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SR AND ND ISOTOPE ANALYSIS AT THE RADIOGENIC ISOTOPE LABORATORY OF THE ISTITUTO NAZIONALE DI GEOFISICA E VULCANOLOGIA, SEZIONE DI NAPOLI - OSSERVATORIO VESUVIANO

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Introduction

Evolution of magmatic systems can be studied by using geochemical and isotopic data. Magmas generated in the mantle, during uprising, can change their characteristics undergoing a variety of chemical evolution processes. The coupling between the study of major and trace element, and radiogenic isotope compositions, may be useful to distinguish the effects of different processes of magma differentiation. The implementation of modern mass spectrometers since the first one designed by Nier [1940] made possible the measurement of variations in the isotopic composition of selected elements in natural materials and thus permitted the spectacular growth of Isotope Geology. Last generation mass spectrometers gave a new impulse to isotopic researches in the Earth Sciences, providing the possibility to strongly reduce the analytical time concomitantly increasing accuracy and precision. A new generation Thermal Ionisation Mass Spectrometer (ThermoFinnigan Triton TI® Mass Spectrometer) and a clean laboratory have been set up at Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Napoli-Osservatorio Vesuviano (OV), since year 2000, using procedures already adopted at the University of Napoli Federico II, as well as standards solutions, in order to measure Sr and Nd isotope compositions of volcanic products for scientific purposes. Particular attention has been dedicated to the procedures set up for extracting Sr and Nd from natural samples (whole rocks, minerals and groundmass) and for measuring Sr and Nd isotope compositions of natural and reference samples. Here we report a data set on certified international standards used to evaluate the quality of data produced in the INGV-OV Radiogenic Isotope Laboratory: NIST SRM 987 for Sr isotopes and La Jolla for Nd isotopes.

The chemical procedures adopted for extracting Sr and Nd from natural samples and the analytical methods for measuring their isotope composition allowed us to develop and perform high precision analysis of small-size samples, such as single crystals, and to detect intra-grain variations (core, rim, growth zones) by using innovative micro-sampling methodologies, such as micro-milling.

1. Procedure adopted in the Clean Chemistry Laboratory

1.1 Sample preparation

In order to study the evolution of magmatic feeding systems by using major and trace element contents and the isotopic composition of the erupted products, samples collected after detailed stratigraphic reconstructions are washed in deionized H_2O for several days, to release possible traces of NaCl. After that, the external part of pumice clasts is removed with a dental drill equipped with a diamond disk, washed again multiple times in deionized H_2O, crushed to lapilli-size particles, then ground and homogenized in an agate mill.

Samples are dissolved in the Clean Chemistry Laboratory of the INGV-OV, equipped with conditioned (ca. 23°C) and over-pressured air, in order to extract by chromatographic technique Sr and Nd for isotope ratios determinations by Thermal Ionisation Mass Spectrometry. Sample dissolution consists in the transformation of constituents, non-dissolvable silicates phases, in soluble phases. This transformation is achieved by acid digestion of a precise amount of sample. Samples selected are whole rock and groundmass powders (their weight ranges from 0.1 to 0.2, depending on Sr and Nd contents), and minerals, either as single grains or as a whole of crystals (the weight of the single grain ranges from slightly less than 0.1 to 0.006 g, depending on their Sr and Nd contents). Groundmass and minerals are hand picked from the bulk sample under binocular microscope, after crushing and sieving. Samples are dissolved in Savillex® Teflon beakers with cups. The cleaning procedure of these beakers consists in variable steps of washing, summarized in Table 1.

Table 1. Procedure adopted for cleaning Teflon beakers.

Step	
1	Fill up the beakers with 6N HCl; then heat them on hot plate for 2-3 hours
2	Wash the beakers with Milli Q® H_2O, then kept on hot plate for ca. 12 hours
3	Rinse the beakers 3 times with Milli Q® H_2O, then left on hot plate for ca. 12 hours in a 1:1 solution of HCl and Milli Q® H_2O
4	Wash the beakers with Milli Q® H_2O, then kept on hot plate for ca. 12 hours
5	Rinse the beakers 3 times with Milli Q® H_2O, then left on hot plate for ca. 12 hours in a 1:1 solution of HNO_3 and Milli Q® H_2O
6	Wash the beakers with Milli Q® H_2O, then kept on hot plate for ca. 12 hours
7	Finally they are rinsed with Milli Q® H_2O and dried

For samples dissolution, high purity (suprapur) chemical reagents are used, in order to measure the isotopic composition of samples without any appreciable external contamination. In particular, high purity nitric acid (HNO_3, 65 wt.%), hydrochloric acid (HCl, 30 wt.%), hydrofluoric acid (HF, 40 wt.%) and H_2O treated with two steps of purification, by using Millipore and Milli Q$^{®}$ systems (18.2 MΩ resistivity) are used. Before starting dissolution, depending on the freshness of the bulk samples, they are acid-leached to limit the effect of post-depositional alteration processes on the measured isotopic ratios. The usual leaching procedure consists in adding a small amount of 6N HCl to the powder. Teflon beakers, containing powder and acid, are kept on hot plate for 10 minutes at 120°C. Then the acid is removed by a pipette and the powder washed with Milli Q$^{®}$ H_2O. Again, 6N HCl is added and kept for 10 minutes into the beakers plate at room temperature. Then the acid is removed by a pipette and samples are re-washed in Milli Q$^{®}$ H_2O.

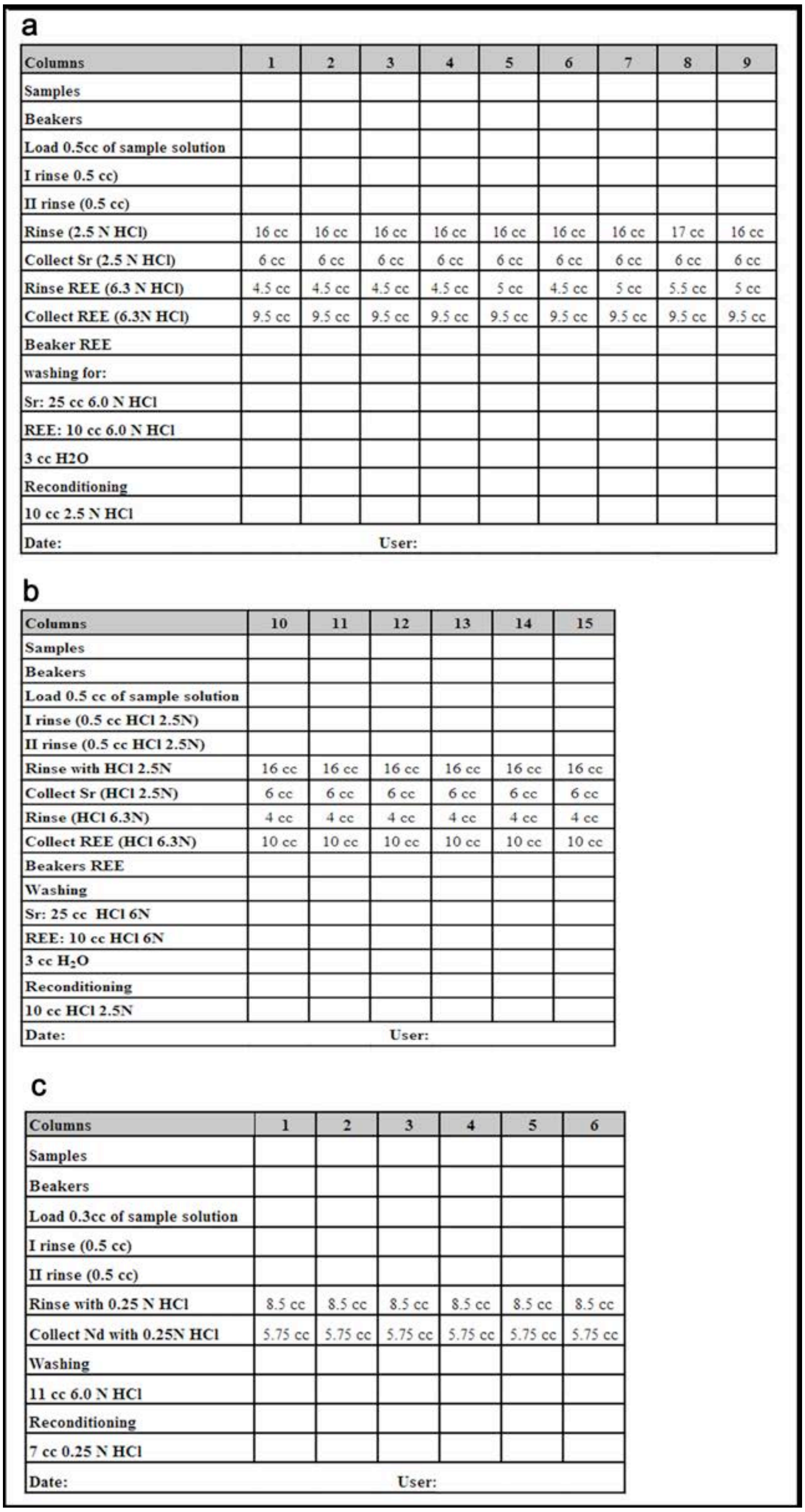
1.2 Sample dissolution

The first step of sample digestion consists in dissolving the weighted amount of sample in concentrated HF. For 0.2 g of sample powder, 1 ml of HNO_3 and 5 ml of HF are used. The solution is left into a closed Savillex beaker on a hot plate, at 120°C for a time variable from 1-2 to 3-5 days, in case of whole-rock powder and mineral phases, respectively. Then, the solution is evaporated to dryness on hot plate. The result of HF dissolution is the formation of fluorides which are insoluble in HCl. Due to the fact that HNO_3 helps to convert the fluorides into nitrates soluble in HCl, the second dissolution step consists of adding 1 ml of HNO_3. The solution is again evaporated to dryness on hot plate. The third step consists in dissolving the sample in 8 ml of 6N HCl. The solution is left in the closed beaker on hot plate for 12 hours at 120°C, and successively evaporated to dryness. At this point the sample is re-dissolved in 1 to 5 ml of 2.5N HCl, depending on its Sr and Nd concentration. The solution is centrifuged for 10 minutes at 5000 rpm; after that it is ready for the chemical separation of Sr and Rare Earth Elements (REE).

1.3 Chemical separation of Sr, REE and Nd

In order to separate Sr and Nd from sample solutions ion-exchange column chromatographic techniques are used, in which the stationary bed is hosted within a tube. In the Clean Laboratory quartz columns with an internal diameter of about 0.5 cm and height of about 22 cm, with a ca. 20 ml reservoir at the top (Figure 1), have been set up and calibrated. In the following, the preparation of columns dedicated to samples containing more than 50 ppm of Sr ("high-Sr samples") is described.

Figure 1. Detail of the quartz columns for Sr and REE separation by chromatographic techniques.



a

Columns	1	2	3	4	5	6	7	8	9
Samples									
Beakers									
Load 0.5cc of sample solution									
I rinse 0.5 cc)									
II rinse (0.5 cc)									
Rinse (2.5 N HCl)	16 cc	16 cc	16 cc	16 cc	16 cc	16 cc	16 cc	17 cc	16 cc
Collect Sr (2.5 N HCl)	6 cc	6 cc	6 cc	6 cc	6 cc	6 cc	6 cc	6 cc	6 cc
Rinse REE (6.3 N HCl)	4.5 cc	4.5 cc	4.5 cc	4.5 cc	5 cc	4.5 cc	5 cc	5.5 cc	5 cc
Collect REE (6.3N HCl)	9.5 cc	9.5 cc	9.5 cc	9.5 cc	9.5 cc	9.5 cc	9.5 cc	9.5 cc	9.5 cc
Beaker REE									
washing for:									
Sr: 25 cc 6.0 N HCl									
REE: 10 cc 6.0 N HCl									
3 cc H2O									
Reconditioning									
10 cc 2.5 N HCl									
Date:				User:					

b

Columns	10	11	12	13	14	15
Samples						
Beakers						
Load 0.5 cc of sample solution						
I rinse (0.5 cc HCl 2.5N)						
II rinse (0.5 cc HCl 2.5N)						
Rinse with HCl 2.5N	16 cc	16 cc	16 cc	16 cc	16 cc	16 cc
Collect Sr (HCl 2.5N)	6 cc	6 cc	6 cc	6 cc	6 cc	6 cc
Rinse (HCl 6.3N)	4 cc	4 cc	4 cc	4 cc	4 cc	4 cc
Collect REE (HCl 6.3N)	10 cc	10 cc	10 cc	10 cc	10 cc	10 cc
Beakers REE						
Washing						
Sr: 25 cc HCl 6N						
REE: 10 cc HCl 6N						
3 cc H_2O						
Reconditioning						
10 cc HCl 2.5N						
Date:			User:			

c

Columns	1	2	3	4	5	6
Samples						
Beakers						
Load 0.3cc of sample solution						
I rinse (0.5 cc)						
II rinse (0.5 cc)						
Rinse with 0.25 N HCl	8.5 cc	8.5 cc	8.5 cc	8.5 cc	8.5 cc	8.5 cc
Collect Nd with 0.25N HCl	5.75 cc	5.75 cc	5.75 cc	5.75 cc	5.75 cc	5.75 cc
Washing						
11 cc 6.0 N HCl						
Reconditioning						
7 cc 0.25 N HCl						
Date:			User:			

Figure 2. Procedures adopted for chemical separation of **a)** Sr and REE from samples having Sr contents higher than 50 ppm; **b)** Sr and REE from samples having Sr contents lower than 50 ppm; **c)** Nd from the REE fraction.

These columns have been prepared adding cation exchange resin Dowex AG 50 W X-8 (200-400 mesh) conditioned in 2.5N HCl, to fill the column for three quarters of its volume. To calibrate the columns a solution sample of known Sr concentration (0.5 ml of 2.5N HCl containing 50 ppm of Sr) has been loaded on each column. Then, several 0.5 ml aliquots of 2.5N HCl have been loaded, each time collecting the eluted aliquots in different, labeled beakers. Sr content of the solutions collected in each beakers has been measured by atomic absorption spectrophotometry. In this way it has been possible to know for each column the 2.5N HCl volume to be eluted and discarded, and the 2.5N HCl volume, containing most of the Sr fraction, to be eluted and collected into a beaker (Fig. 2a). In order to calibrate the column to separate the REE, 0.5 ml of 2.5N HCl solution containing 50 ppm of Sm and 50 ppm of Nd, has been loaded in each column. The amount of 2.5N HCl, corresponding to that necessary to collect Sr (see calibration scheme Fig. 2a), has been eluted and discarded. Afterwards, several aliquots of 0.5 ml of 6.3N HCl have been eluted and collected in variable, labeled beakers. In order to detect the presence of REE in each eluate, *Eriochrome Black T*, a chemical indicator sensible to metal presence in basic solutions, has been used. The indicator changes to pink in presence of metal ions, and to blue in metal ions-free solutions. Thus, each eluate has been converted to pH 9-10 by adding few drops of 50 % by volume NH_3 solution, and checked for the presence of metal ions by adding few drops of *Eriochrome Black T*. This procedure returned, for each column, the 6.3N HCl volume to be eluted and discarded, and the 6.3N HCl volume containing most of the REE to be eluted and collected into a beaker (Fig. 2a). The same procedure described for calibrating the columns dedicated to high Sr samples has been used for calibrating 6 quartz columns, located under a laminar flow hood, to be used for extracting Sr and REE from samples containing less than 50 ppm of Sr, and from single crystals. The "low-Sr samples" chemical separation scheme is reported in figure 2b.

For separating Nd from the dried REE fractions, through column chromatographic techniques, 0.25N HCl has been used as eluent. Columns for Nd separation are smaller than the Sr/REE ones, with a height of 16 cm, an internal diameter of 0.5 cm, and a 10 ml reservoir. They are filled with Ln Spec$^{®}$, an organic acid $\{[CH_3\ (CH_2)\ 3CH\ (C_2H_5)\ CH_2O]\ 2POOH\}$ adsorbed on 100 mesh Teflon spheres, used as cation exchanger. The calibration has been performed by loading 0.5 ml of a 0.25N HCl solution containing about 50 ppm of Nd into each column. Then, several 0.3 ml aliquots of 0.25N HCl have been eluted, and collected in single beakers. Each eluate has been checked for the presence of Nd by adding drops of *Eriochrome Black T,* after basification to pH 9-10 by using few drops of 50 % by volume NH_3 solution. The resulting procedure of Nd separation is illustrated in Fig. 2c.

1.4 Loading procedure of samples on filament

Once the chemical separation (either Sr or Nd) is completed, a few drops of concentrated HNO_3 are added to the collected fractions, then dried on hot plate to convert chlorides to nitrates. The fractions are then re-dissolved in diluted HNO_3 and loaded on previously degassed Rhenium (Re) filaments, to carry out mass spectrometer analysis. The loading procedure is carried out under a laminar flow hood by using a power supply device (Fig. 3 insert).

Sr loading procedure

The Sr fraction is loaded on Re single filaments. First, it is dissolved in diluted nitric acid (10%) and only a small aliquot (1-2 μl) of the solution is then loaded, in order to have approximately 200ng of Sr on the filament. Two different

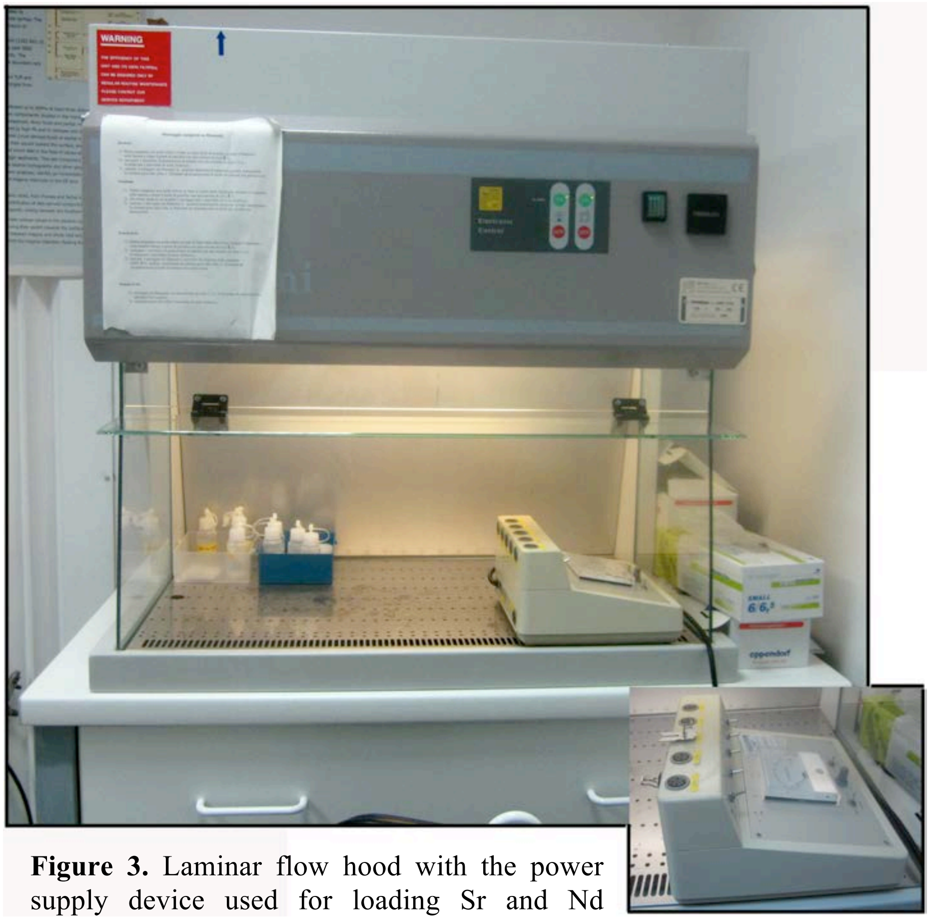


Figure 3. Laminar flow hood with the power supply device used for loading Sr and Nd fractions on single and double Re filaments, respectively.

salts are necessary to paste the Sr fraction on the filament: H_3PO_4 and $TaCl_5$. The loading procedure consists of four steps:

1) load 1 µl of 5 % H_3PO_4 solution on a degassed filament and dry it at 1 A;
2) load 1 µl containing 10 µg of $TaCl_5$ solution on the filament and dry it at 1 A;
3) load the Sr sample in 1 µl of 10% HNO_3 solution on the filament and dry at 1 A;
4) turn up slowly to 2-3 A until burning, and then turn down fast.

Nd loading procedure

The Nd fraction, dissolved in nitric acid as well (usually in 1 or 2 µl of diluted HNO_3), is loaded on a previously degassed Re filament, to be arranged in a double configuration with another, void Re filament in order to optimize thermoionic emission. The loading procedure consists of three steps:

1) load 1 µl containing 10 µg of $TaCl_5$ solution on a degassed filament and dry it at 1 A;
2) load the Nd fraction on the filament and dry it at 1 A;
3) turn up slowly to 2-3 A until burning, and then turn down fast.

1.5 Environmental contamination

All sample preparation procedures unavoidably result in mixing between the element analysed in the sample and the same element occurring in the reagents and laboratory environment. The level of contamination may be determined by performing the entire chemical procedure in the absence of sample, by isotope dilution techniques.

Blank determinations consist in weighting an amount of a spike containing the element to be analysed (available by courtesy of Prof. Riccardo Petrini, University of Pisa), and making the same dissolution and chromatographic separation as for the natural samples and finally measuring its isotopic composition.

Sr Blank contribution in ng has been calculated in the Clean Laboratory by using the following isotope dilution equation:

$$Sr_{blank}\,(g) = P_{Spike}\cdot C_{Sr\text{-}spike*}(Ab^{86}{}_{spike*}\,{}^{84}Sr/{}^{86}Sr_{spike} - Ab^{84}{}_{spike})/(Ab^{84}{}_{nat} - {}^{84}Sr/{}^{86}Sr_{spike}\cdot Ab^{86}{}_{nat})\cdot 8.762,$$

where P_{Spike} is the weight of Spike, $C_{Sr\text{-}spike}$ is the concentration of Sr in the spike, Ab are the isotope abundances in spike and in natural Sr and ${}^{84}Sr/{}^{86}Sr_{spike}$ is the isotopic ratio of the spike. Concentration and mass abundances of the used Sr spike are listed in Table 2. Sr blank, routinely measured in the Clean Laboratory, is of the order of 0.5 ng and 0.08 ng for the "high-Sr" and "low-Sr" samples columns, respectively.

2. The Thermal Ionisation Mass Spectrometer established at the Radiogenic Isotope Laboratory of INGV, Sezione di Napoli-OV

A new generation Thermal Ionisation Mass Spectrometer (TIMS) Finnigan MAT Multicollector Triton TI® (e.g., Wieser and Schwieters, 2005) has been established at the Radiogenic Isotope Laboratory of INGV, Sezione di Napoli-OV, since 2001 (Fig. 4). The instrument has been located in a constant temperature room (24°C) to allow the sophisticated integrated systems and the amplifiers working correctly.

In the Triton TI®, the thermal ionization source is pumped to high vacuum (10^{-7} mbar) with a system consisting of a rotary pump and a turbomolecular pump. It contains a magazine with 21 positions for locating the samples to analyze. They are loaded, in the form of a salt of the element, onto a Re filament, as this element has high work function and low volatility. The filament is heated by an electrical current of several Amperes flowing through the filament to a temperature T sufficient to evaporate the element to be analysed. The resultant ions are accelerated applying a high voltage (10 kV), and are collimated into a tight ion beam applying smaller potentials to a series of slits (source lens), situated between the source and the analyzer magnet. Then ion beam proceeds towards the mass analyser in the analyser tube, pumped at high vacuum (10^{-9} mbar) by ion pumps. Within the analyzer tube, the ion beam is deflected.

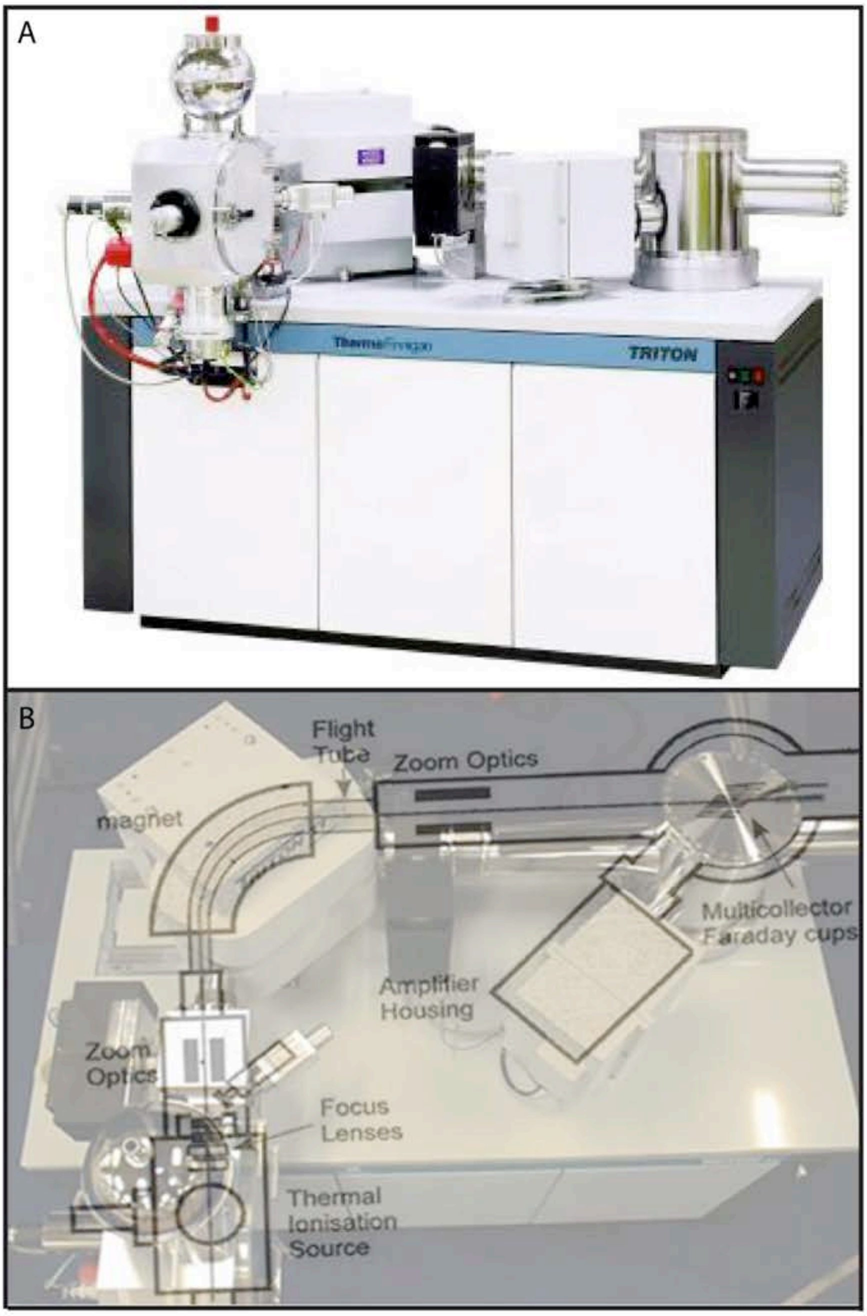


Figure 4. a) Photograph of the Thermal Ionisation Mass Spectrometer (TIMS); b) Schematic representation of the essential components of a TIMS: thermal ionization source, analyzer magnet, detection system, which consists of a cylindrical box which contains the Faraday cups, and amplifier housing. Within the analyzer tube (Flight tube) all ions move from source to detection system.

The calibration of the magnetic field is done by varying opportunely the magnetic field intensity to find the peaks of those elements, surely present on filaments, such as ^{23}Na, ^{39}K, or on standards (^{88}Sr, ^{146}Nd, ^{238}U,ecc.). An example of the calibration curve is shown in Figure 5.

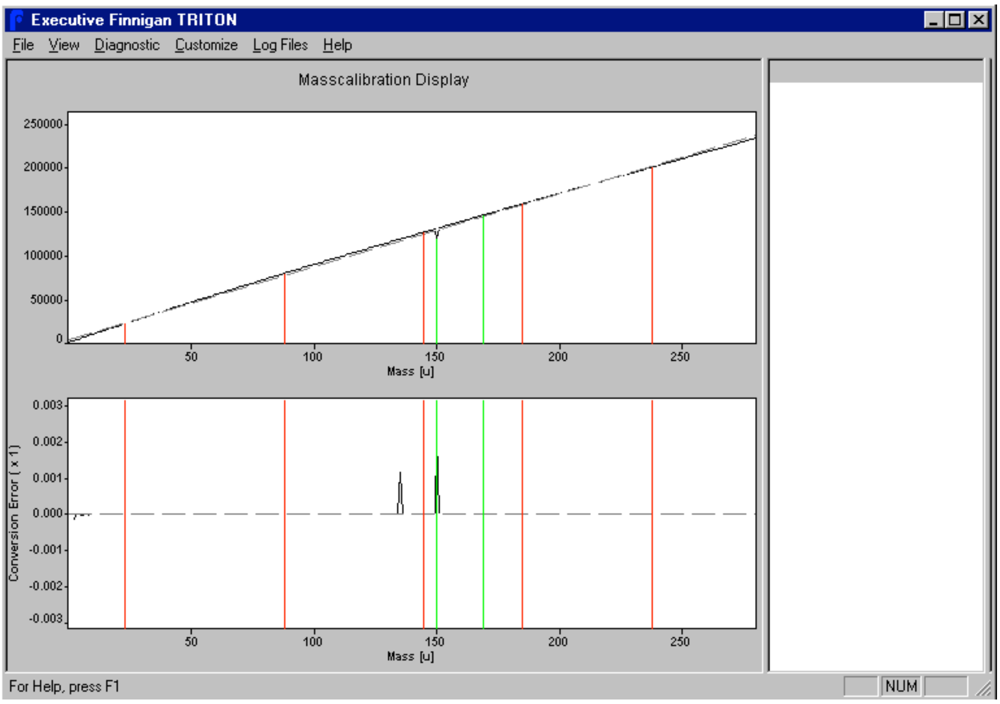


Figure 5. Calibration curve obtained by varying opportunely the magnetic field intensity to find the peaks of elements such as ^{23}Na, ^{39}K, or ^{88}Sr, ^{146}Nd, ^{238}U.

Faraday cups detect the ions as electric charges and have equal response for different ionic masses. The Triton TI® have a multicollector detection system (Fig. 6), consisting in nine collectors, one fixed in the center and other eight placed symmetrically, capable to move respect to the central one with a spatial precision of 10 µm.

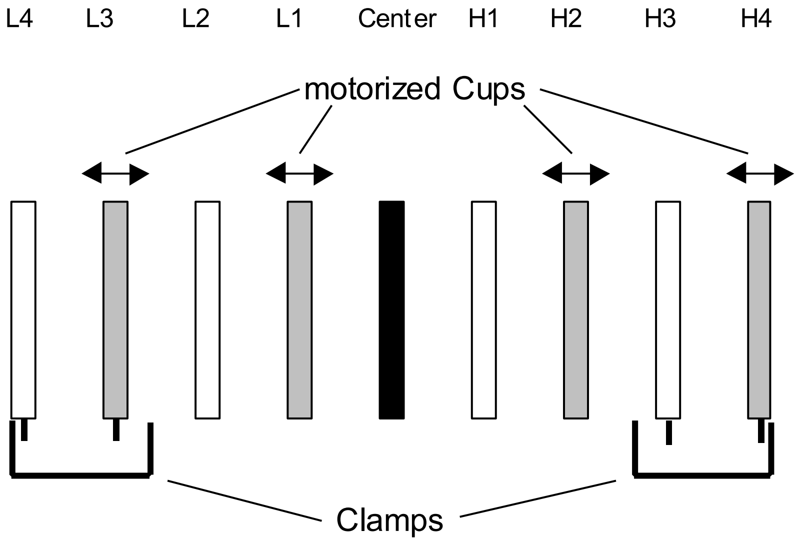


Figure 6. Faraday cup arrangement in the Finnigan™ Triton TI® mass spectrometer.

The multicollector detection system permits two conditions of running measurements: static mode and dynamic mode. In the first one the magnetic field has a specific setting and depends on the element to be analysed. Each isotope of the element is detected at a particular Faraday cup, and up to 9 isotopes can be measured simultaneously. This is the running condition adopted at the Radiogenic Isotope Laboratory for Sr and Nd isotopic ratios determination. It offers three advantages:

- Reduced time of analyses;
- High precision, because Faraday cups can be positioned in the best way to collect ions;
- Constant ratio measurement for increasing or decreasing ion beams intensity, because all isotopic beams are collected together.

For measuring isotope ratios by Triton TI®mass spectrometer, different cup configurations can be used. Their alignment is controlled by the Triton software. Cup configurations shown in Figure 7 are currently used in the Radiogenic Isotope Laboratory. These configurations allow the measured ratios to be corrected for the isobaric interference of ^{87}Rb and ^{144}Sm. This effect is corrected by monitoring ^{85}Rb and ^{147}Sm in case of Sr and Nd isotope ratio determinations, respectively. The example of correction equation for Sr is:

$^{87}Sr_{corr} = {}^{87}Sr_{mis} - ({}^{87}Rb/{}^{85}Rb) \times {}^{85}Rb_{mis}$

where ^{87}Rb/^{85}Rb is the ratio of natural abundances of Rb isotopes. Measured Sr and Nd isotope ratios are also corrected for mass fractionation.

Sr isotopes configuration

Cup	**L4**	**L3**	**L2**	**L1**	**C (Far)**	**H1**	**H2**	**H3**	**H4**
Mass Sr				^{84}Sr	^{85}Rb	^{86}Sr	^{87}Sr	^{88}Sr	

Nd isotopes configuration

Cup	**L4**	**L3**	**L2**	**L1**	**C (Far)**	**H1**	**H2**	**H3**	**H4**
Mass Nd		^{143}Nd	^{144}Nd	^{145}Nd	^{146}Nd	^{147}Sm	^{148}Nd	^{150}Nd	

Figure 7. Cup configurations used for measuring Sr and Nd isotope ratios.

For Sr analyses, fractionation of ^{87}Sr/^{86}Sr is monitored by using the ^{88}Sr/^{86}Sr ratio, since ^{88}Sr and ^{86}Sr are both non radiogenic. The ratio ^{86}Sr/^{88}Sr is constant throughout the Earth and is taken to be 0.1194 by international convention. ^{143}Nd/^{144}Nd isotopic ratios are similarly normalised for fractionation using an internationally agreed value of ^{146}Nd/^{144}Nd = 0.7219.

For example, in order to properly correct for fractionation effects, during the course of the measurement ^{88}Sr/^{86}Sr has to vary in the range 8.33-8.47. The "management software" automatically corrects this ratio according to an exponential law:

$[(A/B)_{mis}/(A/B)_{e.l.}]^{\ln(mC/mD)} = [(C/D)_{mis}/(C/D)_{e.l.}]^{\ln(mA/mB)}$

where e.l. defines normalized ratios with exponential law, A/B and C/D are mean values of measured ratios and m is the mass of the isotope. If the ratio is beyond the aforementioned range, the exponential law is no more able to correct the deviation.

Cycle	Time	146Nd	143Nd/144Nd (1)	146Nd/144Nd (2)	147Sm/144Nd (3)	143Nd/144Nd (4)
139	10:44:37:490	1.0244386e+000	5.1182301e-001	7.2395156e-001	-2.6999985e-006	5.1182330e-001
140	10:44:45:881	1.0224509e+000	5.1177074e-001	7.2391952e-001	4.3384385e-005	5.1176607e-001
141	10:44:54:273	1.0205318e+000	5.1180081e-001	7.2396563e-001	2.2846739e-006	5.1180057e-001
142	10:45:02:664	1.0189642e+000	5.1184996e-001	7.2392241e-001	1.0643965e-005	5.1184882e-001
143	10:45:11:055	1.0171090e+000	5.1180112e-001	7.2395496e-001	8.6075300e-006	5.1180019e-001
144	10:45:19:447	1.0153148e+000	5.1185851e-001	7.2397976e-001	1.9085557e-005	5.1185646e-001
145	10:45:27:838	1.0129688e+000	5.1172677e-001	7.2387124e-001	2.3461129e-005	5.1172424e-001
146	10:45:36:229	1.0106082e+000	5.1186744e-001	7.2393803e-001	3.0429775e-006	5.1186711e-001
147	10:45:44:620	1.0079181e+000	5.1184884e-001	7.2392645e-001	3.2291521e-005	5.1184536e-001
148	10:45:53:012	1.0054299e+000	5.1182135e-001	7.2399140e-001	1.3378395e-005	5.1181991e-001
149	10:46:01:403	1.0026116e+000	5.1177775e-001	7.2391895e-001	1.1754051e-006	5.1177763e-001
150	10:46:09:793	9.9997906e-001	5.1181631e-001	7.2395185e-001	4.1179270e-005	5.1181187e-001
151	10:48:28:404	1.0518788e+000	5.1193396e-001	7.2402647e-001	7.9736403e-006	5.1193310e-001
152	10:48:36:795	1.0477903e+000	5.1184723e-001	7.2396537e-001	-1.1641992e-006	5.1184735e-001
153	10:48:45:186	1.0449509e+000	5.1183737e-001	7.2398123e-001	4.9380990e-006	5.1183684e-001
154	10:48:53:577	1.0414750e+000	5.1183157e-001	7.2401239e-001	1.5816095e-005	5.1182987e-001
155	10:49:01:967	1.0383700e+000	5.1185187e-001	7.2399998e-001	1.7608672e-005	5.1184997e-001
156	10:49:10:358	1.0355002e+000	5.1184899e-001	7.2404516e-001	1.0978218e-005	5.1184781e-001
157	10:49:18:750	1.0326915e+000	5.1187958e-001	7.2406331e-001	8.9937200e-006	5.1187861e-001
158	10:49:27:141	1.0300981e+000	5.1182286e-001	7.2396972e-001	1.8270912e-005	5.1182089e-001
159	10:49:35:532	1.0277196e+000	5.1188214e-001	7.2403228e-001	2.0681916e-006	5.1188192e-001
160	10:49:43:924	1.0245817e+000	5.1180104e-001	7.2392845e-001	9.8192740e-006	5.1179998e-001
161	10:49:52:315	1.0214255e+000	5.1185187e-001	7.2399240e-001	-3.7346146e-006	5.1185227e-001
162	10:50:00:706	1.0187950e+000	5.1189282e-001	7.2405459e-001	5.0765222e-007	5.1189277e-001
163	10:50:09:097	1.0162588e+000	5.1185338e-001	7.2399571e-001	-4.7348172e-006	5.1185389e-001
164	10:50:17:487	1.0135609e+000	5.1191340e-001	7.2408242e-001	8.8142659e-006	5.1191245e-001
165	10:50:25:878	1.0109588e+000	5.1186470e-001	7.2412386e-001	1.6058949e-005	5.1186297e-001
166	10:50:34:271	1.0077298e+000	5.1190903e-001	7.2403744e-001	1.9505523e-005	5.1190692e-001
167	10:50:42:661	1.0050802e+000	5.1191248e-001	7.2404913e-001	-2.1310307e-006	5.1191271e-001
168	10:50:51:052	1.0023579e+000	5.1179183e-001	7.2403744e-001	8.5279637e-006	5.1179091e-001
169	10:50:59:444	9.9944823e-001	5.1192377e-001	7.2405684e-001	2.0074554e-005	5.1192161e-001
170	10:51:07:835	9.9672308e-001	5.1191300e-001	7.2405504e-001	-2.3963049e-006	5.1191326e-001
171	10:51:16:226	9.9419365e-001	5.1189918e-001	7.2409093e-001	1.8961534e-005	5.1189714e-001
172	10:51:24:617	9.9108789e-001	5.1190504e-001	7.2413528e-001	-9.6021882e-007	5.1190514e-001
173	10:51:33:008	9.8741177e-001	5.1185601e-001	7.2405017e-001	2.2165365e-005	5.1185362e-001
174	10:51:41:398	9.8454064e-001	5.1190348e-001	7.2402039e-001	-9.7879930e-006	5.1190454e-001
175	10:51:49:789	9.8200968e-001	5.1187865e-001	7.2408084e-001	3.9013969e-005	5.1187444e-001
***	Cup	C	L3 | L2	C | L2	H1 | L2	L3 | L2
***	Info	tbdgy	ON1e I1 tbdgy - St	O I1 tbdgy - St	ON1e tbdgy - St	ON1e tbdgy - St
***	Mean	9.7895944e-001	5.1184079e-001	7.2364955e-001	1.3601832e-005	5.1183933e-001
***	StdErr (%)	5.0724757e-001	7.1086003e-004	2.7578687e-003	9.1573084e+000	7.1109147e-004
***	StdErr (abs)	4.9657480e-003	3.6384716e-006	1.9957304e-005	1.2455617e-006	3.6396458e-006
***	StdDev (%)	6.7102546e+000	9.3768878e-003	3.6378786e-002	1.2079319e+002	9.3799407e-003
***	StdDev (abs)	6.5690671e-002	4.7994737e-005	2.6325492e-004	1.6430088e-005	4.8010225e-005
***	Valid Values	175(175)	174(175)	174(175)	174(175)	174(175)

Figure 8. Example of acquired isotopic ratios.

3. Sr and Nd Standard measurements

The running conditions for determining the isotope composition of natural samples have been tested by measuring the isotope ratios of reference samples. The National Institute of Standards and Technology (NIST) for USA or the Community Bureau of Reference (BCR) for European Community give reference material of known Sr and Nd isotope composition. Sr and Nd standard samples are routinely measured together with natural samples.

From 2001 to 2013 we systematically measured $^{87}Sr/^{86}Sr$ of the NIST SRM 987 and $^{143}Nd/^{144}Nd$ of the Nd La Jolla standards, respectively. The recommended values for $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ are 0.71025 and 0.51185, respectively (Thirlwall, 1991).

In the Radiogenic Isotope Laboratory measurements are performed with ^{88}Sr and ^{144}Nd signals of ca. 6-8 Volt and 2-3 Volt, and integrating time of 16 and 8 seconds, respectively. The measured isotopic ratios are mean values of 175 ratios, divided in 5 blocks of 35 measures (Fig. 8), because a large number of acquired ratios gives more confidence on the mean value reliability. This confidence is expressed as mean standard error (se), equal to $\sigma/\sqrt{n}$. We generally report the analytical error as ± 2 times the standard error (2se).

Analyses made on the Sr and Nd standards in the time interval from December 2011 to July 2012 are plotted in the figures 9a, b, respectively. Mean values of the measured isotope ratios are 0.710215 ($2\sigma = 1.4x\ 10^{-5}$, N= 50), and 0.511843 ($2\sigma= 1.5x\ 10^{-5}$, N= 27). The mean values of standard isotopic ratios are calculated considering all measurements performed in the time span during which a set of natural samples is analysed (as for example the one here reported from December 2011 to July 2012), while the error is expressed as 2σ, where σ is the standard deviation among all measurements performed in that time span, and represents the external reproducibility [Goldstein et al., 2003].

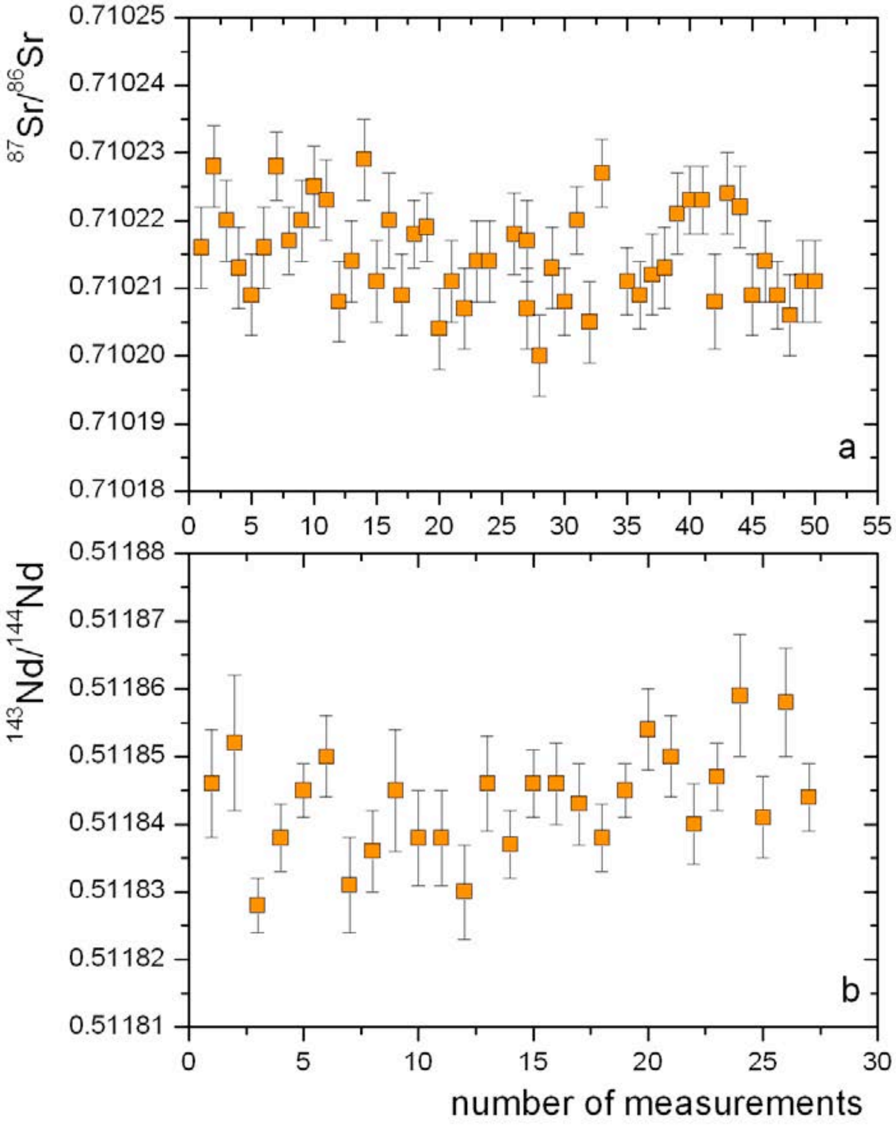


Figure 9. a) $^{87}Sr/^{86}Sr$ (NIST SRM 987) and b) $^{143}Nd/^{144}Nd$ (Nd La Jolla) ratios measured from December 2011 to July 2012.

4. Conclusions

A new generation Thermal Ionisation Mass Spectrometer (ThermoFinnigan Triton-TI® Mass Spectrometer) for radiogenic isotope analyses has been set up at the Radiogenic Isotope Laboratory of the INGV, Sezione di Napoli-OV since 2000. The procedures for extracting Sr and Nd from natural samples and for measuring Sr and Nd isotope compositions of natural and reference samples have been set up. Since the establishment of the Radiogenic Isotope Laboratory data on samples from different geodynamic settings have been acquired and have been object of dissertations, PhD thesis and publications on JRC journals.

The detect isotopic variations have permitted to contribute to the still open scientific debate on topics such as genesis, architecture and temporal evolution of magmatic systems feeding quiescent and active volcanoes. Detailed investigations have been performed on volcanic rocks from Campi Flegrei, Ischia and Procida of the Phlegraean Volcanic District, in which magmatic feeding system processes such as fractional crystallization, crustal contamination and mingling/mixing among distinct magmas/magmatic components have been invoked to explain, at least in part, the isotopic variability of the erupted melts [Arienzo et al., 2009, 2010, 2011; Civetta et al., 2004a, 2007; D'Antonio et al., 2007, 2013; De Campos et al., 2008; Di Renzo et al., 2011; Di Vito et al., 2011; Pabst et al., 2008]. Geochemical and isotopical data (Sr, Nd, Pb, B) acquired on volcanics from Mt. Vesuvius, together with the available literature data, allowed contributing to the reconstruction of the complex history of the Somma-Vesuvius magmatic system [Aulinas at al., 2008; Civetta et al., 2004b; Di Renzo, 2005; Di Renzo et al., 2007].

In recent papers Sr and Nd isotope compositions have been proposed as useful tools for correlating proximal and distal tephra erupted from Colli Albani [Gaeta et al., 2011; Giaccio et al., 2013]. Petrology and geochemistry of West Philippine Basin basalts and early Palau-Kyushu arc volcanic clasts from ODP Leg 195 (Site 1201D), as well as the geochemistry of serpentinized peridotites from the Mariana Forearc Conical Seamount (ODP Leg 125) have been studied in order to highlight the role of the shallow slab fluid release across and along the Mariana arc-basin system [D'Antonio et al., 2006; Savov et al., 2005, 2006, 2007]. Furthermore, by performing geochemical investigation on products from Mt. Etna and Stromboli volcanoes, from the Ethiopian rift volcanoes and from Piton de la Fournaise volcano, it has been possible to contribute in deepen the current knowledge on the geochemical and isotopic variations of the feeding system of these volcanoes [Correale et al., 2012; Corsaro et al., 2009, 2013; Landi et al., 2009; Pompilio et al., 2012; Martelli et al., submitted; Giordano et al., in press; Di Muro et al., submitted].

The INGV-OV Radiogenic Isotope Laboratory has also performed determinations of Sr and Nd isotope compositions of the ~~rocks~~ lavas extruded by the Etna and Stromboli eruptions since 2007. This work has been carried out, in collaboration with colleagues of the INGV-Sezione di Catania (Dr. Rosa Anna Corsaro) in the framework of the monitoring activity of these active volcanoes. Results for Etna suggest the arrival of a new magma more enriched in radiogenic Sr since year 2011. A summary of the monitoring activity is provided to the Civil Protection (Relazioni di monitoraggio).

In conclusion, several papers have been published in international journals testifying our efforts in producing high quality data to improve the current knowledge on magma system processes and to help forecasting future behaviors of active volcanoes (see references list).

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