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Sulphur and oxygen isotope analysis to identify sources of sulphur in gypsum-rich black crusts developed on granites

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HIGHLIGHTS

- Gypsum-rich black crusts on granite and possible sulphur sources were studied.
- Sulphur and oxygen isotope analysis was used to identify sulphate origins.
- Sulphur contributions were marine and anthropogenic.
- Mortars on buildings were enriched by sulphur on buildings.
- Orientation towards different sulphur sources influenced the $\delta^{34}S_{CDT}$ and $\delta^{18}O_{SMOW}$ ratios.

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ABSTRACT

We describe the results of sulphur and oxygen isotope analyses used to identify sources of the gypsum present in black crusts that grow on the granite of historical buildings. The crusts were sampled at various locations in and near the city of Vigo (NW Spain) and were analysed for their sulphur content and $\delta^{34}S$ and $\delta^{18}O$ isotope ratios. Sampled crusts had $\delta^{34}S$ values of 7.3‰ to 12.9‰ and $\delta^{18}O$ values of 6.56‰ to 12.51‰. Sampled as potential sulphur sources were bulk depositions, seawater, foundation, ashlar and construction materials and combustion residues. The results indicated marine and, to a lesser extent, anthropogenic, origins for the sulphur and ruled out the contribution of sub-soil sulphates by capillary rise from building foundations. Isotope analyses would indicate that cement and mortar were enriched in sulphur after their application in buildings. The fact that facade orientation (towards the sea or fossil fuel pollution sources) was correlated with sulphur isotope distribution pointed to various contributions to black crust formation.

1. Introduction

Gypsum-rich black crusts, which are a major cause of deterioration of heritage buildings and monuments, have been widely studied, but mainly for carbonate rocks (Sabbioni, 1995; Schiavon et al., 2004; Brimblecombe and Grossi, 2005 and references therein). This form of deterioration has very serious consequences for the conservation of architectural heritage as the crusts weaken and erode the surface layer of the stone. Gypsum crusts form on carbonate rocks as a result of wet or dry deposition of atmospheric sulphur (Charola and Ware, 2002, and references therein) and the sulphur's subsequent reaction with calcium in the stone.

Stable isotope analysis is used to determine sources of sulphur, calcium, oxygen, nitrogen, carbon and metallic elements in the environment (Faure, 1986; Hoefs, 2004). It has been successfully used to identify contamination sources for inland waters, such as seawater (Otero et al., 2011) and pollutants from human activities like agriculture (Jiang, 2012), mining and industry (Otero and Soler, 2002; Knöller et al., 2004; Otero et al., 2008; Yin et al., 2012). In the heritage conservation field, sulphur and oxygen isotope analyses have been used to identify the source of sulphur in black crusts and efflorescences on sedimentary and metamorphic (marble) stone in buildings and monuments. Several different sources have been identified, including biological sources (Hosono et al., 2006), construction materials, including mortars (Vallet et al., 2006; Schleicher and Recio, 2010; Kloppmann et al., 2011), sea spray (Kloppmann et al., 2011) and pyrite oxidation within the rock substrate (Kramar et al., 2011). However, the most important source of sulphur is SO_2 emissions from fossil fuels burned by road vehicles and for industrial purposes (Torfs et al., 1997; Prikryl et al., 2004; Vallet et al., 2006; Schweigstillová et al., 2009; Schleicher and Recio, 2010; Kloppmann et al., 2011; Kramar et al., 2011). The fact that the isotope ratio for oxygen in sulphate also helps identify the primary or secondary nature of the sulphate (Holt et al., 1981; Holt and Kumar, 1991) has led several authors (Torfs et al., 1997; Vallet et al., 2006; Schleicher and Recio, 2010; Kloppmann et al., 2011; Kramar et al., 2011) to use this

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approach for architectural heritage constructions. A very recent study by Kloppmann et al. (2014) describes a multi-isotope approach to determining sources for different soluble salts.

Studies of gypsum-rich black crust formations on granite are relatively scarce compared to those for sedimentary stone and marble. The few studies that do exist (Prieto et al., 2007; Silva et al., 2009; Schiavon, 2000; Simão et al., 2006; Sanjurjo et al., 2009, 2011) confirm, nonetheless, that this kind of deterioration is possible despite the low calcium content of igneous rocks. Tests conducted on granite prisms joined with mortar in artificial atmospheres reveal that, even for relatively low SO_2 levels (10 ppm), gypsum precipitation as a consequence of the reaction between SO_2 and calcium from mortars is possible (Rivas et al., 1997). Exposure to higher levels of sulphur dioxide (100 ppm) leads to gypsum crust formation if the atmosphere contains pollution-derived particulate matter (Simão et al., 2006), in which case the cation source for the calcium would appear to be acid dissolution in calcium-rich plagioclases and feldspars (andesite, etc).

In case studies of granite constructions, a distinction is drawn between black crusts of biological origin that develop in non-polluted rural environments and gypsum-rich black crusts that develop in urban environments (Silva et al., 2009). Fossil fuel combustion (by factories and road vehicles) is considered the most likely source of sulphur in gypsum-rich black crusts, although the contribution of other sources (such as construction materials) has not been conclusively ruled out. Some authors differentiate between gypsum-rich crusts associated with air pollution and those associated with old plaster or mortar (Sanjurjo et al., 2009, 2011). Silva et al. (2010) suggest that gypsum from old plaster and mortar is a possible source of the sulphates that cause superficial detachments in granitic rocks. In the above-mentioned studies of granite, the most likely source of sulphur was deduced from the orientation of building facades with respect to vehicle emissions and wind-transported industrial emissions, and also from the presence in walls of construction materials capable of contributing gypsum through dissolution processes. There is also uncertainty about the source of calcium, with Schiavon (2000) and Simão et al. (2006) suggesting that the gypsum was the result of sulphur reactions with calcium released from plagioclases. However, studies have reported gypsum-rich black crusts forming even on calcium-poor granites (Prieto et al., 2007; Sanjurjo et al., 2011), which is the case of the pre-Variscan granites used for Galician granite buildings. The most likely source of calcium for both the gypsum-rich black crusts (Silva et al., 2009) and the calcium sulphate responsible for superficial detachments (Charola, 2000; Silva et al., 2003, 2010) is the dissolution of old mortar or lime.

Despite recent interest in gypsum-rich black crust formations on granitic rock, no scientific studies exist that definitively determine sources for the sulphur in these crusts; in particular, no isotope ratio analysis has been conducted for this purpose. In this article we discuss values for $\delta^{34}S$ and $\delta^{18}O$ ratios for gypsum-rich black crust samples collected from granite buildings in the city of Vigo (NW Spain) and analysed for their chemical and mineralogical composition. We considered different possible sources for the sulphur in the sampled crusts, including bulk atmospheric deposition samples (collected over 4 months), seawater, various materials from the sampled buildings, construction materials and combustion residues from vehicles. Sulphur content was determined and $\delta^{34}S$ and $\delta^{18}O$ ratios for the crust samples and possible sulphur sources were compared.

Particular circumstances make the city of Vigo an excellent subject for a case study of the various possible sources of sulphur and oxygen in black crust formations on granite. First, buildings in its old quarter are mostly granite constructions in which the development of gypsum-rich black crusts is notable. Second, Vigo, located at the northern end of the western Iberian Atlantic coast, is exposed to marine influences, it being well known that marine salts play a role in granite deterioration (Silva et al., 2003); also, sea spray is considered, in Galicia, to be a source of the atmospheric sulphur that affects buildings (Silva et al., 2007). Finally, Vigo is also an important industrial city and the literature has cited atmospheric emissions from industrial, maritime and human activities (Torfs et al., 1997; Prikryl et al., 2004; Vallet et al., 2006; Schweigstillová et al., 2009; Schleicher and Recio, 2010; Kloppmann et al., 2011) as sources of sulphur in gypsum-rich black crusts.

This first application of sulphur and oxygen isotope analyses to the identification of the origin of gypsum in black crusts on granite constructions makes a dual contribution to the literature. On a theoretical level, it advances scientific knowledge of the origins of this form of damage to granites. On a practical level, this knowledge can be used to design protocols aimed at minimizing sulphur deposition and sulphate contamination in both existing and planned buildings.

2. Materials and methods

2.1. Study setting

Vigo (population 300,000) is a major Atlantic port city in terms of industrial, commercial, fishing and shipbuilding activities. It is built on a hill (131 m above sea level) on the southern coast of the Autonomous Community of Galicia in NW Spain (Fig. 1). Galicia, influenced by the Western Atlantic and the Bay of Biscay to the north, has, according to FAO's agro-ecological zoning, a humid sub-tropical climate, with rainy winters (1200 mm rainfall) (Martínez-Cortizas, 1987; Martínez-Cortizas and Pérez, 1999) marked by low-pressure S-SW fronts from the Atlantic. The average annual temperature is 13 °C, with significant differences between coastal areas (15 °C) and the interior (6–8 °C).

Air quality data (Xunta de Galicia, 2012) corresponding to the 4-month study period (October 2010 to January 2011) indicate that Vigo was ranked fourth of the main cities of Galicia in terms of atmospheric SO_2, with an average atmospheric concentration of 3.2 $\mu g/m^3$ and a daily maximum value of 83 $\mu g/m^3$ (4.4 $\mu g/m^3$ and 104 $\mu g/m^3$, respectively, for Galicia's most polluted city, A Coruña). Monthly and seasonal variations were negligible during this period. According to Silva et al. (2007), over 50% of the SO_2 in bulk depositions in Galician coastal towns and cities are of marine origin, with the percentage dropping significantly towards the interior; rainfall resulting from low-pressure fronts from the Atlantic accounts for the predominant wet deposition mode for marine ions in coastal areas. Wind dynamics in Vigo is marked by two principal directions directly related to low-pressure S-SW fronts and high-pressure N-NE dynamics.

2.2. Sample description

Sampling was performed both of gypsum-rich black crusts and of different potential sources of sulphur.

Sampled for crusts were 3 buildings in Vigo's old quarter constructed using leucogranite and two-mica granite, both common local stones (IGME, 1985). The joint mortar between granite ashlars was composed of Portland cement mixed with fine-grained granitic aggregate and the ashlars had been laid using sand and concrete. A total of 19 crust samples were collected, as follows:

- Building 1: S-SE facade, heavily affected by traffic, 10 samples (M1-M10), 8 from granite ashlars and 2 from mortar.
- Building 2: NE facade, heavily affected by traffic, 6 samples (M11-M16), 4 from granite ashlars and 2 from mortar.
- Building 3: SW and NW facades, mildly affected by traffic, 3 samples from granite ashlars (M17-M19).

Sampling for possible sulphur sources (6 different kinds) was as follows:

- Bulk atmospheric depositions (BD), collected every 15 days over the 4-month study period (October 2010 to January 2011) except in the first fortnight. Sampling was performed at 5 different sampling sites,