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Original article

Strontium, a new marker of the origin of gypsum in cultural heritage?

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ABSTRACT

A new possible methodology for recognizing the nature of gypsum in artworks, in particular for wall paintings, was developed. Calcium sulfate can be an alteration product of the calcium carbonate, or a component used by the Artist himself; the problem of identification of the presence and the nature of gypsum could be found detecting the presence of strontium. This element could be used as a marker since, differently from the alteration form, in mineral gypsum simultaneous presence of calcium and strontium occurs. The correlation between these two elements may be recognized using non-invasive in situ X-ray fluorescence measurements. In the present work, we tested this occurrence in various mineral samples of gypsum and alabaster as well in tempera, fresco and Egyptian paintings. Considering the new possible role of strontium indicating the presence of natural gypsum, we expect to provide a valuable tool for conservation scientists, restorers and art historians.

1. Research aim

The object of this study is focused on strontium, an element that could be used as a new marker in order to identify the origin of gypsum in cultural heritage: natural or an alteration product?

Several mineral samples, which led to the identification of a possible association of calcium with strontium, were analysed. This correlation was subsequently tested on some real case studies: wall paintings, stucco, icons, and painting on wood.

2. Introduction

The technique of wall painting, known under the Italian term of *a fresco*, is widespread in all age and in every country. Many authors in the past described the good fresco technique, emphasizing the right combination of ingredients and the painting procedure on wet plaster [1–5]. Due to the alkalinity of the medium, a limited number of pigments (chiefly earths of various colours) mixed simply with water or lime water can be used. In order to have a greater colour palette, painters have often used variants of the technique by painting the dried plaster. In this case, different *a secco* techniques and binders have been used, as egg white or egg yolk, various kinds of natural substances as wax, honey, casein, animal glue, resins or oils [6]. In our recent studies, we encountered also the use of gypsum as inorganic medium for the pigments and, in the same time, forming a fine plaster. It is well known that a widespread alteration of mural paintings is due to the phenomenon of sulphating of the lime, caused by the environmental pollution or water penetration, especially in the surface. This phenomenon is very dangerous for the artworks as it may cause the detachment of the paint film. In the same time, if calcium sulfate di-hydrate ($CaSO_4.2H_2O$) in the form of gypsum has been used by the painter, analyses are not able to differentiate between these two possibilities. So, one of the main diagnostic problem remains the correct individuation of the gypsum in the wall paintings if it is really due to alteration processes or not.

We encountered a similar problem in studying the preparation layers and painted layers of some Albanian medieval icons and an ancient Egyptian sarcophagus. In fact, for the paintings made on wood, one of the common preparation layer was usually obtained by mixing animal glue with gypsum [7] or, in fewer cases, with lime [8].

In a recent work conducted on mural paintings, we have encountered a difficulty in determining the source of gypsum presence. In all cases where the study is conducted using micro-sampling and cross-section methods, it is possible to examine the different layers separately, so generally the preparation method used by the painter is clear. On the contrary, in the case of *in situ* study, using X-ray fluorescence, in presence of lead pigments, as lead white or red lead, it is practically impossible to distinguish between a gypsum or a lime preparation. In fact, a peak overlap occurs when sulphur (SKα 2,31 keV) and lead (PbMα 2,35 keV) are present in the same sample and the precise identification of sulphur becomes very difficult. However, if the gypsum presence is confirmed, also with another analytical methods, remains the problem of its formation: natural or alteration gypsum.

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Table 1
Intensity of Ca Kα and Sr Kα peaks in a series of commercial or mineral samples.

Sample	State	Ca Kα	Sr Kα
Merck commercial marble	P	86	2
Carrara marble, from Tuscany (Italy)	P	967	34
Marble stone, from Tuscany (Italy)	B	226	3
Dolomite mineral, from Dolomites (Italy)	B	107	2
Aragonite mineral, from Liguria (Italy)	B	123	n.d.
Carlo Erba commercial $CaSO_4.2H_2O$, 99% pure	P	1174	36
Red bolo, commercial material for art	P	1259	42
Calcite mineral, from Liguria (Italy)	B	1421	98
Calcite from Chihuahua (Mexico)	B	150	8
Calcite from M.Barauis (Brasil)	B	181	13
Limestone I from the National Park of Krka, Croatia	B	59	3
Limestone II from the National Park of Krka, Croatia	B	168	5
Limestone I from the Podbrdo Hill, Medjugorje, Bosnia and Herzegovina	B	137	5
Limestone I from Areopagus Hill, Athens, Greece	B	146	6
Limestone II from Areopagus Hill, Athens, Greece	B	77	8
Limestone III from Areopagus Hill, Athens, Greece	B	89	7
Val Fontanabuona slate, Genoa (Italy)	B	37	17
Portoro of Levanto black zone	B	160	11
Portoro of Levanto white zone	B	173	70
Portoro of Levanto yellow zone	B	136	8
Pietra di Finale red	B	105	6
Pietra di Finale white	B	143	n.d.
Alabaster mineral I, from Tuscany (Italy)	B	32	21
Alabaster mineral II, from Tuscany (Italy)	B	668	577
Alabaster stone I	B	350	255
Alabaster stone II	B	68	36
Gypsum mineral I, from Emilia-Romagna (Italy)	B	27	14
Gypsum mineral II, from Emilia-Romagna (Italy)	B	41	15
Gypsum mineral from Sicily (Italy)	P	72	35
Gesso di Bologna, commercial material for art	P	362	244
Desert rose (Tunisia)	B	24	8
Desert rose (Spain)	B	8	4
Gypsum mineral I from Piedmont (Italy)	B	24	10
Gypsum mineral II from Piedmont (Italy)	B	21	15
Gypsum mineral from Sardinia (Italy)	B	45	19

P: powder; B: block.

Some previous works, conducted on paintings, detected the presence of strontium, but a clear meaning of this element was not given [8–11]. Recently a correlation between calcium and strontium was found in an Ethiopian medieval wall painting [12]. We considered and investigated the presence of this element since we have often noted in our studies a noteworthy correlation between strontium and calcium. Consequently we developed our bibliographical and experimental research.

3. Methodology

Firstly we developed a bibliographical research aimed at collecting most of the published data about the subject. We found an interesting geological work regarding the characterisation of many kinds of gypsum coming from different sites of central Italy, showing that gypsum of these regions contains, in all examined samples, appreciable amounts of strontium [13]. It was not clarified if strontium was related to the mineralogical sulfate *celestine* ($SrSO_4$) or it was present as a solid solution form in gypsum itself. A thermochemical study that has dealt with the theme of the formation of solid solutions between calcium and strontium carbonate was published, in 1996[14]. However, from a geological point of view, the presence of *celestine* in gypsum rocks is well known [15,16].

In order to conduct the experimental study, X-ray fluorescence and X-ray diffraction measurements were performed on several minerals and commercial samples of lime, gypsum and alabaster in use for artistic purposes obtained from different firms (Table 1). Finally we tried to apply our results to real case studies: several samples from Italian and Greek artworks (see Table 2), Albanian Icons painted on wood panels, an important *fresco* of Luca Cambiaso in Villa Imperiale di Terralba in Genoa, Italy, (second half of the XVI century), a wall painting of Bernardo Castello in Villa Paradiso in Genoa, Italy (first half of the XVII century) and the Egyptian sarcophagus of Pasherienaset (VII-VI century b.c.), preserved in an archaeological museum in Genoa.

4. Experimental

4.1. X-ray fluorescence spectrometry

Elemental analysis was performed using a Lithos 3000 portable XRF system by Assing and the Lithos software to process the experimental data. The apparatus consists of a molybdenum tube, a zirconium filter and a semiconductor silicon (Li) detector, cooled by Peltier effect. The operating parameters were: 25 kV, 0.1 mA, and 240 seconds of acquisition time. As calibration standard we used an YBCO ($YBa_2Cu_3O_{7-x}$) sample, that presents a wide spread of lines on energy scale. The identification lines of the elements were: Ca Kα (3,691 keV), Sr Kα (14,165 keV). The analytical signal was taken considering the maximum height of the peak emission. Only semiquantitative analyses were performed due to the great matrix effect which affects XRF measurements. Moreover, a possible correlation can be obtained only from measurements carried out on samples came from the same opera or samples with a matrix very similar.

4.2. X-ray diffraction

X-ray powder patterns were obtained using a PW 1830 Philips Diffractometer (Ni-filtered CuKα radiation); scans over a 2θ range of 5–65° (steps of 0.02° and acquisition time of 5 s for step). Standard samples were analysed in form of powder; the small samples coming from Villa Imperiale and Villa Paradiso were not