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Sr isotopic microanalysis at the Radiogenic Isotope Laboratory of the Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Napoli - Osservatorio Vesuviano

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SR ISOTOPIC MICROANALYSIS AT THE RADIOGENIC ISOTOPE LABORATORY OF THE ISTITUTO NAZIONALE DI GEOFISICA E VULCANOLOGIA, SEZIONE DI NAPOLI - OSSERVATORIO VESUVIANO

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Introduction

Mechanical sampling, conventional dissolution and chemical separation, followed by analysis using the TIMS (Thermal Ionisation Mass Spectrometry), is one of the best methods for highly accurate and precise determinations of Sr isotopic compositions in most geological materials over a wide range of Sr concentrations. Recent technological improvements have provided the opportunity to analyze Sr isotopic compositions at the scale of individual crystals and along core to rim transects of single minerals. Sr isotopic ratio variations, recorded from core to rim of a mineral grain, reflect the progressive changes, if any, in the composition of the magma from which the mineral has crystallized [e.g. Davidson et al., 2001, 2007; Francalanci et al., 2005]. Therefore, the relationship between isotopic variations and petrographic features can be used to constrain magma evolution pathways involving open system processes, such as magma mixing, contamination and recharge.

Here we present the methodology that we have set up at the Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Napoli - Osservatorio Vesuviano (OV) for the precise analysis of ng-levels of Sr, purified either from single crystals or from microgram-sized solid samples, extracted from minerals in thin sections. Physical sampling has been performed by using a computer numerical control milling machine: the MicroMill™ manufactured by the New Wave™.

The chemical procedures routinely adopted at the INGV-OV Radiogenic Isotope Laboratory for extracting Sr and Nd from natural samples, and the analytical methods for measuring their isotopic composition [Arienzo et al., 2013 and references therein], allowed us to develop and perform high precision analyses of single crystals and microgram-sized solid samples collected through this innovative micro-sampling methodologies. We also report the results of the analyses performed on a certified international standard in order to evaluate the quality of data produced by the INGV-OV Radiogenic Isotope Laboratory. In particular, we used the National Institute of Standards and Technology (NIST) SRM 987 standard, with Sr concentration of 3, 6, 12 ng/μl. Results obtained on single feldspar crystals from the Campanian Ignimbrite (39 ka) [Fisher et al., 1993; Civetta et al, 1997; De Vivo et al., 2001; Arienzo et al., 2009 and references therein] and the Agnano Monte Spina tephra (4690-4300 a cal BP) [de Vita et al., 1999; Blockley et al., 2008; Arienzo et al., 2010], are reported to test the quality of the whole analytical procedure.

1. Procedure adopted for single crystal analysis

1.1 Sample preparation

Samples are washed in deionized H_2O for several days, to release possible traces of NaCl adsorbed from sea water aerosols. Then, the external part of pumice clasts is removed with a dental drill equipped with a diamond disk, washed again many times in deionized H_2O, crushed and mechanically sieved through a set of sieves with opening sizes from +1.5 Ø to -1.5 Ø (Fig. 1A).

Crystal grains between 0 to -1.5 Ø fractions are hand-picked under a binocular microscope (Fig. 1B). They are leached for ca. 15 minutes in an ultrasonic bath (Fig. 1C) with 7% HF to remove any glass from the surface, and then rinsed with H_2O Milli Q®. If needed, the leaching procedure is repeated. The selected crystals, fixed on a glass dish with parafilm, are cut under a binocular microscope, possibly along their elongated axes (Fig. 2A), by using a pair of tweezers, cut and bent to create an homemade small scalpel (Fig. 2B, C).

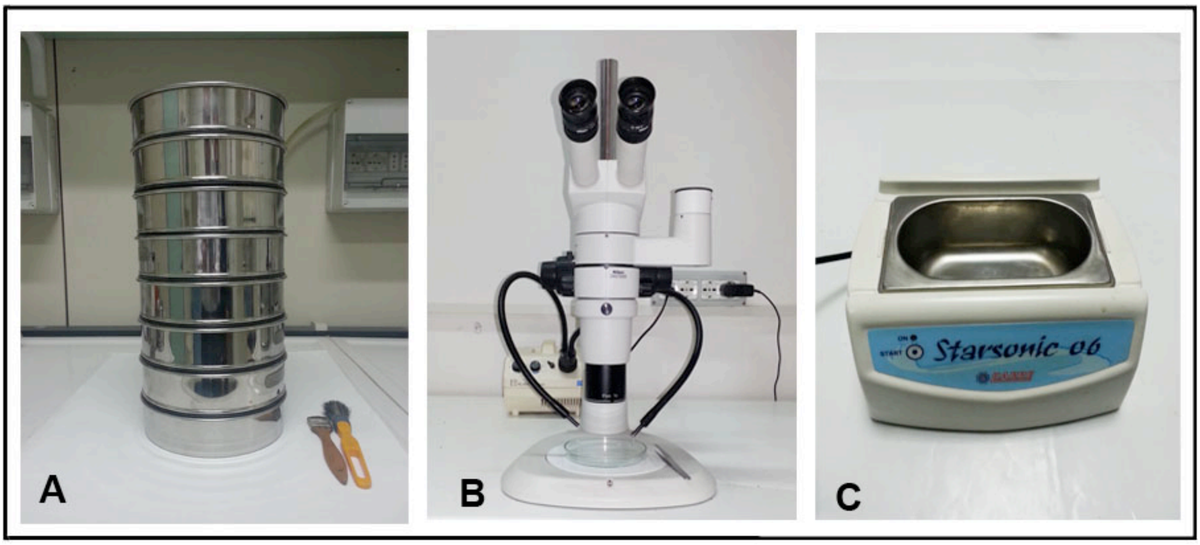


Figure 1. A) Sieves; B) Binocular microscope; C) Ultrasonic bath used for leaching.

Half-crystal is mounted on a glass slide for chemical analysis (major elements and Sr) by electron microprobe. The remaining part of the crystal is washed in a ultrasonic bath with H_2O Milli Q®, in the Clean Chemistry Laboratory, for isotopic analysis.

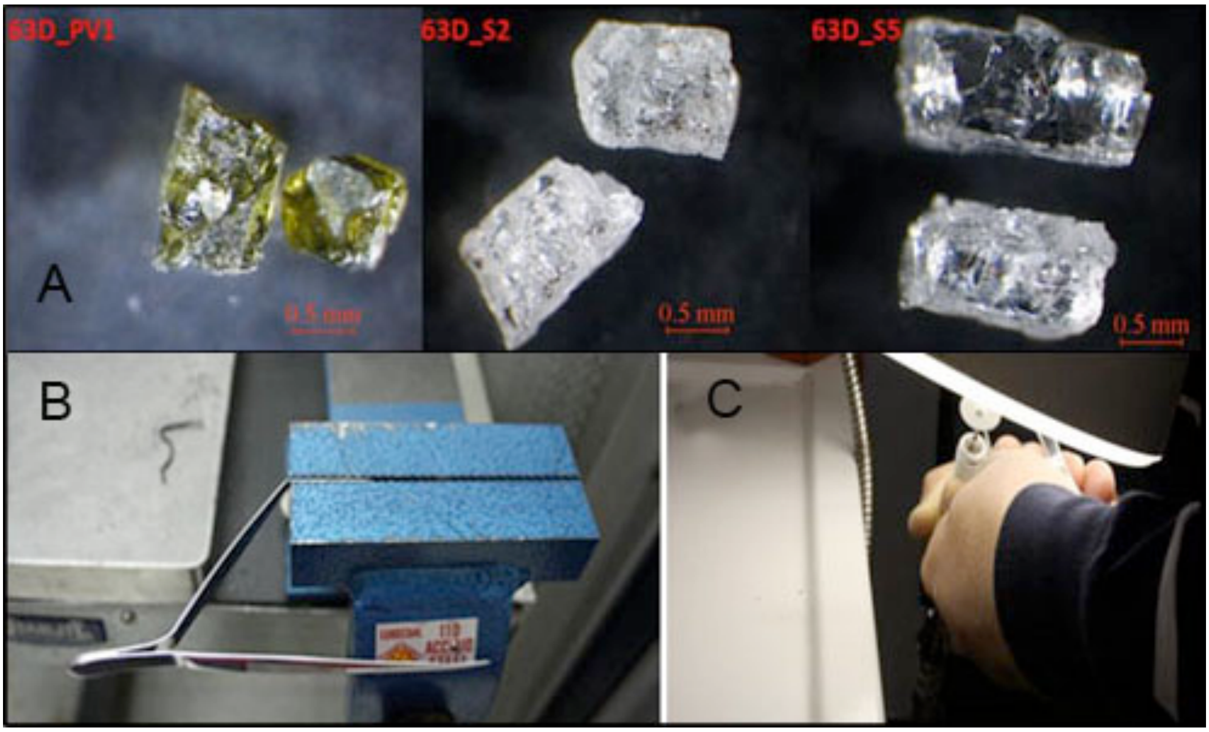


Figure 2. A) Half-crystals, possibly cut along their elongated axes, are washed in the Clean Chemistry laboratory before dissolution starts; B) and C) Photographs of the pair of tweezers cut and bent to create an homemade small scalpel.

1.2 Preparation of micro-columns

Chromatographic columns are made up from standard 0.5-1 ml pipette tips with a circular piece of polypropylene frit (30 μm pore-size) fitted into the tapered end. The portion of the pipette tip below the frit is cut diagonally with a scalpel in order to facilitate emptying of the column during elution [Charlier et al., 2006]. Once made up and checked for flow rate by filling with water, columns are washed in a solution H_2O Milli Q®:15M HNO_3 = 1:1, for one week in a 1 l Savillex™ Teflon beaker, under a laminar flow hood (Fig. 3A) in the Clean Chemistry Laboratory. The cleaned columns are then rinsed in H_2O Milli Q® and left overnight on hotplate at 100°C. They are rinsed with clean H_2O Milli Q® prior to use.

Materials to be used in the Clean Chemistry Laboratory for microanalyses are washed with mixtures of H_2O Milli Q® and ultra-pure HCl and HNO_3. The 3.5 ml screw-cap Savillex™ Teflon beakers, used for samples dissolution and for collecting the Sr fractions, are carefully cleaned, filled with 6M HCl, closed with their cup and left overnight on hotplate at 100°C. Then they are rinsed with H_2O Milli Q® in a 500 ml beaker and left on hotplate at 100°C for ca. 8 hours. Next step consists in washing the 3.5 ml screw-cap Teflon beakers in a 500 ml beaker with 15M HNO_3 and then rinsing them with H_2O Milli Q®.

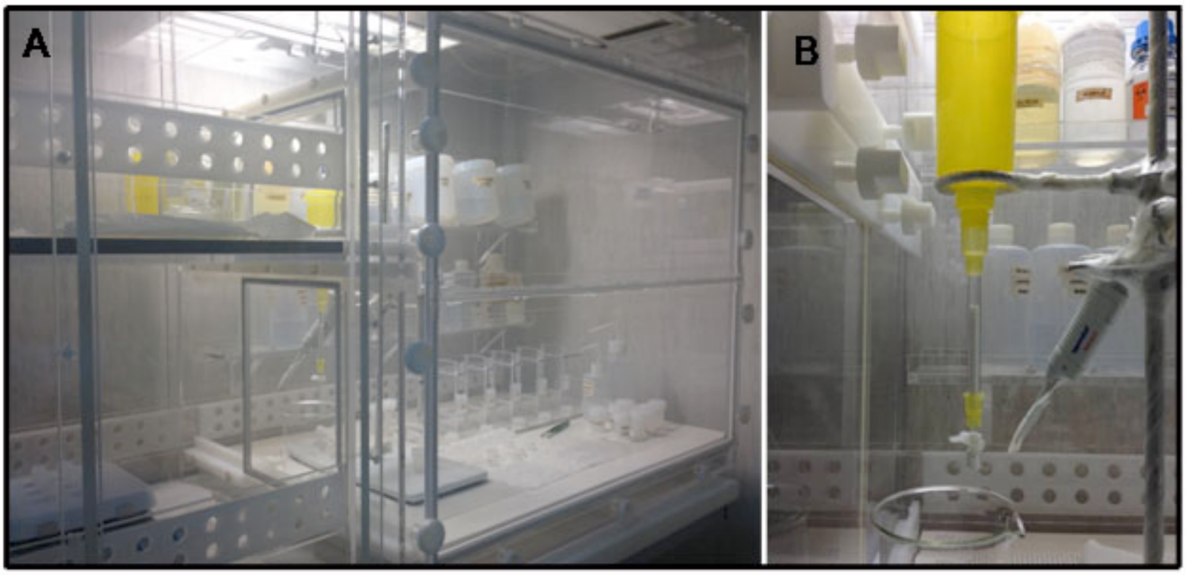


Figure 3. A) Laminar flow hood in the Clean Chemistry laboratory; B) The 2 ml Biorad™ column used for cleaning the resin.

The Sr Spec™ resin, used for the chemical separation of Sr, is cleaned thoroughly before use. 2 ml of resin (enough for 20-30 columns), slurried with water, is placed in a 2 ml Biorad™ column with a 225 ml reservoir attached (Fig. 3B). The following acids, in the reported order, are passed in succession for 10 times:

- 2.5 ml of 6M HCl;
- 22.5 ml of H_2O Milli Q®;
- 22.5 ml of 0.1M H_2SO_4;
- 22.5 ml of 0.05M HNO_3.

This procedure allows removing traces of organic compounds, and minimizing the Sr blank contribution from the resin. The cleaned resin is stored as a slurry with 0.05M HNO_3, in a 50 ml FEP dropper bottle.

1.3 Sample dissolution

Half-crystals are weighted into 3.5 ml screw-cap Savillex™ Teflon beakers, in which they undergo through three steps of sample digestion. The amount of acid needed in each step depends on the sample weight. For samples lighter than 0.5 mg the first dissolution step is achieved by adding 70 µl of 15M HNO_3, 70 µl of 6M HCl and 70 µl of 29M HF; for samples weighting between 0.5 and 5 mg, by adding 70 µl of 15M HNO_3, 70 µl of 6M HCl and 150 µl of 29M HF, and for samples heavier than 5 mg, by adding 70 µl of 15M HNO_3, 70 µl of 6M HCl and 200 µl of 29M HF.

Beakers are then sealed and placed on a hotplate (ca. 100°C) for 2-3 days. Following evaporation, the residues of samples lighter than 0.5 mg, weighting between 0.5 mg and 5 mg and heavier than 5 mg, are taken up in 70, 150 and 200 µl of 6M HCl, respectively and the beakers resealed and replaced on hotplate overnight. Following evaporation, samples lighter than 0.5 mg, weighting between 0.5 mg and 5 mg and heavier than 5 mg, are taken up in 70, 150 and 200 µl of 15M HNO_3, respectively, and again the beakers are sealed and placed on the hotplate overnight. Following a final evaporation step, sample residues are dissolved in 150µl of 3M HNO_3 and placed into the ultrasonic bath (Fig. 1C) for 10-15 minutes, prior to column chemistry. At this stage, the nitric acid solutions are generally clear and free of precipitates.

1.4 Chemical separation of Sr and determination of blank of the resin

Prior to Sr chemical separation by chromatographic techniques, the micro-columns are placed on a Plexiglas support (Fig. 4).

Cleaned columns are washed alternately with H_2O Milli Q® and HCl 6M prior to filling them with approximately 70 µl (column volume - CV) of Sr Spec resin. The resin is further washed with several CVs of 6M HCl and H_2O Milli Q®, before conversion to a nitric acid medium by adding twice 100 µl 3M HNO_3.

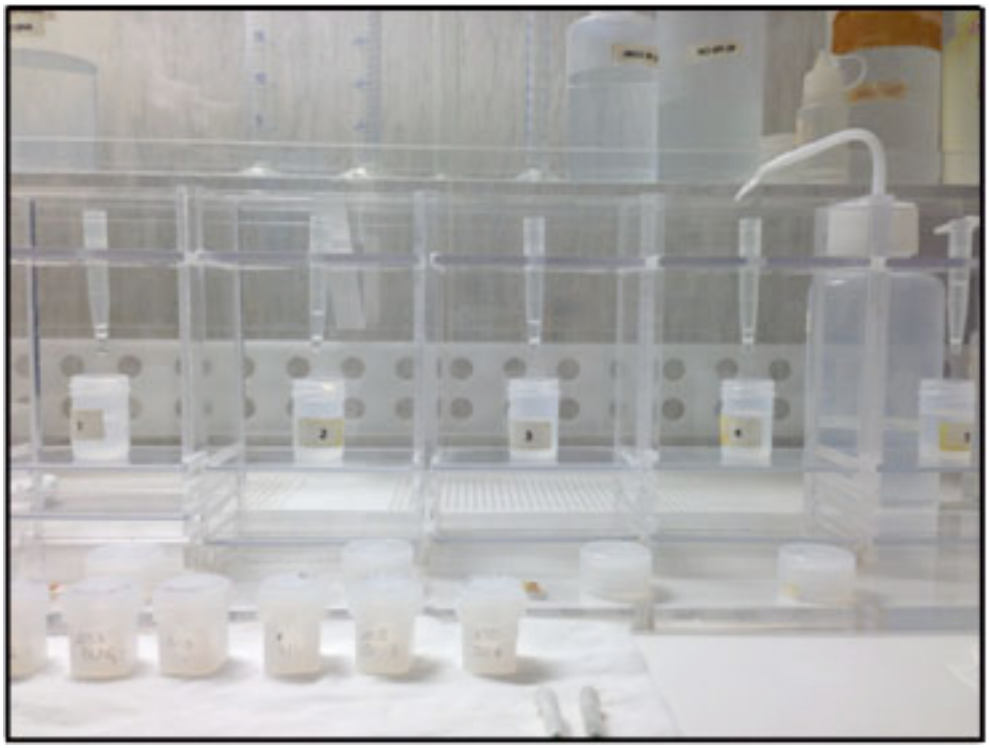


Figure 4. Micro-columns for chemical separation of Sr by chromatographic techniques.

After loading the column with the sample dissolved in 150 µl 3M HNO_3, 550 µl 3M HNO_3 are passed in four stages (50, 100, 200 and again 200 µl). Then Sr is collected in 250 µl 0.05M HNO_3.

However, before being used for the chemical separation of Sr from natural samples, the cleaned resin is loaded on a micro-column in order to measure the blank of the resin. The Spike, a sample enriched in ^{84}Sr (available by courtesy of Prof. Riccardo Petrini, University of Pisa), is weighted, diluted in 150 µl of 3M HNO_3 and loaded on the micro-column.

The blank of the resin for micro-analyses has to be ca. 12 pg (±8), considering a total Sr concentration of 3 ng for the samples to be analyzed. This means that the blank of the resin must be less than 0.5% of the total Sr concentration [Charlier et al., 2006]. Three determinations have been carried out to check the cleaning procedure adopted for the resin (Table 1). Furthermore, two more blank determinations have been performed to check the level of Sr contamination of the total procedure for single crystals digestion. These latter determinations have been performed by weighting an aliquot of spike into a beaker, by adding the amount of acid necessary for dissolving a sample of similar weight, and following the same separation scheme used for natural samples. Blank determinations are reported in Table 1.

Table 1. Results of measurements of blank of the resin and that of the total procedure.

	November 2012	**June 2013**	**July 2013**
Blank of resin	10 pg	10 pg	13 pg
Total blank 1	36 pg		
Total blank 2		32 pg	
Blank of H_2O MilliQ®	10 pg		
Total blank MicroMill™			12 pg

2. Chemical procedure adopted for drilled sample powders

2.1 MicroMill™

A MicroMill™, produced by Merchantek-New Wave Research, has been set up at the Radiogenic Isotope Laboratory of INGV-OV. It is located in a laminar flow hood to limit external contamination (Fig. 5). Crystals selected for microanalyses are hand-picked from the largest (> 0 Ø) fractions. They are embedded in a bi-component resin, then grinded with abrasive paper and polished with alumina powder (0.3 µm). Before being positioned under the microscope of the MicroMill™, the polished section is cleaned with H_2O Milli Q® and then with ethanol in ultrasonic bath. Conical tungsten carbide mill bits are used for milling the samples. Prior to accurate sampling, a number of parameters need to be determined or selected, using the instrument software. Such parameters include mill tip location, sample surface position, offset between the mill axis and the optical axis of the microscope (*XY* offset), and milling depth. It is also possible to mill out multiple shallow points along particular zones of interest. The number of points to be milled is defined according to the a-priori knowledge of i) the Sr concentration in the sample, ii) the geometry of the milling bits, and iii) the milling depth, calculated taking into account that approximately 3 ng of Sr is required for high-precision analysis [see Charlier et al., 2006 for details]. The milling is carried out under a drop of H_2O Milli Q®, that prevents the generated fine sample powder from being dispersed over the sample surface, and it is confined by a square of Parafilm™ with a hole cut at the center, firmly pressed to the polished sample surface (Fig. 6).

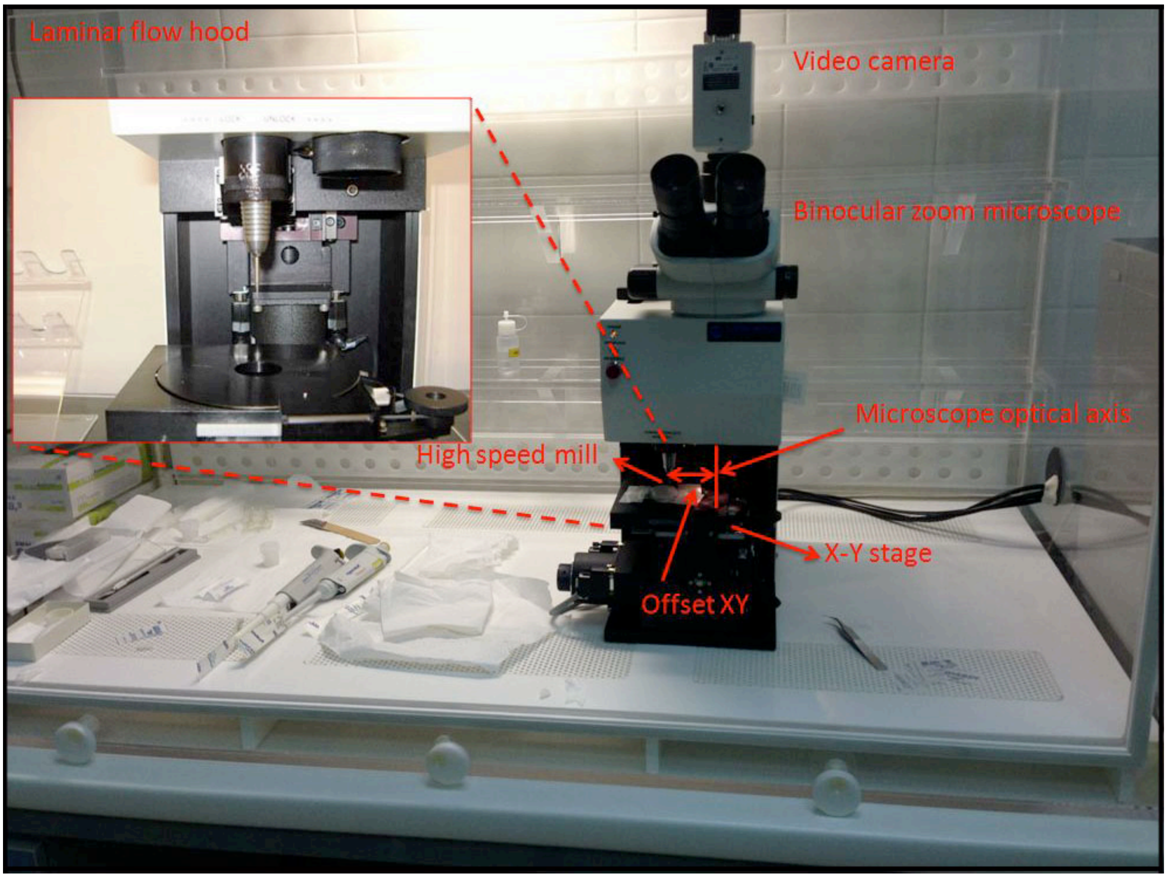
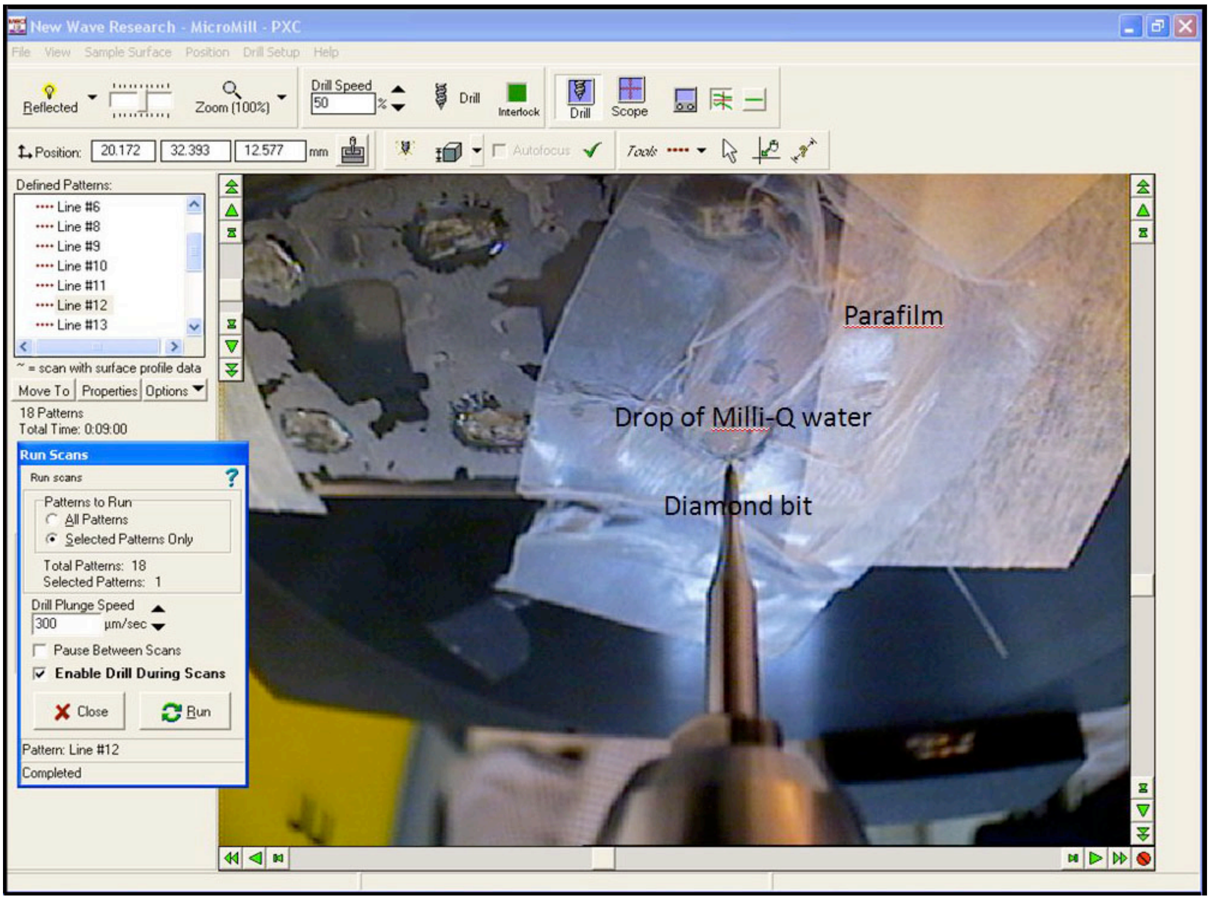


Figure 5. Photograph of the MicroMill™ set up at the INGV-OV laboratory.

2.2 Dissolution and chemical separation of the Sr from the drilled samples

The produced powder is pipetted from the polished sample surface in H_2O Milli Q® and transferred directly to the 3.5 ml volume digestion beaker. The solution is then dried on a hotplate in the Clean Chemistry Laboratory. Sample decomposition is achieved by adding 70 µl 15M HNO_3, 70 µl 6M HCl and 70 µl 29M HF, and placing the beaker on a hotplate (ca. 100°C) overnight. The residue is taken up in 150 µl 6M HCl and placed on a hotplate for two hours. Following evaporation, the sample is taken up in 150 µl of 15M HNO_3 and placed on a hotplate (ca. 100°C) for few hours. Then, sample is dissolved in 150 µl 3M HNO_3 and placed in a ultrasonic bath for twenty minutes before chromatographic separation. The same procedure described for single crystals and blank is adopted for the chemical separation of Sr from the drilled samples.



Drill Speed 50 %

Position: 20.172 32.393 12.577 mm

18 Patterns
Total Time: 0:09:00

○ All Patterns
● Selected Patterns Only

Total Patterns: 18
Selected Patterns: 1

Drill Plunge Speed 300 µm/sec

☐ Pause Between Scans
☑ Enable Drill During Scans

Pattern: Line #12
Completed

Figure 6. Screen shot of the software controlling the milling machine.

2.3 Blank determination

Total procedure blank relative to the drilled samples is determined by milling within a drop of H_2O Milli Q®, placed on a polished portion of the section. The mill bit is left into the drop of water for a time equal to that necessary to mill the selected crystals. Once inserted the clean mill in the drop of H_2O Milli Q® the latter is recovered by a pipette and left in the same beaker where an aliquot of Sr spike has been previously weighted. The blank solution is treated as the drilled samples in the Clean Chemistry laboratory in order to measure, by TIMS, the total procedure blank. The measured value is reported in Table 1 as "Total blank MicroMill™".

3. Sr isotopic analyses by Thermal Ionization Mass Spectrometry (TIMS)

3.1 Sr standard measurements

The running conditions for determining the Sr isotopic composition of single crystals and drilled samples is tested by measuring the isotopic ratios of the National Institute of Standards and Technology (NIST) SRM 987 standard, which recommended value for $^{87}Sr/^{86}Sr$ is 0.71025 (Thirlwall, 1991). The NBS standard solution has been supplied by Prof. Massimo D'Antonio and Prof. Lucia Civetta, University of Napoli Federico II. In the Radiogenic Isotope Laboratory measurements of the NIST SRM 987 standard, having Sr concentration of 3 ng/µl, 6 ng/µl and 12 ng/µl, are performed. Sr standards are loaded in a laminar flow hood by using a power supply device and suitable solutions, as reported in Arienzo et al. (2013).

Sr isotopic ratio determinations have been performed with ^{88}Sr signals of 2-4 Volt and integration time of 4 seconds [Charlier et al., 2006]. The measured Sr isotopic ratios are mean values of 150 ratios, divided in 10 blocks of 15 measures. The confidence on the mean value reliability is expressed as mean standard error (se), equal to $\sigma/\sqrt{n}$, where σ is the standard deviation and n is the number of measurements. We generally report the analytical error as ± 2 times the standard error (2se).

Analyses made on the Sr standard in the time interval from April 2013 to July 2013 are plotted in Figure 7. The mean value of the $^{87}Sr/^{86}Sr$ measured on standards having Sr concentration of 3 ng/µl is 0.710210 ($2\sigma = 1.7\text{x } 10^{-5}$; n=17), that relative to the standards having 6 ng/ µl of Sr is 0.710210 ($2\sigma = 2.5\text{x } 10^{-5}$; n=17), whereas the mean value relative to the standards having Sr concentration of 12 ng/µl is 0.710208 ($2\sigma = 2.3\text{x } 10^{-5}$; n=21). The external precision (2σ) can be expressed in ppm according to the equation:
$2\sigma_{ppm} = (2\sigma/m) \text{ x } 10^6$,
where σ is the standard deviation and m is the mean of measurements [Charlier et al., 2006]. For our standards it ranges from 24 to 35 ppm.

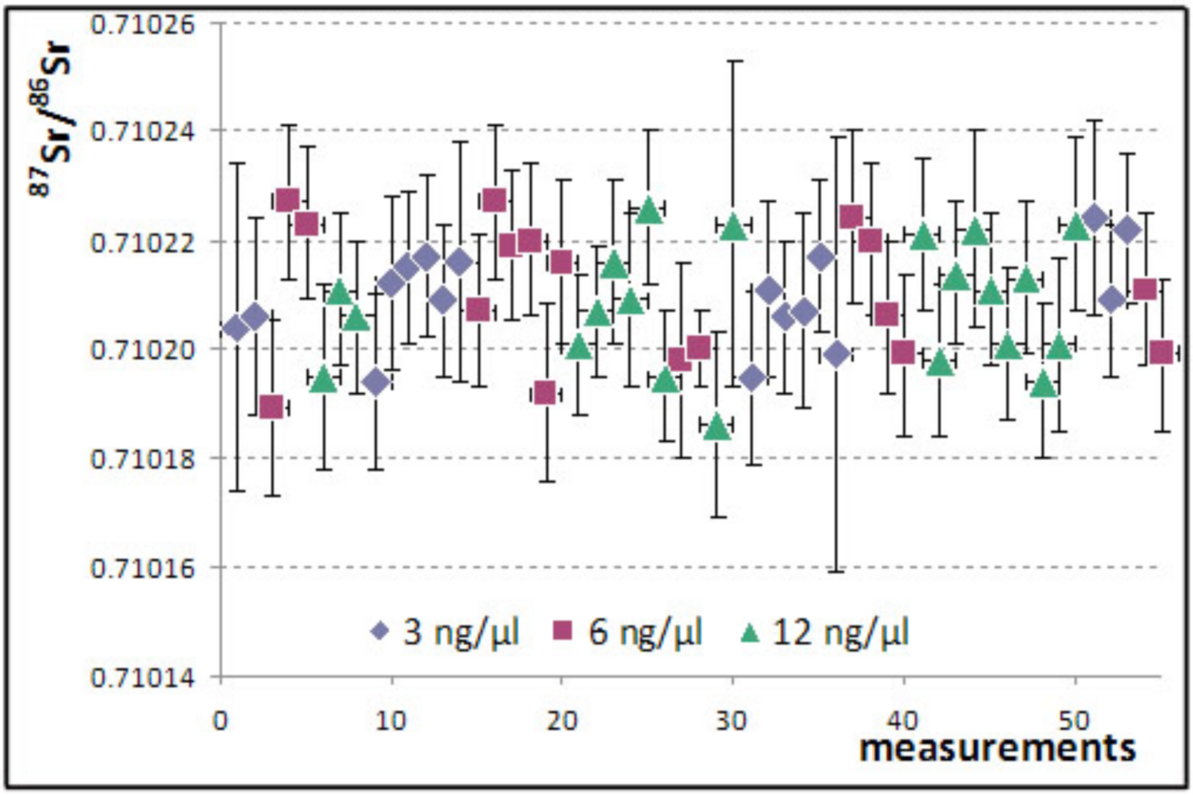


Figure 7. Sr isotopic ratios of NIST SRM 987 with Sr concentration of 3 ng/µl, 6 ng/µl and 12 ng/µl performed in the time span April-July 2013.

3.2 Sr isotopic composition of selected Campi Flegrei feldspar crystals

On the basis of total procedure blank (12 pg), of the measured isotopic ratios of NIST SRM 987 standard and, in order to test the procedures described previously, we performed Sr isotopic determinations of single feldspar crystals from the Campanian Ignimbrite erupted products, and of an Agnano Monte-Spina, microgram-sized solid sample, obtained by MicroMill^{TM}.

We analyzed the isotopic composition of two single sanidine crystals (IC CR1, weighting 5.7 mg and IC CR2, weighting 1.2 mg) hand-picked from a sample collected at the San Marco Evangelista (Caserta) outcrop and belonging to the Campanian Ignimbrite deposit [Arienzo et al., 2009]. Both crystals have been digested and dissolved by adopting the procedures already described. The measured $^{87}Sr/^{86}Sr$ are 0.707304 ± 0.000007 and 0.707296 ± 0.000006 for IC CR1 and IC CR2, respectively. These values are similar to the average Sr isotopic composition (~ 0.707300) of feldspar crystals from the same sample, measured through conventional procedures for Sr isotopic analysis [Arienzo et al., 2009].

For testing the chemical procedures and performing high precision analyses of microgram-sized solid samples, through the micro-sampling methodology, we have chosen a feldspar crystal (AMS F1), incorporated in a bi-component resin, hand-picked from products of the Agnano Monte-Spina eruption (Fig. 8).

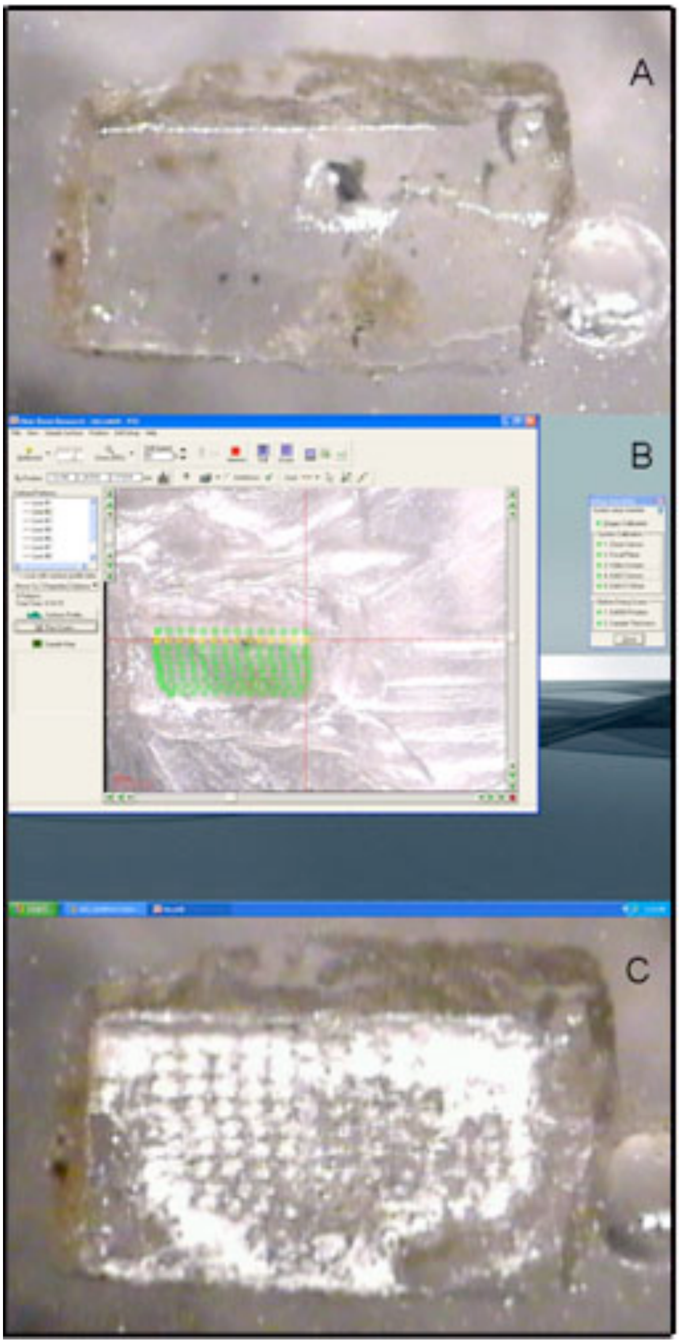


Figure 8. Feldspar crystal hand-picked from the Agnano-Monte Spina erupted products, before (A) and after (B) and (C) microdrilling.

In this test 12 lines, for a total of 140 holes, with a drilling depth of 75 µm, have been performed on the crystal, in order to have ca. 10 ppm of Sr in the recovered sample powder. The measured $^{87}Sr/^{86}Sr$ is 0.707460 ± 0.000016. This value is similar to the lowest Sr isotopic compositions measured through conventional procedures on feldspar crystals selected from the Agnano-Monte Spina erupted products, characterized by $^{87}Sr/^{86}Sr$ ranging from 0.70746 to 0.70750 [de Vita et al., 1999].

4. Conclusions

The obtained results show the feasibility of performing mechanical sampling by MicroMill™, conventional dissolution and chemical separation of Sr followed by analysis by TIMS, at the Radiogenic Isotope Laboratory of the INGV-OV. This innovative methodology, coupled with conventional geochemical analyses, could greatly improve the ability to decipher magmatic processes, particularly in those volcanic areas characterized by the emission, over a wide time span, of compositionally similar magmas. In these areas major oxide and trace element variations cannot be used to unequivocally discriminate between open and closed system processes. For example, in the last decades detailed petrographic, mineral chemistry, geochemical and isotopic investigations on volcanic rocks spanning the history of the Campi Flegrei volcanic area, have been variably combined in order to define the role of these magmatic processes in the evolution of its magmatic feeding system [e.g. Civetta et al., 1997; D'Antonio et al., 1999, 2007; Pappalardo et al., 2002; Tonarini et al., 2004; 2009; Arienzo et al., 2009; 2011; Perugini et al., 2010; Di Renzo et al., 2011; Di Vito et al., 2011 and references therein]. The results obtained by testing the use of the microanalytical technique in the Radiogenic Isotope Laboratory on crystals from the Campi Flegrei erupted products (Minolfi, 2013), represent a new impulse, offered to our research, for further investigating magma chamber processes such mingling/mixing among chemically similar, but isotopically distinct magmas, by performing high precision determination of Sr isotopic ratios on single crystals and drilled sample powders, this latter obtained by using the MicroMill^{TM} instrument.

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