

# WEATHERING SURFACES ON CLASSICAL MARBLE SCULPTURES: ISOTOPIC AND X-RAY DIFFRACTION ANALYSES

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**Abstract.** We have proposed elsewhere the use of a minimally-destructive, integrated approach towards the provenance determination of classical marble sculptures, using stable isotope analysis, X-ray diffraction, grain-size determination, stylistic analysis, literary information, and archaeological data. Stable isotope analysis and X-ray diffraction require only a few milligrams of clean marble powder, which can easily be removed from unobtrusive parts of sculptures, many of which already have damaged surfaces. Care must be taken in sample removal, however, since weathered marble surfaces are likely to have altered crystalline properties and to have markedly different isotopic values. The alteration of both carbon and oxygen isotopes by just a few parts per thousand is more than sufficient to produce an erroneous source attribution.

Experimental work by others has suggested that marble crusts may be used as evidence for the antiquity of a particular sculpture if the isotopic and crystallographic values of both the crust and fresh marble are determined. We present a comparison of stable isotope and X ray diffraction data for weathered and fresh marble samples from 28 Classical marble sculptures. These data are interpreted in light of biologically and geochemically mediated alteration mechanisms, and some suggestions are made regarding sampling techniques for provenance analysis, and on the authentication of marble sculptures.

**Key-words.** Marble - Weathering - Stable isotope analysis - X-ray diffraction - Sampling

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## Introduction

We have proposed elsewhere the use of a minimally-destructive, integrated approach towards the provenance determination of classical marble sculptures, using stable isotope analysis, X-ray diffraction, grain-size determination, stylistic analysis, literary information, and archaeological data (van der Merwe *et al.*, 1995; this volume). Stable isotope analysis and X-ray diffraction require only a few milligrams of clean marble powder, which can easily be removed from unobtrusive parts of sculptures, many of which already have damaged surfaces. Care must be taken in sample removal, however, since weathered marble surfaces are likely to have altered crystalline properties and to have markedly different isotopic values. The alteration of both carbon and oxygen isotopes by just a few parts per thousand is more than sufficient to produce an erroneous source attribution. Detailed comparison of isotopic and physical properties of weathering layers with those of fresh marble interiors may be useful in the authentication of marble sculptures (Newman, 1990).

## Stable isotope and XRD analyses

Samples weighing several milligrams were removed from Classical marble sculptures in the Museum of Fine Arts, Boston, and the Sackler Museum, Harvard University, using a stainless steel knife blade. Surface material was removed first and labelled; fresh marble powder was then collected from the cleaned area.

Stable isotope analyses of paired samples were performed using a VG Prism II mass spectrometer located in the Department of Earth & Planetary Sciences at Harvard University. The results are reported using the delta notation ( $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ ) in parts per mil relative to the PDB marine limestone standard. Our analytical precision is  $\pm 0.1\text{‰}$  for carbon and  $\pm 0.2\text{‰}$  for oxygen.

XRD analyses were done initially to identify dolomitic marble sculptures which could be attributed to the Cape Vathy (Thasos) source (Herrmann, 1990; 1992; Herrmann and Newman, 1995). These analyses of fresh

marble were done by Richard Newman at the MFA and by Robert Tykot at Harvard using a Scintag 2000 X-ray diffraction spectrometer.

## Weathering

Isotopic shifts in weathered surfaces of marble have been reported by several researchers (Ulens *et al.*, 1995; Doehne *et al.*, 1992; Newman, 1990; Margolis and Showers, 1988; 1990). We report here the isotopic analyses of fresh and surface marble from 28 sculptures, including 14 already preliminarily published (van der Merwe *et al.*, 1995). Thirteen of the surface samples exhibit enough alteration to preclude accurate provenance determination, and illustrate the importance of removing clean marble samples for analysis (Table 1; Fig. 1).

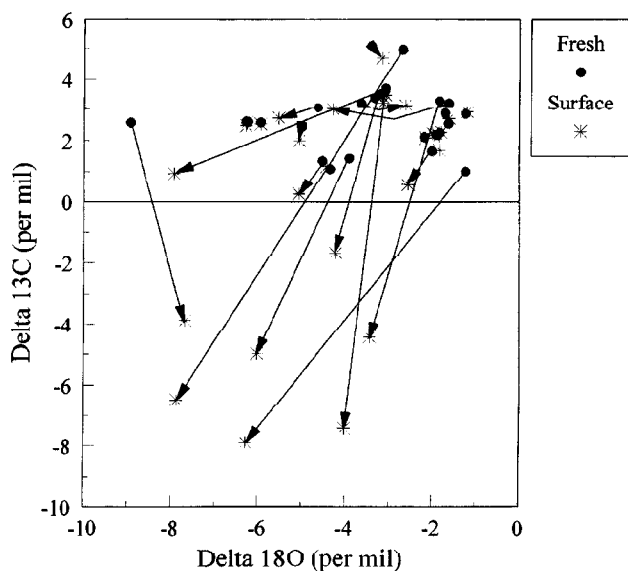


Figure 1. Isotopic analysis of fresh and surface marble samples

The alteration of the isotopic signature may be explained in many cases by the contribution of isotopically-negative ground and meteoric water, and atmospheric  $\text{CO}_2$ , to recrystallized dolomite and calcite on marble surfaces (Salomons and Mook, 1986). The isotopic alterations observed in Classical marble sculptures are similar to those reported for naturally weathered marble from ancient marble quarries (Ulens *et al.*, 1995); some of the quarry marble, presumably weathered for longer periods of time, exhibits even greater shifts in  $\delta^{13}\text{C}$  than our sculptural samples.

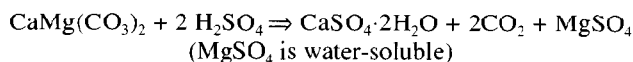
The biological mediation of microorganisms and/or lichens has also been suggested as an important weathering mechanism. Experimental work by Heller and Herz (1995) has documented the organic production of oxalic acid, which reacts with marble to form calcium oxalate and can significantly shift isotopic values in a matter of months (see also de Santis and Allegrini, 1991; del Monte, 1991; del Monte and Sabbioni, 1987).

Our XRD analyses of the marble sculptures showing the largest isotopic shifts between fresh and surface samples suggest additional weathering mechanisms and sampling procedures that must be considered:

- 1 The first is simple contamination from soil and clay material. The fresh marble sample from sculpture MFA 1961.86 demonstrates that it is a pure calcite, but the surface sample contains about 4% illite or other clay minerals. It is unclear whether the isotopic shift is due to the inclusion of illite in the analyzed sample, or to the alteration of the calcite itself by groundwater and/or biological mediation during the same exposure conditions that led to the clay contamination.

- 2 No differences were observed using XRD for fresh and surface samples from sculpture MFA Res.53.63 despite an isotopic depletion in carbon by more than 1%. This alteration may be due to simple recrystallization of surface calcite.

- 3 Surface samples from both a calcite marble sculpture (MFA 16.62) and a dolomite sculpture (MFA 98.641) contain 2-3% gypsum, which is not present in the fresh marble. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) forms when marble reacts with sulphuric acid, which is commonly present in acid rain but which can also be produced from elemental sulphur and water. Sculptures which have been acid cleaned may still retain isotopically-altered marble even if the dark patina itself has been removed.



- 4 Calcium oxalate was not found in any of the surface samples with significant isotopic depletion that were also analyzed by XRD, and thus we were unable to document biologically mediated alteration in our Classical sculptures.

- 5) One problematic sculpture (MFA 76.729), initially thought to be dolomitic based on the presence of magnesium (measured using the electron microprobe) but with isotopic values inconsistent with Thasos, was resampled in several locations. This piece is actually Mt. Pentelikon calcite with small bands of dolomite and pure muscovite (white mica).

## Conclusion

Isotopic and XRD analyses of fresh and weathered marble demonstrates that extreme care must be taken during sample removal for marble provenance studies. While marble may appear "clean" at "fresh" breaks and in acid-washed sculptures, rapid alteration may have occurred due to atmospheric circumstances (even inside museums), or previous weathering effects may not have been totally removed. Alterations may have penetrated more deeply along minute cracks and fissures, and would still have a great effect on the tiny samples typically used for stable isotope analysis. Our results suggest that samples removed for provenance studies should come from at least 1-2 mm

Lab. No.	Museum No.	Sample Type	$\delta^{13}\text{C}$	$\delta^{18}\text{O}$	Material
HI-001a HI-001b	Sackler 1905.8	fresh marble surface	+2.60 +2.47	-6.27 -6.27	calcite
HI-002a HI-002b	Sackler 1961.86	fresh marble surface	+1.00 -7.89	-1.23 -6.28	pure calcite 4% illite
HI-090 HI-091	MFA 08.205	surface surface	+3.48 -7.42	-3.06 -4.01	pure dolomite
HI-104 HI-105	MFA 84.25	fresh marble surface	+2.84 +2.92	-1.23 -1.20	pure calcite
HI-111 HI-112	MFA 63.2760	fresh marble surface	+3.58 -1.67	-3.09 -4.21	pure dolomite
HI-113 HI-114	MFA 84.64	fresh marble surface	+3.50 +3.44	-3.22 -3.14	pure dolomite
HI-115a HI-116	MFA 41.909	fresh marble surface	+3.20 +3.15	-3.62 -2.61	pure dolomite
HI-117 HI-118	MFA 69.2	fresh marble surface	+3.39 +3.23	-3.32 -3.13	pure dolomite
HI-238 HI-239	MFA 67.948	fresh marble surface	+1.43 -4.97	-3.90 -6.01	calcite
HI-240 HI-241	MFA 1988.327	fresh marble surface	+5.08 +4.70	-3.39 -3.14	calcite
HI-242 HI-243	MFA 1980.212	fresh marble surface	+3.29 -4.44	-1.83 -3.42	pure dolomite
HI-256 HI-257	MFA 1924.150 B	fresh marble surface	+2.87 +2.70	-1.70 -1.61	calcite
HI-258 HI-259	MFA 1924.150 A	fresh marble surface	+2.53 +2.27	-1.62 -1.80	calcite
HI-348 HI-347	Sackler 1991.640	fresh marble surface	+3.06 +2.71	-4.62 -5.52	dolomite
HI-713 HI-714	MFA 01.8200	fresh marble surface	+2.43 +2.00	-4.99 -5.05	calcite
HI-1526 HI-715	MFA 01.8203	fresh marble surface	+1.66 +0.56	-2.00 -2.55	calcite
HI-721 HI-722	MFA 03.755	fresh marble surface	+2.24 +2.23	-1.82 -1.99	calcite
HI-726 HI-727	MFA 16.62	fresh marble surface	+4.96 -6.48	-2.67 -7.87	pure calcite 3% gypsum
HI-1531 HI-732	MFA 1971.209	fresh marble surface	+2.56 -3.87	-8.92 -7.67	calcite
HI-737 HI-738	MFA 1972.971	fresh marble surface	+2.57 +2.52	-5.94 -5.94	calcite
HI-1535 HI-742	MFA 1978.227	fresh marble surface	+3.21 +3.02	-1.61 -4.28	calcite
HI-743 HI-744	MFA 1979.523	fresh marble surface	+2.17 +2.16	-1.90 -1.85	calcite
HI-746 HI-747	MFA 1983.681	fresh marble surface	+1.08 +1.18	-4.34 -4.42	calcite
HI-750 HI-751	MFA 1986.885	fresh marble surface	+2.58 +2.56	-6.23 -6.26	calcite
HI-755 HI-756	MFA 30.543	fresh marble surface	+2.17 +1.69	-1.88 -1.83	calcite
HI-759 HI-760	MFA 51.1404	fresh marble surface	+2.10 +2.08	-2.18 -2.15	calcite
HI-778 HI-779	MFA Res.53.63	fresh marble surface	+1.35 +0.26	-4.52 -5.06	pure calcite pure calcite
HI-358 HI-774	MFA 98.641	fresh marble surface	+3.71 +0.94	-3.06 -7.92	pure dolomite 2% gypsum

Table 1. Stable isotope values for fresh and surface marble samples from Classical sculptures.

below the present surface regardless of whether it appears "clean" or not.

Additional isotopic and X-ray diffraction analyses of fresh and weathered marble samples are in progress, while an experiment to evaluate the isotopic effects of sulphuric acid-induced gypsum production would be a worthwhile endeavor. When all weathering mechanisms are better understood, we will have greater confidence in isotopic and other analytical results, and perhaps in the authentication of particular marble sculptures.

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