

Supplementary Information for

Beautiful Pietàs in South Tyrol (Northern Italy) – local or imported works of art?

Petra Dariz¹, Ulrich Wortmann², Jochen Vogl³, Thomas Schmid^{3*}

¹ heritagelab, 39100 Bozen, Italy.

² University of Toronto, Department of Earth Sciences, M5S 3B1 Toronto, Canada.

³ Federal Institute for Materials Research and Testing, Department of Analytical Chemistry; Reference Materials, 12489 Berlin, Germany.

Additional File 1

Materials and Methods

Description of the analytical procedures for Sr isotope and mass fraction analysis

Materials

For all sample solution preparations and subsequent dilutions, only precleaned labware and high-purity water and acids were used. Further details can be obtained from Ref. [S1]. All sample manipulations were carried out in a metal-free cleanroom at the Federal Institute for Materials Research and Testing (BAM, Berlin, DE). The certified reference material NIST SRM 987 *Strontium Carbonate Isotopic Standard* was purchased from the National Institute of Standard and Technology (NIST, Gaithersburg, MD, US), the certified reference material NASS-6 *Seawater reference material for trace metals* was purchased from the National Research Council of Canada (NRC, Ottawa, CA).

Sample preparation

Gypsum stones and gypsum mortars were packed in polyethylene zip bags, padded at the outside with soft tissues and gently struck with a hammer to obtain smaller particles. Subsamples of the crumbled material of 10 mg to 20 mg each were weighed in Savillex beakers and 10 mL of Milli-Q water was added. The sample was left for 7 to 10 days for extraction, sometimes supported by gently heating at 80 °C on a hotplate. Similar approaches for gypsum were applied by Alonso-Azcarate et al. 2006 [S2] and Yesilova et al. 2020 [S3]. Thereafter, the samples were centrifuged to separate very few remaining and mostly coloured particles; alternatively, the supernatant was taken. For quantitative strontium analyses with inductively coupled plasma mass spectrometry (ICP-MS) in dependence of the current equipment capacity a subsample of the centrifugate of 10 µL (sector field ICP-MS Element 2, Thermo Fisher Scientific, Bremen, Germany) or 100 µL (quadrupole ICP-MS iCAP Q, Thermo Fisher Scientific, Bremen, Germany), respectively, was made up to 5 mL with nitric acid (0.32 mol/L). Based on the quantitative measurements, a subsample containing approximately 5 µg strontium was withdrawn and further prepared for strontium isotope ratio analysis by thermal ionisation mass spectrometry (TIMS) as follows. First, the subsample was evaporated to dryness on a hotplate and redissolved in 350 µL of nitric acid (3 mol/L). This solution was then loaded on mini columns with a volume of 0.5 mL (Evergreen Scientific, Buffalo, NY, US) which beforehand were filled with 300 µL Eichrom Sr Spec resin (Triskem International, Bruz, FR), prewashed with 6 x 350 µL Milli-Q water and conditioned with 6 x 350 µL nitric acid (3 mol/L). After carefully loading the sample onto the column, the matrix was eluted by 6 x 350 µL nitric acid (3 mol/L). Subsequently, the strontium fraction was eluted by 6 x 350 µL Milli-Q water into Savillex beakers. The strontium fraction was then evaporated to dryness on a hotplate, 0.5 mL nitric acid (65 %) and 250 µL hydrogen peroxide (30 %) was added and the sample was again evaporated to dryness. The sample was then redissolved in dilute nitric acid (1 mol/L) to yield a final strontium mass fraction of 100 ng/µL.

Sr mass fraction and isotope analysis

The samples prepared for quantitative Sr analysis as described above were diluted to a nominal mass fraction of 1 µg/kg to 100 µg/kg for measurements by sector field ICP-MS and to a nominal mass fraction of 10 µg/kg to 200 µg/kg for analyses by quadrupole ICP-MS. In both cases ICP multi-element standard IV (Merck KGaA, Darmstadt, DE) was applied as external calibrant. At the iCAP Q rhodium was used as internal standard, while at the Element 2 no internal standard was used, because samples were diluted so much that the Ca mass fraction $w(\text{Ca}) < 1$ mg/kg and drift effects did not occur. The relative expanded measurement uncertainty was assessed to be 20 %, based on the sample preparation, dilutions, the repeatability of the measurement and the calibration standards.

Sr isotope ratio analyses were carried out on a Sector 54 multi-collector TIMS instrument (Micromass, Manchester, UK). In the first step, 1 µL of the finally prepared sample was loaded on Re single filaments together with a tantalum pentachloride activator. The measurements were carried out in dynamic multi-collection mode using automated measurement procedures for obtaining conventional $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios (also known as radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$). The achieved signal intensity for ^{88}Sr was 3 V and the number of measurement replicates was 200. The data treatment includes corrections for the ^{87}Rb interference on ^{87}Sr , the correction of the instrumental isotope fractionation via the fixed value of $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ using the power law, and a normalisation of measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios via a correction factor obtained from the $^{87}\text{Sr}/^{86}\text{Sr}$ reference value for NIST SRM 987 divided by the measured $^{87}\text{Sr}/^{86}\text{Sr}$ value for NIST SRM 987. The reference value for NIST SRM 987, $^{87}\text{Sr}/^{86}\text{Sr} = 0.710250$, can be obtained from Ref. [S4] or as median from the published data for NIST SRM 987 listed in GeoReM [S5]. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ value for NIST SRM 987 was 0.710220 with a repeatability of 0.000006 expressed as twice the standard deviation of the mean (2SE, N = 43). The final correction factors, calculated for each measurement campaign, ranged between 1.000001 and 1.000055. The typical internal precision, expressed as 2SE of 200 replicates, was 0.000012. The reproducibility obtained on 8 independently processed samples of NASS-6 with 31 measurements (filaments) in total, was 0.000004 (2SE, N = 31). For quality control purpose NIST SRM 987 and NASS were processed the same way as the samples, but without the extraction step. The finally obtained values were compared to the published data as listed in GeoReM [S5] and good agreement with the reference values within the stated measurement uncertainties was achieved. This is documented by E_n values (formerly termed *normalised error*) of less than 1, which state the metrological compatibility of two values [S6]. Based on these validation data and the repeatability and reproducibility of the NASS-6 and NIST SRM 987 measurements an expanded measurement uncertainty U ($k=2$) of 0.000024 was calculated (Table S1).

Table S1. Conventional $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of reference materials NASS-6 and SRM 987 as well as measurement uncertainties U ($k=2$) and calculated E_n values

Sample	Measured data			Reference data			E_n ^b
	N_1/N_2 ^a	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{con}}$	U ($k=2$)	$^{87}\text{Sr}/^{86}\text{Sr}_{\text{con}}$	U ($k=2$)	Ref.	
NASS-6	8/31	0.709182	0.000024	0.709179	0.000024 ^c	[S5]	0.075
SRM 987	3/12	0.710264	0.000024	0.710250	0.000008	[S5]	0.534

^a N_1 represents the number of independent sample preparations, while N_2 represent the total number of measurements

^b the E_n value is a measure for the metrological compatibility [S6]

^c as only a value without uncertainty statement is available from GeoReM, the uncertainty of our values is applied here

References

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