First coupled Sr and Pb isotopic measurements in volcanic gas condensates and groundwaters of Vulcano Island (Italy)

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[1] For the first time, coupled Sr-Pb concentrations and isotopic compositions have been measured on four crater fumaroles and six groundwaters sampled between 1999 and 2001 at Vulcano Island, southern Italy. Sr concentrations and isotopic compositions of groundwaters show that the Sr budget results mainly from the leaching of volcanic rock by groundwaters. Leaching intensity is controlled by the variable dissolution of volcanic gases into shallow aquifers. The data do not reveal any influence of seawater except at one coastal site. Low Pb concentrations together with calculated saturation indexes with respect to mineral phases indicate that Pb content in groundwaters is strongly influenced by adsorption and/or precipitation processes. Pb isotopic ratios of two steam-heated waters display a clear anthropized meteoric water signature, suggesting gas dissolution or wall rock alteration to be a negligible process for this element in this particular context. Low ($\approx$0.5) and high ($10^2 - 10^3$) enrichment factors were calculated for Sr and Pb, respectively, indicating their refractory and volatile behavior in volcanic gases. Most of the gas samples display Sr and Pb isotopic ratios similar to parent rocks. These data suggest that Sr is mainly derived from wall rock or particle contamination during gas ascent, whereas Pb results mainly from magma degassing. However, two gas condensates collected from two different fumarolic vents and at different periods show a dramatic Pb and Sr isotopic shift with a clear atmospheric/anthropogenic signature. Episodic permeability variations of the volcanic structure, probably arising from microseismicity swarms, changes of local stress field, and migration of self-sealing processes lead to changing interactions between freshly infiltrated meteoric water and volcanic gases that temporarily modify the trace metal signature of the fumarolic gas.

1. Introduction

[2] Active hydro-volcanic systems are sites of complex interactions between magmatic gases, wall rock and aquifers fed by meteoric water and/or seawater. These interactions are usually investigated by using classical parameters such as temperature, major and trace compounds chemistry, oxygen fugacity, and δD, $^3He/^4He$, $\delta^{13}C$ or $\delta^{18}O$ isotopic compositions applied to fumarolic gases and shallow groundwaters [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Capasso et al.*, 1999; *Chiodini et al.*, 1993; *Harris and Maciejewski*, 2000; *Quisefit et al.*, 1989; *Symonds et al.*, 1987, 1996; *Taran et al.*, 1995; *Tedesco*, 1997; *Tedesco et al.*, 1995]. More recently, boron and sulfur isotope compositions were also used to constrain these interactions [*Cortecci et al.*, 2001; *Leeman et al.*, 2005; *Pennisi et al.*, 2000]. Using these parameters provide insights on source effects, mixing and alteration processes, possibly interpreted in terms of volcanic/magmatic processes.

[3] Volcanic exhalations are also a source of heavy metals to the atmosphere [*Dongarra and Varrica*, 1998; *Ferrara et al.*, 1995; *Piccardi et al.*, 1979; *Quisefit et al.*, 1989; *Symonds et al.*, 1987; *Taran et al.*, 1995; *Toutain et al.*, 2003; *Vallelonga and Mather*, 2003]. Gases emitted through occasional eruptions or quiescent degassing are mainly composed of H_2O and CO_2 steam with minor amounts of H_2S, SO_2, HCl, HF and trace gases. Gases contain also metallic trace elements (MTE), that are more or less enriched with respect to the magma [*Symonds et al.*, 1987; *Taran et al.*, 1995; *Toutain et al.*, 2003] as evidenced by highly contrasted Enrichment Factors (EF) defined as follows:

$$EF_X = \left[(X/X_R)_g / (X/X_R)_r \right]$$

for an element X, g and r being the gas condensate sample and the rock, respectively, X_R corresponding to an element displaying a refractory behavior with respect to volcanic fluids. [*Quisefit et al.*, 1989]. High EF elements (Se, Re, Bi, Te, As, Cd, Pb, Tl, among others) are volatile elements mainly produced by selective distillation at the magma chamber level. Low EF elements (Sr, Al, Fe, Mg, Mn among others) are refractory elements mainly present in the gas phase through wall rock and or ash alteration processes in highly acidic context. By coupling the study of both a refractory and a volatile element, one should make available a powerful tool to discriminate processes that contribute to MTE transport in the volcanic pile.

[4] As Sr and Pb isotopes do not fractionate measurably in nature [*Barbieri and Morotti*, 2003; *Bollhöfer and Rosman*, 2001], their variations are controlled by radioactive processes only and Sr and Pb isotopic compositions are powerful geochemical tracers to identify natural, anthropogenic or atmospheric sources [*Bollhöfer and Rosman*, 2001; *Freydier and Viers*, 2003; *Monna et al.*, 1997, 1999], to study water rock interactions [*Barbieri and Morotti*, 2003; *Goff et al.*, 1991; *Möller et al.*, 2004; *Pennisi et al.*, 2000] or to describe magmatic evolution [*Clocchiatti et al.*, 1994; *De Astis et al.*, 1997, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003]. However, probably as the result of sampling or analytical difficulties, and because most of the metals (including Pb) are strongly partitioned in the particulate phase of volcanic plumes [*Hinkley*, 1991], Sr and Pb isotopic data on volcanic gases totally lack. Only few Pb isotopic data have been recently published on volcanic aerosols [*Monna et al.*, 1999; *Vallelonga and Mather*, 2003] and secondary solid phases [*Ferrara et al.*, 1995]. On the contrary, in thermal waters, Sr and Pb isotopes are common tools for sources identifications and characterization of water-rock interactions [*Barbieri and Morotti*, 2003; *Goff et al.*, 1991; *Möller et al.*, 2004; *Pennisi et al.*, 2000].

[5] In this work, we propose the first coupled isotopic study of Sr and Pb in fumarolic gases and thermal waters from Vulcano Island. Data are processed together with rock data [*Clocchiatti et al.*, 1994; *De Astis et al.*, 1997, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003] and local anthropogenic/atmospheric signatures [*Monna et al.*, 1999]. The aim of this work is to document the isotopic variability in the hydro-volcanic environment, to identify sources of elements and to constrain processes that control Sr and Pb transfers.

2. Geological Setting and Hydrovolcanic Context

[6] Vulcano is the southernmost island of the Aeolian volcanic Archipelago, southern Tyrrhenian Sea (Figure 1). Its magmatic activity began in the upper Pleistocene with leucitic tephrites to highly potassic trachytes, followed in historic time by alkali-rhyolitic obsidian [*Keller*, 1980]. Since the last eruption in 1888–1890, the volcanic activity is restricted to (1) a wide fumarolic field located on
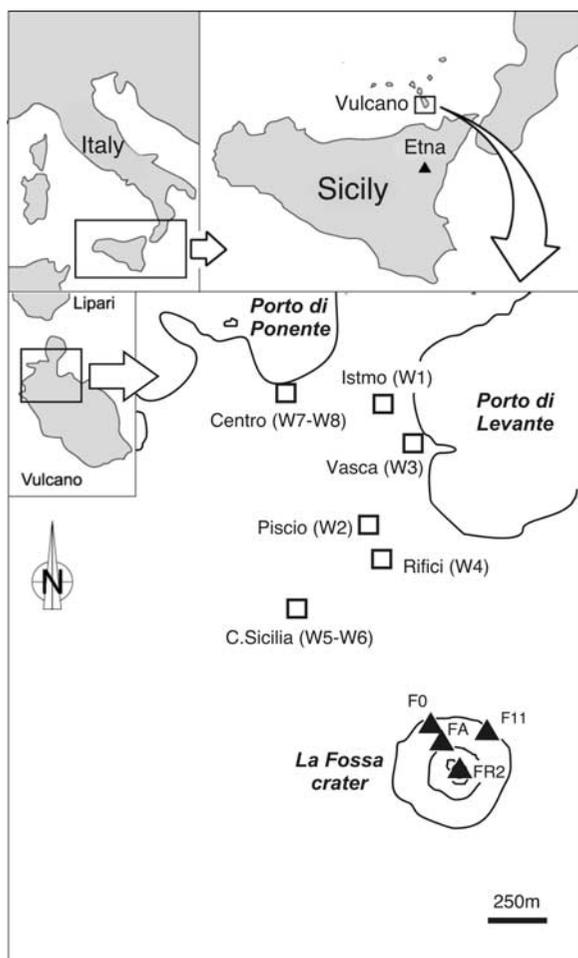
Figure 1. Geographic location of Vulcano Island and sampling sites, modified from *Bolognesi and D'Amore* [1993]. Groundwater (square plot) and fumarole (triangle plot) sampling sites are shown.

the rim and the internal wall of the "La Fossa" crater (391 m a.s.l.), (2) low temperature fumaroles (close to 100°C) located on the "Porto di Levante" beach, (3) CO_2-dominated soil gas emissions in the Vulcano porto area and around the "La Fossa" crater edifice, and (4) thermomineral waters related to an active hydrothermal system and accessible from shallow water wells. During the last century, the fumarolic field of "La Fossa" crater has displayed wide variations in outlet temperature (from 200°C to 700°C) and gas composition [*Barbieri et al.*, 1991; *Harris and Maciejewski*, 2000]. Fluctuations of the size and location of fumarolic vents have also been reported [*Harris and Maciejewski*, 2000] and interpreted in terms of variable magma degassing generating permeability modifications of the volcanic edifice by fracturation processes and self-sealing of the fumarolic conducts.

[7] Previous studies display chemical and light stable isotope evidences that shallow waters and fumarolic gases compositions result from multiple interactions between magmatic, hydrothermal, meteoric and seawater components [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Capasso et al.*, 1991, 1992, 1999, 2001; *Cortecci et al.*, 2001; *Dongarra et al.*, 1988; *Leeman et al.*, 2005; *Martini*, 1980; *Panichi and Noto*, 1992]. Seismic events, leading to variable fracture permeability, are supposed to modulate mixing processes between geothermal waters, shallow thermal waters and ascending magmatic vapor [*Bolognesi and D'Amore*, 1993]. The involvement of seawater in the hydrothermal system of Vulcano Island remains a controversial question [*Bolognesi*, 1996; *Chiodini et al.*, 1995; *Cortecci et al.*, 2001; *Leeman et al.*, 2005]. Seawater signature modified by wall rock interactions seems obvious in crater-rim fumaroles [*Leeman et al.*, 2005; *Panichi and Noto*, 1992] whereas the contribution of seawater to the shallow aquifers appears unlikely except for selected samples close to sea-side [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Cortecci et al.*, 2001].

3. Sampling Techniques

[8] Four crater fumaroles and waters from six wells were sampled between 1999 and 2001 (Figure 1). Fumarolic gases were channeled through a silica tube to an acetone-cooled condenser [*Chevrier and Le Guern*, 1982] allowing the fast condensation of water, acid gases and associated trace elements. In order to ensure a continuous flow of gas, a weak and constant aspiration was applied with a hand-pump. Gas condensates were sampled from F11 (G1, G2, G3 samples), FA (G4, G5 samples), F0 (G6, G7, G8 samples) and FR2 (G9 sample) fumarolic vents.

[9] Water samples were filtered in the field through 0.2 μm Millipore filters, stored in suprapur HBr pre-washed Teflon bottles and acidified with suprapur HNO_3 to avoid Sr and Pb adsorption on bottles walls. A sampling and filtration blank was made with ultra-pure water. Waters were sampled from the following wells: Istmo (W1 sample), Piscio (W2 sample), Vasca (W3 sample), Rifici (W4 sample), C.Sicilia (W5, W6 samples) and Centro (W7, W8 samples).

4. Analytical Methods

[10] Temperature, pH and redox potential (Eh) were measured directly in the field. Alkalinity

was obtained by titration with 0.01N HCl. SO_4^{2-}, Cl^- and F^- concentrations were measured by High Pressure Liquid Chromatography (DX 300, Dionex). Na, K, Ca and Mg concentrations were determined by Atomic Adsorption (5100 ZL, Perkin Elmer SCIEX). Sr and Pb abundances were measured using a quadrupole-based ICP-MS (Elan 6000, Perkin-Elmer SCIEX). Accuracy and precision of the measurements were controlled by analyzing SLRS-4 certified reference material. Analytical errors are in the range of 5–10%.

[11] The amount of gas condensate and water samples needed for Sr and Pb isotopic measurements was calculated from Sr and Pb concentrations and evaporated. The solid deposits were submitted to acid digestion (HF + HNO_3), oxidation (H_2O_2) and dried at $50°C$. The final deposits were then dissolved with 0.5 mL of suprapur 2N HNO_3 and centrifuged before chemical extraction. Each dissolution was performed using ultrasonic agitation. The Sr and Pb chemical separation was on polypropylen columns containing 150 μl of Sr-spec resin, following the protocol described by *Deniel and Pin* [2001]. Blank contributions with respect to the total amount of sample analyzed were generally <0.25%. Higher blank contributions are discussed later.

[12] Sr and Pb isotopic compositions were measured using a Thermal-Ionization Mass Spectrometer (Finnigan MAT 261). Pb was loaded on a double Re filament using the silica gel/phosphoric acid loading technique. Sr was loaded on a single W filament together with "Ta-activator." Regular measurement of NBS-981 Pb standard allowed the correction of the Pb isotopic data for mass fractionation (1.30 ± 0.05‰ per amu) using a linear law [*Doucelance and Manhès*, 2001]. For Sr, regular measurement of NBS-987 Sr standard was used to monitor accuracy. Sr isotopic ratios were normalized to $^{88}Sr/^{86}Sr = 0.1194$. Duplicates of four waters (W2, W4, W5, W8) and one fumarole (G3) show good reproducibility and confirm the significance of analytical data.

4.1. Blank Contributions

[13] The blank of the bulk procedure (dissolution + chemical extraction) was measured by ICP-MS for each set of eight samples. The mean values obtained were 0.45 ng and 0.92 ng for Sr and Pb, respectively. For some samples, Sr or Pb blank contribution appears to be potentially significant (i.e., from 0.25% to 5.9%) with respect to the total amount of element analyzed. This is due to the

limited quantities of sample available and to the low Sr and/or Pb concentrations observed in some cases. In order to evaluate the impact of the blanks on our isotopic data, binary mixtures calculations were performed on the basis of the assumption that the total amount of the element analyzed was a combination of blank and sample contribution. Sr-Spec procedural blanks were analyzed by TIMS for their Sr isotopic composition by *Dessert* [2002] at the LMTG, Toulouse. As our analyses were performed in nearly similar conditions (laboratory, reagents, material), the $^{87}Sr/^{86}Sr$ blank value = 0.72108 ± 0.00008 determined by *Dessert* [2002] appears to be suitable for our blank impact calculations. No isotopic compositions of Sr-spec procedural blanks were available for Pb. Moreover, Pb blanks display a high variability between the different chemical extractions (from 0.2 ng to 1.9 ng). This phenomenon was ascribed to variable atmospheric contamination during the chemical procedure and Pb blank was then supposed to result mainly from this source. As a consequence, the Pb isotopic composition of Toulouse airborne ($^{206}Pb/^{207}Pb = 1.1042 ± 0.0001$; $^{208}Pb/^{206}Pb = 2.1563 ± 0.0004$, station 6, ORAMIP) analyzed by *Monna et al.* [1997] was used for the calculation and all isotopic data associated with blank contribution > 0.25% were corrected by this method. The maximum Sr blank contribution (5.9%) was observed for sample G7 whereas the maximum Pb blank contribution (3.6%) was observed in W2 and W3 samples. Maximum corrections applied correspond to 0.1% for $^{87}Sr/^{86}Sr$ ratio of G7 sample, and to 0.16% and 0.085% of W3 $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotopic ratios, respectively. The minimum corrections applied correspond to 0.006% of the G3 $^{87}Sr/^{86}Sr$ isotopic ratio and to 0.15% to 0.08% of G4 $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotopic ratios, respectively. Such corrections have no significant implication on our interpretations of Sr and Pb isotopic compositions.

5. Results and Discussion

5.1. Thermomineral Waters

5.1.1. Major Element Geochemistry

[14] Sampling temperatures, pH and Eh vary between 21.2 to $81°C$, 1.15 to 7.62 and −361 to 194 mV, respectively (Table 1). The major elements geochemistry of Vulcano groundwaters is extensively described in literature [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993; *Capasso et al.*, 2001; *Cortecci et al.*, 2001]. Our major ele-

Table 1. Major Element Composition, T, pH, Eh, and Total Dissolved Solids in Vulcano Island Groundwaters[a]

| Water Well	Number	Date	T	pH	Eh	SO_4	Cl	F	Alk	Na	K	Ca	Mg	TDS
Chloride-rich waters														
Istmo	W1	24.02.2001	61.0	5.7	−361	2863	19834	2	694	11214	655	600	1341	35862
Steam-heated waters														
Piscio	W2	24.02.2001	27.3	7.1	194	1713	287	4	357	383	152	438	61	3333
Vasca	W3	24.02.2001	81.0	1.1	−47	8210	1511	7	0	1071	379	255	180	11433
Rifici	W4	24.02.2001	31.0	6.7	186	1787	430	3	409	314	161	602	89	3705
Volcanic groundwaters														
C.Sicilia	W5	24.02.2001	49.5	7.6	161	1704	2084	9	411	1656	627	140	88	6631
C.Sicilia	W6	18.05.1999	56.4	7.5	n.d.	1962	1788	8	390	1469	463	95	71	6176
Shallow groundwaters														
Centro	W7	24.02.2001	21.2	6.9	33	328	411	14	405	348	90	88	32	1685
Centro	W8	20.05.1999	22.0	6.7	n.d.	418	366	13	210	352	80	88	33	1527

[a] Units: major element composition, mg/kg; T, °C; Eh, mV; Total Dissolved Solids (TDS), mg/kg. n.d. stands for nondetermined. Sampling dates are also shown.

ments data presented are in agreement with previous studies. Therefore, in order to avoid redundancy, only general points will be presented. Sampled waters observed in classical anionic triangular plot (Figure 2) are far from the "mature water" field defined by *Giggenbach* [1988]. This indicates that Vulcano groundwaters are far from equilibrium with their host rocks. Following *Aiuppa et al.* [2000], Vulcano groundwaters can be classified in four groups:

[15] W1 water, sampled at the sea-side (Figure 1) can be classified as a chloride-rich water. W1 displays the highest Total Dissolved Solids (TDS = 35862 mg/kg) and lowest Eh (−361 mV) as the result of seawater contribution and bubbling of reducing gases (CH_4, H_2S).

[16] W2, W3 and W4 waters were sampled between the coastal area and the volcanic edifice (Figure 1). Their anion contents (Figure 2) correspond to the steam-heated water group. These waters are supposed to result from the interaction of shallow groundwaters of meteoric origin and H_2S-rich geothermal steam released from a deep (≈200 m) boiling geothermal aquifer fed by ascending volcanic gases. This hypothesis is actually supported by geothermal explorative drillings as
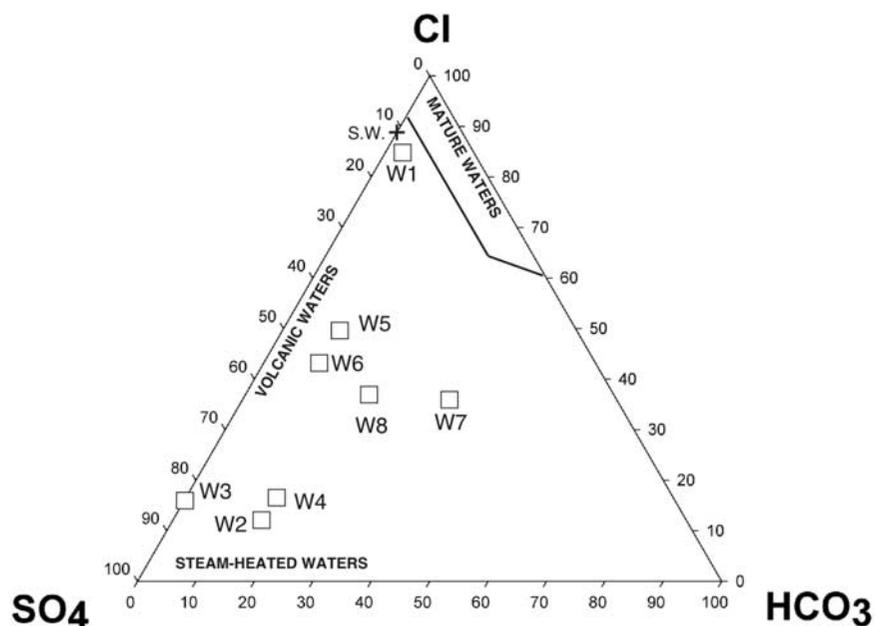
Figure 2. Ternary plot (Cl, SO_4, HCO_3) for thermomineral waters of Vulcano Island.

Table 2. Sr and Pb Concentrations and Isotopic Compositions of Vulcano Island Groundwaters[a]

Number	Sr	Pb	$^{87}Sr/^{86}Sr$	2 S.D	$^{206}Pb/^{207}Pb$	2 S.D	$^{208}Pb/^{206}Pb$	2 S.D	$^{206}Pb/^{204}Pb$	2 S.D
W1	9731.8	0.78	0.70799	0.00001						
W2	635.9	5.4	0.70474	0.00001	1.1437[b]	0.0009[b]	2.1184[b]	0.0013[b]	17.750[b]	0.026[b]
Duplicate			0.70473	0.00001						
W3	3710.2	89.6	0.70516	0.00001	1.1576[b]	0.0004[b]	2.1056[b]	0.0016[b]	18.017[b]	0.018[b]
W4	1106.7	3.0	0.70466	0.00001						
Duplicate			0.70466	0.00001						
W5	3608.2	0.84	0.70462	0.00001						
Duplicate			0.70461	0.00001						
W6	2154.2	1.3	0.70463	0.00001						
W7	6.7	0.15	0.70619[b]	0.00001[b]						
W8	4.4	0.18	0.70601[b]	0.00001[b]						
Duplicate			0.70616	0.00001						

[a] Sr and Pb concentrations are in μg/kg.
[b] Results corrected for blank contribution (see text).

reported by *Sommaruga* [1984]. An intense interaction of geothermal steam with W3 aquifer, leading to the oxidation of H_2S to H_2SO_4, is likely to be responsible of the low pH, low Eh, high sulfate and high TDS value of this sample.

[17] W5 and W6 waters were sampled close to the volcanic edifice (Figure 1) and fall in the compositional field of volcanic waters (Figure 2), also named chloride-sulfate groundwaters or magmatic waters [*Aiuppa et al.*, 2000; *Bolognesi and D'Amore*, 1993]. As described in these studies, these groundwaters result from a mixing be-

tween meteoric water and HCl/H_2SO_4 condensates of volcanic origin and subsequent water-rock interaction.

[18] W7 and W8 were sampled far from the volcanic edifice, close to the "Porto di Ponente area" (Figure 1). These waters can be classified as shallow groundwaters because of their low TDS samples ascribed to the meteoric recharge.

[19] When plotted in the classical *Giggenbach* [1988] Na, K, Mg triangular diagram, most of the

Table 3. Main Sr and Pb Chemical Species in 2001 Vulcano Island Groundwaters[a]

	W1	W2	W3	W4	W5	W7
Aqueous Species, μg/kg						
Sr^{2+}	8521	424	3650	761	2654	5.7
$SrCl^+$	1698	1.2	84	3.3	61	<0.1
$SrSO_4$	<0.1	439	<0.1	717	1868	1.9
Pb^{2+}	<0.1	1	52	1.2	0.05	0.03
$PbCl_2$	0.46	<0.1	6	<0.1	<0.01	<0.01
$PbCl^+$	0.3	0.1	38	0.2	0.04	<0.01
$PbCl_3^-$	0.14	<0.1	<0.1	<0.1	<0.01	<0.01
$PbCO_3$	<0.1	5.4	<0.1	2	0.9	0.14
Mineral Phase Saturation Indexes, log(SI)						
Strontium minerals						
SrF_2	−4.5	−4.7	<−5	−4.7	−3.3	<−5
Strontianite ($SrCO_3$)	<−5	−0.59	<−5	−0.84	0.78	−2.56
Celestite ($SrSO_4$)	<−5	−2.25	<−5	−2	−1.46	−4.6
Lead minerals						
Cerussite ($PbCO_3$)	<−5	−0.74	<−5	−1.19	−1.65	−2.3
Galena (PbS)	6.3	<−5	0.27	<−5	<−5	<−5
Pb	−2.8	<−5	<−5	<−5	<−5	<−5
Alamosite ($PbSiO_3$)	<−5	−2.7	<−5	−3.4	−2.9	−4.9
Anglesite ($PbSO_4$)	<−5	−3	<−5	−3	−4.5	−5
Paralauriaunite (PbCl(OH))	<−5	−4	<−5	−4.1	−4	<−5
Hydrocerussite ($Pb_3(CO_3)_2(OH)_2$)	<−5	−4.1	<−5	<−5	<−5	<−5
Lanarkite ($Pb_2(SO_4)O$)	<−5	−4.8	<−5	<−5	<−5	<−5

[a] Calculated saturation indexes with respect to Sr and Pb mineral phases (log(SI) > −5) are also shown.

thermal waters fall in the field of immature waters along a line characteristic of the isochemical rock dissolution [*Bolognesi and D'Amore*, 1993; *Capasso et al.*, 2001; *Cortecci et al.*, 2001]. This confirms the observation previously made with the anionic triangular diagram (Figure 2) which evidence that waters are far from thermodynamical equilibrium with the host rocks.

5.1.2. Sr and Pb Concentrations and Aqueous Speciation

[20] As shown in Table 2, Sr content ranges from 4.4 to 9731.8 μg/kg, whereas Pb is considerably less abundant with concentrations from 0.15 to 89.6 μg/kg. These values are similar to previous studies [*Aiuppa et al.*, 2000; *Cellini Legittimo et al.*, 1980]. Thermodynamical modeling of our samples was performed with the CHESS 3.0 software program [*Van der Lee and De Windt*, 2000] with T°C, pH, Eh, major element and Sr, Pb concentrations as inputs. This software was used for the determination of the aqueous elemental speciation and for the calculation of saturation indexes (SI) with respect to solid phases with the aim to determine the influence of mineral precipitation to the Sr, Pb content in groundwaters. The results are reported in Table 3, and show that Sr aqueous chemistry in groundwaters is dominated by Sr^{2+} free ion and sulfate complexes, whereas the most abundant Pb species are respectively $PbCO_3$ and Pb^{2+} free ion. However, in the case of high Cl concentrations and/or reducing environment (i.e., W1 and W3 samples), chloride complexes become significant for Sr ($SrCl^+$) and Pb ($PbCl_2$, $PbCl^+$, $PbCl_3^-$) and even dominant for lead in W1 sample which presents the highest Cl concentration and the lowest Eh. Saturation indexes (SI) with respect to mineral phases show that Sr contents in Vulcano groundwaters can be controlled by carbonate mineral precipitation in oxidizing environment. Indeed, $SrCO_3$ was found to be supersaturated in W5 sample and close to equilibrium values for W2 and W4 samples. In reducing and/or low pH environment (i.e., W1 and W3 samples) sulfide mineral precipitations are possible for Pb.

[21] Major mineral phases (silica, carbonates, sulfates and fluorides minerals) are close to equilibrium or supersaturated. We did not calculate the saturation indexes for clay minerals because of the poor quality of the relevant thermodynamic data, but it is clear that they dominate the alteration facies at least for the more acidic fluids. In any case, this short thermody-

namic analysis indicates that adsorption on and/or coprecipitation with these minerals have also to be considered as partially influencing the trace metals abundances in Vulcano groundwaters and might be responsible of the low Pb contents measured in our samples.

5.1.3. Sr and Pb Isotopic Compositions

[22] Sr concentrations and isotopic compositions of Vulcano groundwaters are displayed in Table 2. In Figure 3, 87Sr/86Sr ratios are plotted versus Sr concentrations, together with the seawater (SW) value (Sr = 8100 μg/g; $^{87}Sr/^{86}Sr$ = 0.70918) derived from the study of Etna groundwaters by *Pennisi et al.* [2000]. In meteoric waters (MW), Sr concentrations and isotopic compositions fluctuate accordingly to the variable aerosol sources (sea-salt, soil dust, biological or anthropogenic emissions). *Pennisi et al.* [2000] assigned a 10 μg/kg concentration and the typical $^{87}Sr/^{86}Sr$ isotopic ratios of seawater to their hypothetical meteoric water end-member. However, *Negrel and Roy* [1998] obtained Sr contents as low as 0.35 μg/kg in Massif Central rainwaters. North African aerosols might also influence the Vulcano's rainwater budget [*Monna et al.*, 1999]. Saharan dust [*Krom et al.*, 1999] displays $^{87}Sr/^{86}Sr$ isotopic ratios ranging from 0.7160 to 0.7192. Concerning southern Europe, *Grousset et al.* [1998] have measured $^{87}Sr/^{86}Sr$ isotopic ratios in Corsican aerosols and obtained values ranging from 0.71925 to 0.72451. This shows that direct measurements of Vulcano rainwater are required to characterize more precisely the Sr concentrations and isotopic compositions of MW in this area. As a consequence, MW water possible values are represented as a range in Figure 3, with Sr concentrations ranging from 0.35 to 10 μg/kg and a minimum $^{87}Sr/^{86}Sr$ ratio corresponding to the SW value from *Pennisi et al.* [2000]. The rock values, selected from literature data [*Clocchiatti et al.*, 1994; *De Astis et al.*, 1997, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003] are also presented in Figure 3. The lower rock isotopic value corresponds to sample VL229/1a+b from *De Astis et al.* [1997] displaying a $^{87}Sr/^{86}Sr$ = 0.70412 whereas the higher value corresponds to sample VL90/3La from *De Astis et al.* [2000] with a $^{87}Sr/^{86}Sr$ = 0.70588.

[23] In Figure 3, W1 sample display a higher Sr content than SW and a $^{87}Sr/^{86}Sr$ ratio between the higher Vulcano rock signature
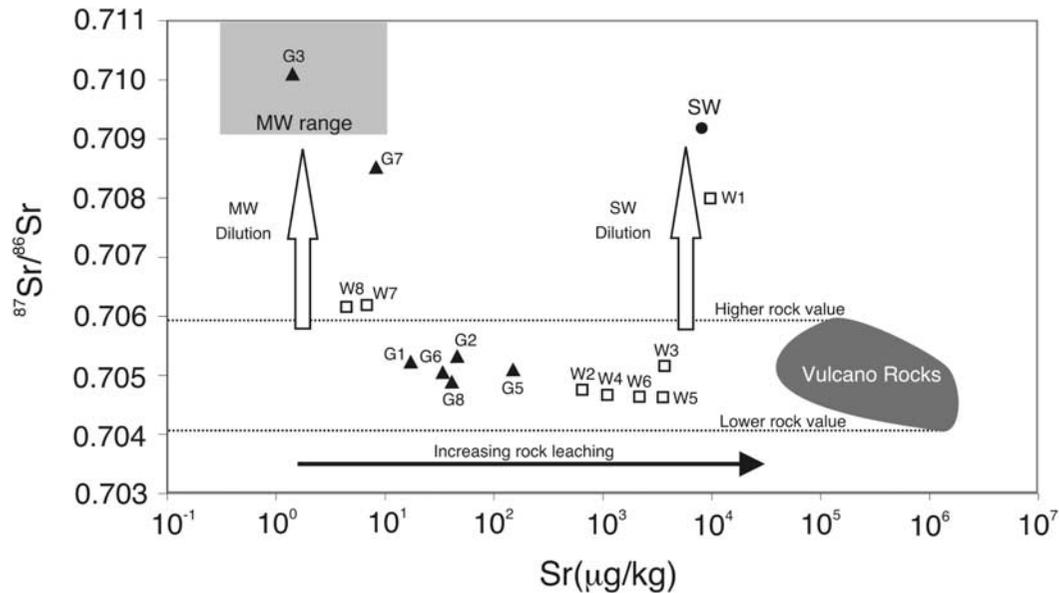
Figure 3. ^{87}Sr/^{86}Sr ratios versus Sr (μg/kg) in acid condensates (triangle plot) and thermomineral waters (square plot) from Vulcano Island. The seawater value (round plot) is taken from the study of *Pennisi et al.* [2000]. The clear shaded area corresponds to the MW range, whereas the dark shaded area corresponds to the rock values from literature (see text for details). Vulcano rock extreme isotopic values are from *De Astis et al.* [1997] and *De Astis et al.* [2000]. The Sr concentrations and isotopic compositions of fluid samples are related both to the intensity of rock leaching (horizontal arrow) and to the influence of SW and MW (vertical arrows).

and the SW value. This confirms the seawater main contribution for this sample already suggested by major elements chemistry. All other waters display significantly lower Sr concentrations, and most of them have ^{87}Sr/^{86}Sr ratios in the range of rock values. Steam-heated and volcanic waters both display low ^{87}Sr/^{86}Sr ratios and high Sr concentrations with respect to shallow groundwaters, likely as the result of enhanced rock leaching due to a higher input of geothermal and/or magmatic fluids. Together with major elements geochemistry, these observations suggest that the Sr budget of steam-heated and volcanic waters results mainly from a balance between two end-members (meteoric water and parent rock) modulated by acid gases influx. Indeed, variable dissolution of rising gases into shallow aquifers modifies the physico-chemical parameters of groundwaters and therefore controls the intensity of rock leaching. W7 and W8 samples display the lowest Sr concentrations and ^{87}Sr/^{86}Sr signatures between the Vulcano rock and the MW range. This suggests a strong influence of MW for these samples together with a lower efficiency of

rock leaching which is in agreement with major elements geochemistry.

[24] Due to the low Pb contents, only two Pb isotopic data are available for water samples (see Table 2). In Figure 4, W2 and W3 samples plot far from the Vulcano rocks isotopic compositions and in the field of recent anthropogenic signatures [*Monna et al.*, 1999]. For these steam-heated waters, these results suggest a strong influence of anthropogenic Pb either via meteoric water infiltrations or contamination of the relative aquifers by geothermal drillings performed in the 50s [*Sommaruga*, 1984]. Natural Pb influence due to wall rock interactions, magmatic gas dissolution or re-entrainment of volcanogenic aerosols in MW during rainfall appears negligible for these samples. Any marine contribution can also be ruled out due to the very low Pb content (about 10^{-12} g/g) in seawater [*Yuan-Hui*, 1991].

5.2. Fumarolic Gas Condensates

[25] Sampling temperature, Sr and Pb concentrations and isotopic compositions of gas condensates from La Fossa crater fumarolic field are reported in
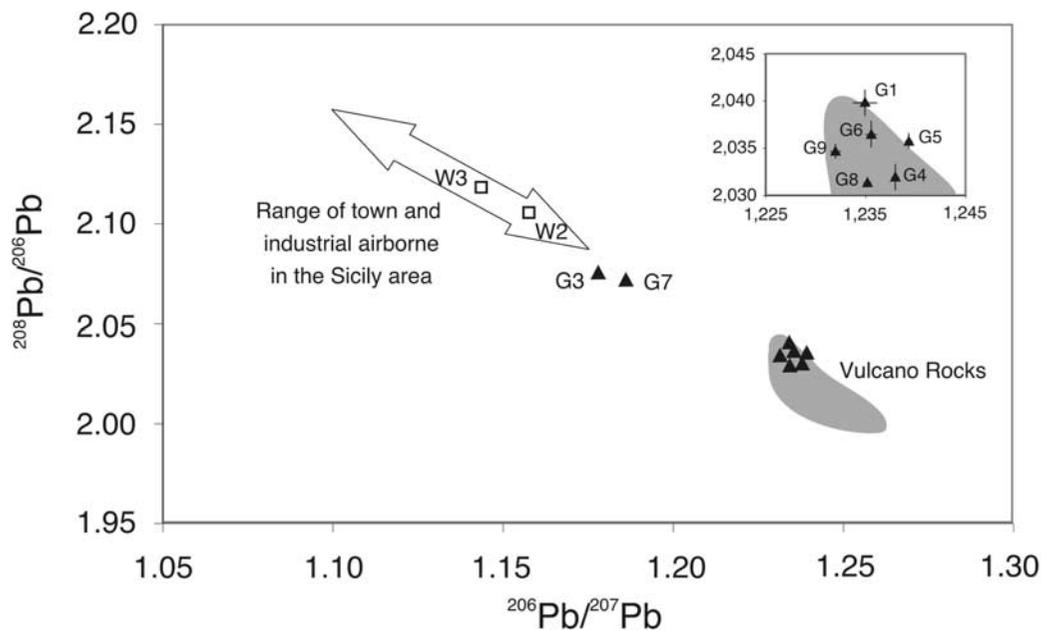
Figure 4. $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ in acid condensates (triangle plot) and thermomineral waters (square plot) from Vulcano Island. In this type of diagram, any linear trend can be interpreted in terms of mixing between two end-members. The shaded area includes Vulcano rock data [*Clocchiatti et al., 1994; De Astis et al.*, 1997, 2000; *Del Moro et al.*, 1998; *Ellam et al.*, 1989; *Esperança et al.*, 1992; *Gioncada et al.*, 2003]. The range of town and industrial airborne in the Sicily area (arrow) is also plotted for comparative purposes [*Monna et al.*, 1999].

Table 4. Sr and Pb enrichment factors (EF) with respect to Al are also shown in Table 4. Al is chosen because of its refractory behavior in volcanic fluids. Ti or Zr may also be chosen with little effect for global results. EF were calculated using the mean of Vulcano rocks analyses from *Clocchiatti et al.* [1994].

[26] The outlet temperatures of fumarolic vents, sampled during the 1999–2001 period, range from 104°C (G9) to 446°C (G3). Sr concentrations are ranging from 1.4 μg/kg (G3) to 151.7 μg/kg (G5) whereas Pb is much more abundant with concentrations ranging from 90.3 μg/kg (G7) to 7968.5 μg/kg (G8). $^{87}Sr/^{86}Sr$ ratios vary from 0.70487 ± 0.00002 (G8) to 0.71009 ± 0.00002 (G3). $^{206}Pb/^{207}Pb$ ratios range from 1.1780 ± 0.0001 (G3) to 1.2396 ± 0.0001 (G5) and $^{208}Pb/^{206}Pb$ ratios vary from 2.0314 ± 0.0003 (G7) to 2.0756 ± 0.0002 (G3). No clear correlations were observed between the outlet temperature of the fumarolic vents and Sr and Pb concentrations or isotopic compositions.

[27] Pb and Sr display respectively high ($10^2–10^3$) and low (≈0.5) EF in volcanic fluids (Table 4), as the result of their respective volatile and refractory behaviors. This accounts for the very contrasted elemental and isotopic compositions for Sr and Pb in Vulcano condensates.

[28] In Figure 3, most of the gas samples (G1, G2, G5, G6, G8) display low Sr isotope ratios, within the bulk rock range, suggesting both Sr content in volcanic gases to be mainly derived from wall rock or particle leaching during gas ascent and Sr contamination from meteoric water infiltrations to have a negligible impact on the $^{87}Sr/^{86}Sr$ isotopic ratios. However, two samples (G3, G7) display a definitely contrasted isotopic signature, close to, or inside the meteoric water range. These samples also display the lowest Sr concentrations observed in gas condensates.

[29] In the $^{208}Pb/^{206}Pb$ versus $^{206}Pb/^{207}Pb$ diagram (Figure 4), G1, G4, G5, G6, G8 and G9 samples plot in the field of parent rocks. This observation is in accord with previous studies performed in plume aerosols from Masaya [*Vallelonga and Mather*, 2003] and in lead sulfosalts sublimates of Vulcano [*Ferrara et al.*, 1995] displaying lead isotopic ratios of volcanic exhalations similar to respective

Table 4. Sr and Pb Concentrations and Isotopic Compositions in Vulcano Fumarolic Gases[a]

Fumarolic Vent	Number	Date	T	Sr	Pb	EF_{Sr}	EF_{Pb}	$^{87}Sr/^{86}Sr$	2 S.D	$^{206}Pb/^{207}Pb$	2 S.D	$^{208}Pb/^{206}Pb$	2 S.D	$^{206}Pb/^{204}Pb$	2 S.D
F11	G1	23.02.2001	365	17.6	1392.8	0.5	8×10^2	0.70520[b]	0.00001[b]	1.2349	0.0010	2.0397	0.0013	19.531	0.131
F11	G2	28.05.2000	410	46.8	828.3			0.70530[b]	0.00005[b]						
F11	G3	19.05.1999	446	1.4	127.6					1.1780	0.0001	2.0756	0.0002	18.407	0.036
Duplicate								0.71009[b]	0.00002[b]	1.1782	0.0007	2.0754	0.0026	18.413	0.023
Duplicate								0.71008[b]	0.00003[b]	1.1789	0.0007	2.0727	0.0025	18.386	0.026
FA	G4	23.02.2001	363	6.4	692.5	0.5	1.2×10^3			1.2379[b]	0.0004[b]	2.0319[b]	0.0013[b]	19.445[b]	0.011[b]
FA	G5	28.05.2000	404	151.7	7470.3			0.70507	0.00001	1.2396	0.0001	2.0352	0.0003	19.448	0.003
F0	G6	23.02.2001	307	34.8	1289.6	0.4	3×10^2	0.70502[b]	0.00001[b]	1.2355	0.0003	2.0365	0.0013	19.457	0.010
F0	G7	27.05.2000	313	8.4	90.3			0.70848[b]	0.00004[b]	1.1859	0.0001	2.0717	0.0002	18.539	0.003
F0	G8	20.05.1999	343	41.9	7968.5					1.2352	0.0001	2.0314	0.0003	19.388	0.003
FR2	G9	21.05.1999	104	3.7	335.9			0.70487[b]	0.00002[b]	1.2320	0.0004	2.0346	0.0004	19.344	0.005

[a] Sr and Pb concentrations are in μg/kg.

[b] Results corrected for blank contribution (see text). Sr and Pb enrichment factors (EF) with respect to Al are also shown (see text). The vent temperature T (°C) and the collection date are also listed. F0, F11, FA, and FR2 refer to the classical denomination of fumaroles used at Vulcano (see text).

parent rock. Some Pb may originate, as Sr, from acid fluid-rock interactions. However, due to high EF (10^2–10^3) in gas condensates, the Pb budget is likely to be dominated by magma degassing. Because isotopic mass fractionation during Pb degassing does not induce measurable effects, gases and rocks should display similar Pb isotopic compositions. Therefore it is not possible to discriminate if small Pb isotopic variations between samples G1, G4, G5, G6, G8 and G9 are due to interactions with isotopically different pathways during gas ascent or to limited magmatic signature variations.

[30] G3 and G7 samples display large differences in both Sr and Pb isotopic ratios with signatures close to the meteoric/anthropogenic values. These samples display the lowest Sr and Pb concentrations measured in gas condensates and one may suggest a possible contamination. However, an artifact due to a rainfall-induced contamination is unlikely because sampling was performed during sunny days and the percentage of contamination should be almost total due to the low concentrations generally observed in meteoric water. Contamination of samples by solid particles can be also ruled out, as it would induce higher Sr and Pb contents. Therefore episodic variations of both Sr and Pb isotope ratios between magmatic/rock signatures and atmospheric/anthropogenic signatures are obvious for F11 (G1, G2, G3 samples) and F0 (G6, G7, G8 samples) fumaroles. As the timescale is quite short between the different sampling campaigns (from 1999 to 2001), a deep process, such as the involvement of Calabrian meta-sediment [*Caggianalli et al.*, 1991] in deep fluid circulation can be ruled out as already concluded by *Ferrara et al.* [1995]. Moreover, a marine contribution by deep infiltration within the volcanic pile is unlikely to affect Sr and Pb isotopic compositions of the crater fumaroles because (1) Sr has a refractory behavior in volcanic gas and large amounts of this element could not be transported in fumarolic fluids from deep levels to the volcano/atmosphere interface and (2) Pb content in seawater is very low [*Yuan-Hui*, 1991] and can be considered as a negligible source of Pb in fumaroles. As suggested by several studies [*Ferrara et al.*, 1995; *Harris and Maciejewski*, 2000], local fluctuations of the volcanic structure permeability are likely to occur due to both seismic events and self-sealing processes that continuously change the circulation pathways and local fluxes of fumarolic fluids. Such changes may lead ascending volcanic gases to undergo variable interactions with meteoric water, which has recently filtered into the shallow volcanic

edifice, therefore accounting for the meteoric/anthropogenic isotopic signature of samples G3 and G7. As discussed above, MW measurements are required to define more precisely the MW range in the Vulcano Island area because Sr concentrations and isotopic compositions of rainwater are dependent on aerosols sources.

6. Conclusion

[31] These new coupled Sr-Pb concentrations and isotopic measurements clearly indicate that the Metallic Trace Elements (MTE) budget of fumarolic gases and shallow waters of Vulcano Island is influenced by both natural and atmospheric/anthropogenic sources. The Sr budget in groundwaters appears to result mainly from water/rock interaction modulated by volcanic gas input into shallow aquifers. The Pb isotope ratios measured in two steam-heated waters reveal the dominant anthropogenic origin of this element at least in these shallow waters. In most gas samples, the data indicate that Pb is originated from magma degassing whereas Sr results mainly from wall rock or particle contamination during gas ascent. Two gas samples were found to display clear anthropogenic/atmospheric Sr and Pb isotopic signatures. This might indicate that variable permeability of the volcanic edifice allows the recycling of fresh meteoric water by ascending volcanic fluids. Because of the short time-scale of variations of the isotopic signatures for a single fumarole (one year period), modifications of the fluid migration network within the volcanic pile appears as a fast-operating process. The 3-D permeability distribution appears as highly dependent on local stress field changes, micro-fracturation due to small volcanic earthquakes and migrating self-sealing processes. These interpretations, performed on the first set of Sr and Pb isotopic ratios in Vulcano gases and groundwaters, have to be confirmed by future Sr and Pb isotopic measurements, coupled with multiparameter data (fluid geochemistry, seismicity, deformations). This will allow a considerable improvement of the comprehension of interactions between ascending gases, shallow aquifers, infiltered meteoric water and wall rock in a continuously permeability changing structure.

Acknowledgments

References

Aiuppa, A., G. Dongarra, G. Capasso, and P. Allard (2000), Trace elements in the thermal groundwaters of Vulcano Island (Sicily), *J. Volcanol. Geotherm. Res.*, *98*, 189–207.

Barbieri, M., and M. Morotti (2003), Hydrogeochemistry and strontium isotopes of spring and mineral waters from Monte Vulture Volcano, Italy, *Appl. Geochem.*, *18*, 117–125.

Barbieri, F., G. Neri, M. Valenza, and L. Villari (1991), 1987–1990 unrest at Vulcano, *Acta Vulcanol.*, *1*, 95–106.

Bollhöfer, A., and K. J. R. Rosman (2001), Isotopic source signature for atmospheric lead: The Northern Hemisphere, *Geochim. Cosmochim. Acta*, *65*(11), 1727–1740.

Bolognesi, L. (1996), Comment on "Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance" by G. Chiodini, R. Cioni, L. Marini, and C. Panichi, *Bull. Volcanol.*, *58*, 319–320.

Bolognesi, L., and F. D'Amore (1993), Isotopic variation of the hydrothermal system on Vulcano Island, Italy, *Geochim. Cosmochim. Acta*, *57*, 2069–2082.

Caggianalli, A., A. Del Moro, A. Paglionico, G. Piccarreta, L. Pinarelli, and A. Rottura (1991), Lower crustal granite genesis connected with chemical fractionation in the continental crust of Calabria (Southern Italy), *Eur. J. Mineral.*, *3*, 159–180.

Capasso, G., G. Dongarra, R. Favara, S. Hauser, and M. Valenza (1991), Chemical changes in waters from Vulcano Island: An update, *Acta Vulcanol.*, *1*, 199–209.

Capasso, G., G. Dongarra, R. Favara, S. Hauser, and M. Valenza (1992), Isotope composition of rain water, well water and fumarole steam on the island of Vulcano, and their implications for volcanic surveillance, *J. Volcanol. Geotherm. Res.*, *49*, 147–155.

Capasso, G., R. Favara, S. Francofonte, and S. Inguaggiato (1999), Chemical and isotopic variations in fumarolic discharge and thermal waters at Vulcano Island (Aeolian Islands, Italy) during 1996: Evidence of resumed volcanic activity, *J. Volcanol. Geotherm. Res.*, *88*, 167–175.

Capasso, G., W. D'Alessandro, R. Favara, S. Inguaggiato, and F. Parello (2001), Interactions between the deep fluids and the shallow groundwaters on Vulcano Island (Italy), *J. Volcanol. Geotherm. Res.*, *108*, 187–198.

Cellini Legittimo, P., M. Martini, and G. Piccardi (1980), Il contenuto di metalli pesanti nelle acque freatiche di Vulcano e l'influenza di fluidi idrotermali, *Rend. Soc. Ital. Mineral. Petrol.*, *36*, 253–260.

Chevrier, R. M., and F. Le Guern (1982), Prélèvement et analyses des condensats de fumerolles sur volcans actifs: Soufrière de la Guadeloupe (1976–1977) et Pouzzoles et Vulcano (Italie) (1978), *Bull. Volcanol.*, *45*, 173–178.

Chiodini, G., R. Cioni, and L. Marini (1993), Reactions governing the chemistry of crater fumaroles from Vulcano Island, and implications for volcanic surveillance, *Appl. Geochem.*, *8*, 357–371.

Chiodini, G., R. Cioni, L. Marini, and C. Panichi (1995), Origin of the fumarolic fluids of Vulcano Island, Italy and implications for volcanic surveillance, *Bull. Volcanol.*, *57*, 99–110.

Clocchiatti, R., A. Del Moro, A. Gioncada, J. L. Joron, M. Mosbah, L. Pinarelli, and A. Sbrana (1994), Assessment of shallow magmatic system: The 1888–90 eruption, Vulcano Island, Italy, *Bull. Volcanol.*, *56*, 466–486.

Cortecci, G., E. Dinelli, L. Bolognesi, T. Boschetti, and G. Ferrara (2001), Chemical and isotopic compositions of water and dissolved sulfate from shallow wells on Vulcano Island, Aeolian Archipelago, Italy, *Geothermics*, *30*, 69–91.

De Astis, G., L. La Volpe, A. Pecerrillo, and L. Civetta (1997), Volcanological and petrological evolution of Vulcano island (Aeolian Arc, southern Tyrrhenian Sea), *J. Geophys. Res.*, *102*(B4), 8021–8050.

De Astis, G., A. Peccerillo, P. D. Kempton, L. La Volpe, and T. W. Wu (2000), Transition from calc-alkaline to potassium-rich magmatism in subduction environments: Geochemical and Sr, Nd, Pb isotopic constraints from the island of Vulcano (Aeolian arc), *Contrib. Mineral. Petrol.*, *139*, 684–703.

Del Moro, A., A. Gioncada, L. Pinarelli, A. Sbrana, and J. L. Joron (1998), Sr, Nd, and Pb isotope evidence for open system evolution at Vulcano, Aeolian Arc, Italy, *Lithos*, *43*, 81–106.

Deniel, C., and C. Pin (2001), Single stage method for the simultaneous isolation of lead and strontium from silicate materials for isotopic measurements, *Anal. Chim. Acta*, *426*, 95–103.

Dessert, C. (2002), Impact du volcanisme sur le climat et sur les cycles géochimiques globaux, Ph.D. thesis, Univ. Paul Sabatier, Toulouse, France.

Dongarra, G., and D. Varrica (1998), The presence of heavy metals in air particulate at Vulcano island, *Sci. Total Environ.*, *212*, 1–9.

Dongarra, G., S. Hauser, G. Capasso, and R. Favara (1988), Characteristics of variations in water chemistry of some wells from Vulcano island, *Rend. Soc. Ital. Mineral. Petrol.*, *43*, 1123–1131.

Doucelance, R., and G. Manhès (2001), Reevaluation of precise lead isotope measurements by thermal ionisation mass spectrometry: Comparison with determinations by plasma source mass spectrometry, *Chem. Geol.*, *176*, 361–377.

Ellam, R. M., C. J. Hawkesworth, M. A. Menzies, and N. W. Rogers (1989), The volcanism of southern Italy: Role of subduction and the relationship between potassic and sodic alkaline magmatism, *J. Geophys. Res.*, *94*(B4), 4589–4601.

Esperança, S., G. M. Crisci, R. de Rosa, and R. Mazzuoli (1992), The role of crust in the magmatic evolution of the island of Lipari (Aeolian Islands, Italy), *Contrib. Mineral. Petrol.*, *112*, 450–462.

Ferrara, G., A. Garavelli, L. Pinarelli, and F. Vurro (1995), Lead isotope composition of the sublimates from the fumaroles of Vulcano (Aeolian Islands, Italy): Inferences on the deep fluid circulation, *Bull. Volcanol.*, *56*, 621–625.

Freydier, R., and J. Viers (2003), Isotopic study of lead transfer at the interface soil-plants-atmosphere, *Geophys. Res. Lett.*, *30*(5), 1227, doi:10.1029/2002GL016145.

Giggenbach, W. F. (1988), Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geoindicators, *Geochim. Cosmochim. Acta*, *52*, 2749–2765.

Gioncada, A., R. Mazzuoli, M. Bisson, and M. T. Pareschi (2003), Petrology of volcanic products younger than 42 ka on the Lipari-Vulcano complex (Aeolian Island, Italy): An example of volcanism controlled by tectonics, *J. Volcanol. Geotherm. Res.*, *122*, 191–220.

Goff, F., H. A. Wollenberg, D. C. Brookins, and R. W. Kistler (1991), A Sr-isotopic comparison between thermal waters, rocks, and hydrothermal calcites, Long Valley caldera, California, *J. Volcanol. Geotherm. Res.*, *48*, 265–281.

Grousset, F. E., M. Parra, A. Bory, P. Martinez, P. Bertrand, G. Shimmield, and R. M. Ellam (1998), Saharan wind regimes traced by the Sr-Nd isotopic composition of sub-tropical Atlantic sediments: Late glacial maximum vs today, *Quat. Sci. Rev.*, *17*, 395–409.

Harris, A. J. L., and A. J. H. Maciejewski (2000), Thermal surveys of the Vulcano Fossa fumarole field 1994–1999: Evidence of migration and sealing, *J. Volcanol. Geotherm. Res.*, *102*, 119–147.

Hinkley, T. K. (1991), Distribution of metals between particulate and gaseous forms in a volcanic plume, *Bull. Volcanol.*, *53*, 395–400.

Keller, J. (1980), The Island of Vulcano, in *The Aeolian Islands—An Active Volcanic Arc in the Mediterranean Sea*, edited by L. Villari, *Rend. Soc. Ital. Mineral. Petrol.*, *36*, 369–414.

Krom, M. D., R. A. Cliff, L. M. Eijsink, B. Herut, and R. Chester (1999), The characterisation of Saharan dusts and Nile particulate matter in surface sediments from the Levantine basin using Sr isotopes, *Mar. Geol.*, *155*, 319–330.

Leeman, W. P., S. Tornarini, M. Penissi, and G. Ferrara (2005), Boron isotopic variations in fumarolic condensates and thermal waters from Vulcano Island, Italy: Implications for evolution of volcanic fluids, *Geochim. Cosmochim. Acta*, *69*(1), 143–163.

Martini, M. (1980), Geochemical survey on the phreatic waters of Vulcano (Aeolian Islands, Italy), *Bull. Volcanol.*, *43*(1), 265–274.

Möller, P., P. Dulski, Y. Savascin, and M. Conrad (2004), Rare earth elements, yttrium and Pb isotope ratios in thermal spring and well waters of West Anatolia, Turkey: A hydrochemical study of their origin, *Chem. Geol.*, *206*, 97–118.

Monna, F., J. Lancelot, I. W. Croudace, A. B. Cundy, and J. T. Lewis (1997), Pb isotopic composition of airborne particulate material from France and southern United Kingdom: Implications for Pb pollution sources in urban areas, *Environ. Sci. Technol.*, *31*(8), 2277–2286.

Monna, F., A. Aiuppa, D. Varrica, and G. Dongarra (1999), Pb isotope composition in lichens and aerosols from eastern Sicily: Insight into the regional impact of volcanoes on the environment, *Environ. Sci. Technol.*, *33*, 2517–2523.

Negrel, P., and S. Roy (1998), Chemistry of rain water in the Massif Central (France): A strontium isotope and major element study, *Appl. Geochem.*, *13*(8), 941–952.

Panichi, C., and P. Noto (1992), Isotopic and chemical composition of water, steam and gas samples of the natural manifestations of the island of Vulcano (Aeolian Arc, Italy), *Acta Vulcanol.*, *2*, 297–312.

Pennisi, M., W. P. Leeman, S. Tonarini, A. Penissi, and P. Nabelek (2000), Boron, Sr, O and H isotope geochemistry of groundwaters from Mt. Etna (Sicily)—Hydrologic implications, *Geochim. Cosmochim. Acta*, *64*(6), 961–974.

Piccardi, G., M. Martini, and P. Cellini Legittimo (1979), On the presence of Cu, Zn, Cd, Sb, Bi and Pb in the fumarolic gases of Vulcano (Aeolian island), *Rend. Soc. Ital. Mineral. Petrol.*, *35*(2), 627–632.

Quisefit, J. P., J. P. Toutain, G. Bergametti, M. Javoy, B. Cheynet, and A. Person (1989), Evolution versus cooling of gaseous volcanic emissions from Momotombo Volcano, Nicaragua: Thermochemical model and observations, *Geochim. Cosmochim. Acta*, *53*, 2591–2608.

Sommaruga, C. (1984), Le ricerche geotermiche svolte a Vulcano negli anni '50, *Rend. Soc. Ital. Mineral. Petrol.*, *39*, 355–366.

Symonds, R. B., W. I. Rose, M. H. Reed, F. E. Lichte, and D. L. Finnegan (1987), Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia, *Geochim. Cosmochim. Acta*, *51*, 2083–2101.

Symonds, R. B., Y. Mizutani, and P. H. Briggs (1996), Long term geochemical surveillance of fumaroles at Showa-Shinzan dome, Uzu volcano, Japan, *J. Volcanol. Geotherm. Res.*, *73*, 177–211.

Taran, Y. A., J. W. Hedenquist, M. A. Korzhinsky, S. I. Tkachenko, and K. I. Shmulovich (1995), Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands, *Geochim. Cosmochim. Acta*, *59*(9), 1749–1761.

Tedesco, D. (1997), Systematic variations in the ^{3}He/^{4}He ratio and carbon of fumarolic fluids from active volcanic areas in Italy: Evidence for radiogenic ^{4}He and crustal carbon addition by the subducting African plate?, *Earth Planet. Sci. Lett.*, *151*, 255–269.

Tedesco, D., G. Miele, Y. Sano, and J. P. Toutain (1995), Helium isotopic ratio in Vulcano island fumaroles: Temporal variations in shallow level mixing and deep magmatic supply, *J. Volcanol. Geotherm. Res.*, *64*, 117–128.

Toutain, J. P., F. Sortino, B. Reynier, B. Dupre, M. Munoz, A. Nonell, M. Polve, and S. Chancha Do Vale (2003), A new collector for sampling volcanic aerosols, *J. Volcanol. Geotherm. Res.*, *123*(1–2), 95–103.

Vallelonga, P., and T. A. Mather (2003), Lead (Pb) fluxes and Pb isotopic compositions from Masaya Volcano, Nicaragua, *Atmos. Environ.*, *37*, 4453–4460.

Van der Lee, J., and L. De Windt (2000), CHESS Tutorial and Cookbook: Updated for Version 3.0, *User Manual LHM/RD/02/13*, Ecole des Mines de Paris, Fontainebleau, France.

Yuan-Hui, L. (1991), Distribution patterns of the elements in the ocean: A synthesis, *Geochim. Cosmochim. Acta*, *55*, 3223–3240.