quarrying and comparison with the sample from the drain indicates two specific positions.

106. Archaeometric Characterization and First Distribution Study of a Spanish Marble used in Antiquity: The Marble from O Incio

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During the last decades, the characterization and study marble use in Roman Spain has leapt forward yet some areas, such as the northwestern territories, remained quite obscure as they still lack significant work. Thus, we addressed the study of this region with the aim of not only to gather data to determine which marbles reached an area as far apart from the Mediterranean as Gallaecia but to do so from an interdisciplinary perspective to enable a chronological sequence of its presence as well to understand of the trade routes and mechanisms of the economy and society that produced or enjoyed these objects.
The work presented here is part of an ongoing project and stems from the fact that a significant number of a first marble objects assemblage did not match the features