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Pb Isotope Composition in Lichens and Aerosols from Eastern Sicily: Insights into the Regional Impact of Volcanoes on the Environment

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A total of 25 lichen thalli of *Parmelia conspersa* (Ehrh), collected at Vulcano island and at Mt. Etna, during a one-year biogeochemical survey, were analyzed for Pb, Br, Al, Sc, $^{206}Pb/^{207}Pb$, and $^{208}Pb/^{206}Pb$ ratios. Lead isotope ratios were also measured on aerosols samples from urban areas and industrial sites of Sicily. The observed $^{206}Pb/^{207}Pb$ range for urban and industrial aerosols (1.103−1.174) closely matches the anthropogenic signature (1.080−1.165). Lichens ($^{206}Pb/^{207}Pb$ = 1.156−1.226), instead, are closer to the compositional field of ^{206}Pb rich geogenic sources. This natural input is more evident at Vulcano island than at Mt. Etna, where the anthropogenic activities are considerably more effective. On the basis of lead isotope data, Pb/Br ratios and calculated lead enrichment factors, a "natural" lead pollution from volcanoes is suggested. Volcanic lead contribution ranges from 10 to 30% at Mt. Etna to 10−80% at Vulcano island.

Introduction

Dongarrà and Varrica (*1*) and Varrica et al. (*2*) recently reported data on trace metal contents in lichen samples collected around Mt. Etna and on the island of Vulcano, two of the most active volcanic areas in Italy. The aim of their studies was to evaluate the effect of volcanic activity on the environmental dispersion of trace metals. One of their underlying working hypotheses was the following: if the amount of lead introduced into the atmosphere by volcanoes may be considered as a small fraction of the global lead budget, it may become considerably more important in the surroundings of volcanic areas, where lead and other trace metals are constantly released by volcanic plumes and high-temperature fumarole gases. The above authors demonstrated that even passive volcanic degassing tends to increase the background levels of some metals in air. This means that, in towns and cities near volcanic areas, natural emissions are added to those due to anthropogenic activities and may enhance the risk level for populations living nearby. In particular, they observed high enrichment factors for Pb, Br, and Sb which could not be attributed exclusively or prevalently to automotive fuel combustion but were partly the result of volcanic exhalations.

From a different point of view, the intense lead release due to human activities during the last two centuries has led scientists to investigate possible perturbations induced by anthropogenic emissions on atmospheric geochemical cycling. Industrial lead has been introduced in the atmosphere from several sources (mainly fossil fuel combustion and smelting), so that such an industrial lead flux has largely altered natural concentrations in oceans (*3*, *4*), lakes (*5*), and recent snow layers in Antarctica and Greenland (*6*, *7*). On a global scale, anthropogenic lead has been estimated at 95% of the total budget (*8*, *9*). Currently, the restricted use of lead additives in gasoline and the introduction of catalytic converters requiring unleaded gasoline have led to a worldwide decrease in Pb emissions (*10*).

The purpose of the present work was to investigate and possibly to apportion volcanic and anthropogenic additions to air and soils of Eastern Sicily by means of the Pb isotope compositions in lichens.

Lead isotopes have been widely used within the environmental sciences as tracers of pollution sources (see the Clair C. Patterson Special Issue, *Geochim. Cosmochim. Acta* **1994**, *58*). Lead introduced in the environment by human activities has the isotope composition of the ore body from which it was extracted. Each lead ore deposit is characterized by its own isotope composition which depends on initial Pb isotope compositions, U/Pb−Th/Pb ratios, and age (actually, the time elapsed since the lead separated from its source rock) (*11*). At least in Western Europe, soil-derived Pb has an isotope signature which is distinct from that of industrial lead(s), so that, once the isotope compositions of the various potential sources are known, mixing processes may be quantified. Another clue can be given by the Pb/Br ratios. As a matter of fact Harrison and Sturges (*12*) have shown that the Pb/Br ratio can be used as a marker of anthropogenic emissions. The rationale of this fingerprint is based on the fact that leaded gasoline contains brominated compounds added to reduce the formation of lead oxides inside the automotive engines. According to gasoline composition, the Pb/Br mass ratio in fresh automotive produced leaded particles should be around 2.5 (*12*). While many data have been published on lead content and isotope compositions of airborne particles collected in urban and rural sites (*13*, *14*), only a few papers deal with stable lead isotope ratios in lichens (*15*, *16*). Lichens have been widely used in environmental science as they act as bioaccumulators of pollutants (*1*, *17*−*21*). Lichens are an extraordinary symbiotic association of fungi and algae with peculiar physiology and morphology (thallous structure; absence of cuticle and stomata) which forces them to absorb and accumulate chemical elements in gaseous, liquid, or particulate form from the atmosphere. Owing to the absence of excretion mechanisms in lichens, the xenobiotic substances cannot be expelled and accumulate over the years. Therefore, data from lichens may provide integrated measurements over a long period of time (10−20 years) and thus furnish important insights on lead contributions to the atmosphere from varying sources over past decades.

Study Area

Volcanism in eastern Sicily results from collision between the African plate and the European continental block (*22*). Mt. Etna and Vulcano are two of the most active volcanoes in the area (Figure 1).

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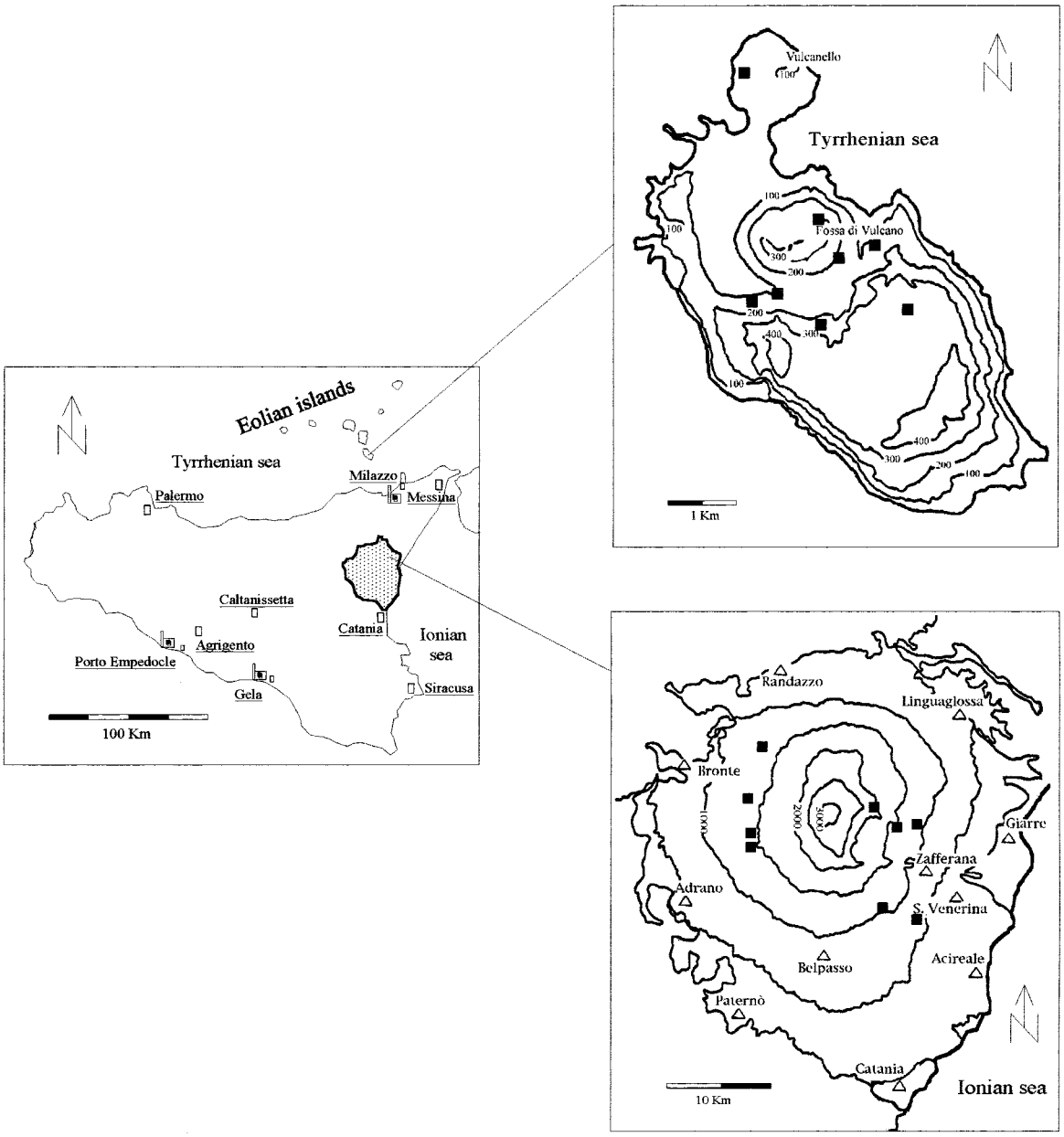

FIGURE 1. Map of Sicily and sampling location.

Mt. Etna formed 500 000−700 000 years ago and is in a persistent effusive-degassing state of activity. The volcano has a complex structure (a basic "old" shield volcano overlaid by a "recent" strato-volcano) which formed during successive phases of accretion (*23*). Volcanic products range in composition from alkali basalts to hawaiites. After the last eruption (1991−1993), the volcano is now in a state of continuous degassing from central craters.

The island of Vulcano belongs to the Aeolian volcanic arc. Volcanic activity started around 120 000 years ago (*24*), but recent eruptions (younger than 15 000 years) started from the pyroclastic and lava cone of La Fossa, where present-day hydrothermal activity is concentrated. The island is entirely made up of volcanic rocks.

The climate in eastern Sicily is ascribed to the typical "Mediterranen Regime", characterized by a dry hot summer season (with minimum precipitation during July−August) and a rainy cold season (October−February). In the Mt. Etna area, the prevailing westerly winds drive the volcanic plume over the eastern slope of the edifice, where it is funneled into a fan-shaped volcanogenic-gravitational depression called Valle del Bove. At Vulcano Island, winds blow mainly from the northern sectors.

Sampling and Analytical Techniques

A total of 25 thalli of *Parmelia conspersa* (Ehrh), a foliose species of lichen, collected on Vulcano and Mt. Etna during a one-year biogeochemical survey, were analyzed for their $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ isotope ratios and Pb, Br, Al, and Sc contents. Samples were all collected from a rocky substrate (cf. Figure 1). No lichen samples were found on Mt. Etna at an altitude higher than 1800 m above sea level or on the Vulcano crater. Each sample was dried at 40 °C, carefully separated from substrate particles with a toothbrush and toothpicks under a low-magnification stereomicroscope, and then finely powdered. For further insight into the source of lead, aerosol samples from five Sicilian cities (Messina, Palermo, Catania, Siracusa, and Caltanissetta) and three industrial areas (Gela, Milazzo, and Porto Empedocle) were collected using a Tecora Bravo H2 sampler (Figure 1), working at a fixed flow-rate of 25 L/mn over 24 h. Sartorius cellulose-nitrate membrane filters (porosity 0.8 μm; diameter 47 mm)

TABLE 1. Pb Isotopic Compositions and Pb, Br, and Sc Contents in Lichens Sampled at Mt. Etna and Vulcano Island[a]

sample	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	Br ($\mu g \cdot g^{-1}$)	Sc ($\mu g \cdot g^{-1}$)	Pb ($\mu g \cdot g^{-1}$)	Pb/Br	EF_{Pb}
Etna Lichens							
71 EP	1.175 ± 0.002	2.088 ± 0.002	23	1.4	17	0.74	23
72 EP	1.178 ± 0.003	2.074 ± 0.006	22	2.7	22	1.00	16
74 EP	1.178 ± 0.002	2.085 ± 0.006	21	1.9	14	0.67	14
76 EP	1.171 ± 0.004	2.090 ± 0.008	24	2	32	1.33	31
81 EP	1.168 ± 0.002	2.095 ± 0.006	22	1	44	2.00	85
81 EP dupl	1.168 ± 0.002	2.094 ± 0.004					
87 EP	1.167 ± 0.003	2.093 ± 0.003	22	1.4	47	2.14	65
90 EP	1.170 ± 0.002	2.093 ± 0.005	36	2.1	48	1.33	44
96 EP	1.178 ± 0.002	2.084 ± 0.005	20	1.9	5	0.25	5
97 EP	1.180 ± 0.002	2.080 ± 0.005	21	1.4	23	1.10	32
99 EP	1.161 ± 0.002	2.104 ± 0.001	19	1.8	26	1.37	28
100 EP	1.156 ± 0.005	2.105 ± 0.006	26	1.2	22	0.85	35
Vulcano Lichens							
5 VUP	1.182 ± 0.004	2.073 ± 0.003	25	1.9	5	0.20	3
10 VUP	1.204 ± 0.003	2.045 ± 0.004	25	1.5	30	1.2	21
13 VUP	1.226 ± 0.002	2.034 ± 0.002	27	1.4	11	0.41	8
16 VUP	1.181 ± 0.002	2.078 ± 0.001	55	1.3	26	0.47	21
17 VUP	1.193 ± 0.004	2.067 ± 0.007	38	3	29	0.76	10
22 VUP	1.167 ± 0.002	2.094 ± 0.004	15	1.1	18	1.2	17
23 VUP	1.208 ± 0.002	2.060 ± 0.005	36	1.2	40	1.1	34
25 VUP	1.177 ± 0.001	2.085 ± 0.001	41	2.2	42	1.0	20
25 VUP dupl.	1.176 ± 0.001	2.081 ± 0.004					
38 VUP	1.184 ± 0.003	2.077 ± 0.005	31	2.7	26	0.84	10
40 VUP	1.191 ± 0.001	2.071 ± 0.001	80	4.3	24	0.30	6
40 VUP dupl.	1.190 ± 0.001	2.067 ± 0.003					
43 VUP	1.176 ± 0.001	2.085 ± 0.004	55	4	24	0.44	6
46 VUP	1.200 ± 0.002	2.064 ± 0.005	38	3	19	0.5	7
48 VUP	1.184 ± 0.001	2.078 ± 0.002	37	2	40	1.1	21
50 VUP	1.184 ± 0.004	2.078 ± 0.003	23	3.2	14	0.61	5

[a] Enrichment factor of Pb (EF_{Pb}) is computed as described in the text. The errors of Pb/Pb ratios correspond at 95% confidence level. Duplicate is abbreviated as dupl.

were used. Some airborne particulate samples, collected in a similar way as previously described, were provided by local municipal agencies.

Sc and Br were analyzed by INAA, Pb and Al by inductively coupled plasma mass spectrometer (ICP-MS) after microwave digestion with $HNO_3 + HF + HClO_4$ added to the filter. Indium was used as internal standard during ICP-MS analyses.

For isotopic analysis, approximately 200 mg of lichens were totally dissolved with 2 mL each of concentrated HNO_3 and HCl of suprapure grade. The digestion was achieved under microwave assistance (MLS ETHOS) in pressured Teflon bombs. A blank was systematically measured for each set of eight unknown samples and was always found negligible by comparison to the total amount of Pb in lichens. Extraction of particulate material from the filters and Pb purification on AG1 × 4 resin were achieved following the procedure described elsewhere (*25*). The Pb isotopic ratios were measured by quadrupole-based ICP-MS (POEMS1-TJA and HP 4500). More details about settings, analytical time management, and correction of mass bias via NBS 981 can be found in Monna et al. (*26*). Few duplicates showed that the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratio measurements are quite reproducible, considering the analytical precision (0.1%−0.2% at 95% confidence level). Although the ratios including the ^{204}Pb isotope were measured when possible, they are not presented here because a complete discussion of these ratios in addition to the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios may appear redundant.

Enrichment factors for Pb, relative to local volcanic rocks, were computed according to the following formula: $EF_{Pb} = (Pb/Sc)_{lich}/(Pb/Sc)_{subst}$. On the basis of several rock chemistry determinations (Dongarrà, unpublished data), a $(Pb/Sc)_{subst}$ ratio of 0.56 was used for the Etna and 0.98 for Vulcano. Metal concentrations and lead isotopic compositions in lichens are reported in Table 1. Lead isotope ratios in urban aerosols and gasoline samples are reported in Table 2.

Results and Discussion

Isotopic Signatures of Pb Sources. Lead in a natural environment usually derives from distinct sources: organo-lead used as antiknock additives in gasoline, industrial activities, and natural inputs. At the studied sites, two main natural sources can be expected: soil dust derived particles and volcanic emissions. Lead isotopic compositions of volcanics from Mt. Etna ($^{206}Pb/^{207}Pb$: 1.240−1.280; av: 1.260; $^{208}Pb/^{206}Pb$: 1.981−2.009; av: 1.990) and sublimates from the Fossa Crater of Vulcano island ($^{206}Pb/^{207}Pb$: 1.230−1.235; av: 1.234; $^{208}Pb/^{206}Pb$: 2.011, 2.045; av: 2.030) have been determined by Carter and Civetta (*27*) and Ferrara et al. (*28*), respectively. A few measurements carried out during our survey on fresh scoriae and on plume particles collected at Bocca Nuova crater, Mt. Etna ($^{206}Pb/^{207}Pb$: 1.211−1.260; $^{208}Pb/^{206}Pb$: 1.999−2.048), fall close to the range previously defined by Carter and Civetta (Table 2). A further natural contribution, as often has been invoked, may come from desert-derived dust, as Saharan winds often spread over Sicily. However, given the low Pb content in desert aerosols (less than 20 $\mu g/g$, (*9*)), Saharan lead is probably of minor importance. Seawater was not considered as its contribution to the total lead content in lichens is rather low.

It has been shown that lead isotope ratios in gasoline in Western Europe have frequently shifted during the past decades in response to changing lead ores used as additives (*29*). In France, a decrease of the $^{206}Pb/^{207}Pb$ ratios from 1.162 in 1966 (*30*) to much lower values of 1.069−1.094 (av: 1.084) in 1995 has been explained by the increasing use of a major component of Pb coming from Australian and Canadian lead ores, all characterized by low radiogenic signatures (*25, 31*). However, the situation can be quite different from one country to another, depending on the main suppliers and on the location of their importation. Regarding Italy, the only data to our knowledge are those reported by Facchetti et al.

TABLE 2. Pb Isotopic Compositions and Pb/Br Ratios of Airborne Particulate Matter and Gasoline in Eastern Sicily[a]

sampling location	name	characteristics	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{206}Pb$	Pb/Br
Palermo	G.51	town	1.119 ± 0.001	2.144 ± 0.004	2.2
Palermo	G.66	town	1.118 ± 0.001	2.143 ± 0.005	2.2
Palermo	G.137	town	1.106 ± 0.001	2.149 ± 0.004	2.8
Palermo	G.37	town	1.123 ± 0.002	2.142 ± 0.004	2.5
Palermo	G.39	town	1.117 ± 0.002	2.148 ± 0.005	2.5
Siracusa	SR2	town	1.167 ± 0.001	2.102 ± 0.003	2.7
Siracusa	SR3	town	1.168 ± 0.003	2.098 ± 0.004	2.8
Messina	Mess 27	town	1.103 ± 0.002	2.152 ± 0.004	1.8
Messina	Mess C7	town	1.104 ± 0.002	2.153 ± 0.005	2.2
Milazzo	Mess 122	town/industrial	1.119 ± 0.002	2.136 ± 0.004	3.9
Milazzo	Mess 117	industrial	1.141 ± 0.003	2.116 ± 0.006	3.9
Caltanissetta	SC	town	1.107 ± 0.002	2.150 ± 0.003	
Caltanissetta	CL	town	1.113 ± 0.002	2.145 ± 0.005	3.1
Caltanissetta	CL2	town	1.126 ± 0.001	2.134 ± 0.004	3.2
Gela	GELA 1	town/industrial	1.113 ± 0.001	2.147 ± 0.004	3.4
Gela	GELA 2	industrial	1.165 ± 0.002	2.098 ± 0.003	4.1
Porto Empedocle	PE1	industrial area	1.149 ± 0.003	2.110 ± 0.008	2.4
Porto Empedocle	PE2	industrial area	1.149 ± 0.003	2.109 ± 0.009	3.2
Catania	CAT F	town	1.165 ± 0.003	2.108 ± 0.005	3.2
Catania	CAT C	town	1.161 ± 0.001	2.110 ± 0.004	3.1
Catania	CAT D	town	1.174 ± 0.002	2.090 ± 0.006	3.2
Catania	CAT XI	town	1.168 ± 0.003	2.095 ± 0.004	3.2
AGIP		gasoline	1.066 ± 0.004	2.205 ± 0.009	
SHELL		gasoline	1.137 ± 0.006	2.112 ± 0.008	
IP		gasoline	1.084 ± 0.004	2.166 ± 0.006	
ASH1		Bocca Nuova Mt. Etna	1.211 ± 0.004	2.043 ± 0.005	
ASH2		Bocca Nuova Mt. Etna	1.260 ± 0.004	1.999 ± 0.010	

[a] The errors of Pb/Pb ratios correspond at 95% confidence level.

(*32*) giving a mean value of 1.18 in Turin (North Italy) for 1974−1975 and by Colombo et al. (*33*) with a mean value of 1.16, for the same town, in 1985. This radiogenic isotopic signature reflected the use of young U.S. and Western European (Greece, Yugoslavia) lead ores.

To establish the lead isotope compositions in gasoline used at the present time in Sicily, samples were collected directly from petrol stations of the most important suppliers (AGIP, IP, and ESSO). The $^{206}Pb/^{207}Pb$ ratios (Table 2) vary rather widely from 1.067 to 1.137 (av: 1.085), proving that the different supplier companies have added Pb having a variable primary origin but always including a significant proportion of unradiogenic Pb.

The isotopic composition of lead emitted by industries is more difficult to assess given the high variability of the possible origins due to the presence of a Pb market much more open than that of gasoline additives. Excluding Gela 1 and Mess 122 samples, likely contaminated by leaded gasoline because of the surrounding car traffic, the observed range of $^{206}Pb/^{207}Pb$ ratios (1.141−1.165) for samples collected near Sicilian industrial sites (Gela, Milazzo, and Porto Empedocle) is similar to that reported for German and French industrial emissions (1.142−1.159) (*25*−*34*). Such a range is considerably more radiogenic than gasoline-derived lead. In our study we will therefore assume the range 1.141−1.165 as characterizing the industrial lead isotopic composition.

Lead Isotope Composition in Urban Airborne Particulate Material. Lead isotope ratios measured on aerosols samples from five Sicilian urban areas (Palermo, Catania, Messina, Siracusa, and Caltanissetta) and from three industrial sites (Gela, Milazzo, and Porto Empedocle) are plotted in Figure 2. We must keep in mind that aerosol samples only reflect a punctual situation, and it is therefore hazardous to draw general conclusions from these data. Temporal variation in atmospheric $^{206}Pb/^{207}Pb$ ratios in urban site can be high, depending on the day of the week and on the wind direction (*25*).

The observed $^{206}Pb/^{207}Pb$ ratios range between the gasoline-derived lead signature and natural input values. Samples

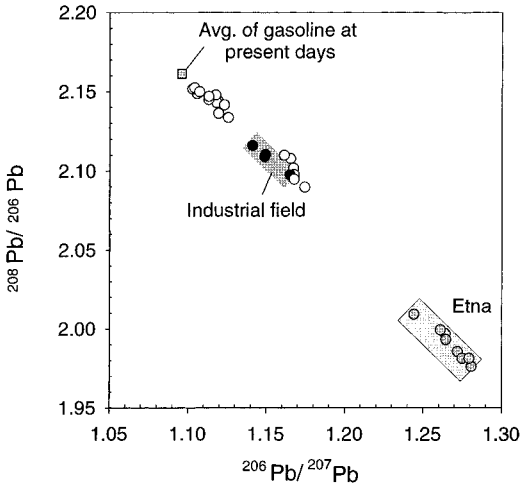

FIGURE 2. $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ in aerosols collected in urban environment (○), and industrial areas (●). The compositional fields of the natural and anthropogenic lead sources are also plotted for comparative purposes.

from Messina, Caltanisseta, and Palermo urban areas show the less radiogenic isotope signatures ($^{206}Pb/^{207}Pb$ = 1.103−1.126), and they are the most affected by automotive lead. In Figure 3 are plotted the $^{206}Pb/^{207}Pb$ isotopic ratios against the Pb/Br ratios observed in airborne particles as well as the compositional fields of anthropogenic (gasoline and industrial) and natural sources (*35*, *36*). The measured Pb/Br ratios in urban particulate material from Messina (1.8−2.2) and Palermo (2.2−2.8) are very close-to-this ratio, confirming the importance of automobile combustion in the dispersion of lead and bromine in the urban atmosphere.

Urban aerosols from southeastern Sicily (Catania and Siracusa), on the contrary, are considerably more radiogenic ($^{206}Pb/^{207}Pb$ = 1.161−1.174) and present higher Pb/Br ratios (2.8−3.2), suggesting a more significative contribution of industrial lead, while the contribution of soil dust is rather

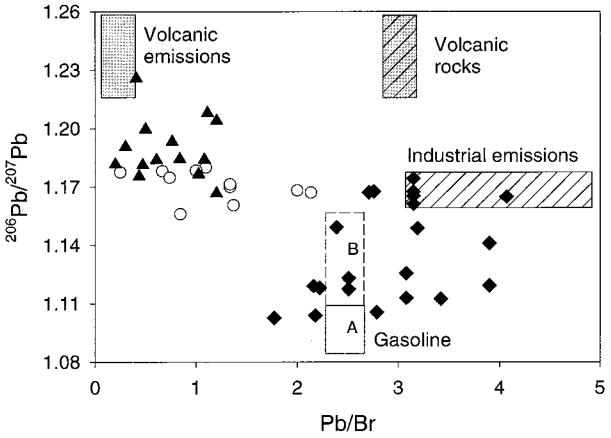

FIGURE 3. $^{206}Pb/^{206}Pb$ vs Pb/Br in aerosol (◆) and lichen samples from Mt. Etna (○) and Vulcano island (▲). Potential lead sources are also shown.

limited on the basis of the very low content of Sc and Al, considered as totally natural occurring elements.

Airborne particulate matter collected on filters indicates therefore that automobile exhausts and industrial emissions are the prominent source of atmospheric lead in the studied urban sites. This means that, over short term, no risk seems to be associated with lead emissions from volcanic activity, at least in urban areas far from the volcanoes.

Lead Isotopic Composition in Lichens. Figure 4 (parts a and b) displays the lead isotopic ratios in lichens sampled at Mt. Etna and Vulcano island, respectively. Both isotopic patterns fit straight lines, defined by extreme end-members corresponding to gasoline and the natural sources. The geogenic input is much more evident at Vulcano island ($^{206}Pb/^{207}Pb = 1.176-1.226$) than at Mt. Etna ($^{206}Pb/^{207}Pb = 1.156-1.180$), where the surrounding anthropogenic activities are considerably more effective. The same observations can be drawn from Figure 3, where lichens are clearly shifted toward the compositional field of a low Pb/Br natural (volcanic) source. As a consequence, a mixture of anthropogenic Pb (gasoline + industrial) with one (or more) geogenic source has to be invoked. Two possible geogenic sources may be suggested: soil(substrate)-derived dust and volcanic emissions. Unlikely, their relative contribution cannot be apportioned on the basis of the sole isotopic data, because of their similar isotopic signatures. However, substratum-derived lead (Pb_{subst}) in each lichen sample can be estimated by

$$Pb_{subst} = (Pb/Sc)_{subst} \times (Sc)_{lich}$$

where $(Pb/Sc)_{subst}$ and $(Sc)_{lich}$ are the average ratio in local volcanics and the total Sc concentration in lichens, respectively. Both Sc and Al may be used due to their very low solubility and because they have no apparent biological function in lichens. Soil-derived lead, as estimated by the above equation, always results in a minor fraction of the total lead content. Such a minor contribution is consistent with the high values (up to 85) of lead enrichment factors (Table 1).

As a matter of fact, although volcanic aerosols (i.e. solid and liquid particles emitted by volcanic plumes and fumaroles) have a lead isotope composition similar to the local substrate, they are characterized by higher Pb/Sc ratios (and high Pb EFs). During magma degassing, volatile elements (as Pb) are preferentially partitioned into the rising gas phase with respect to lithophile elements (as Sc or Al). Therefore, according to the estimated lead fluxes from Mt. Etna and Vulcano island (*37*), a "natural" pollution from volcanoes may be suggested.

TABLE 3. Proposition of Pb Coming from Substratum, Volcanic Emissions, and Anthropogenic Sources in the Lichens of Mt. Etna and Vulcano Island[a]

	substratum %	volcanic emissions %	anthropogenic %
		Etna Lichens	
71 EP	4 ± 1	24 ± 11	72 ± 11
72EP	6 ± 2	25 ± 10	69 ± 10
74 EP	7 ± 2	24 ± 10	69 ± 10
76 EP	3 ± 1	22 ± 11	74 ± 11
81 EP	1 ± 1	22 ± 12	77 ± 12
87 EP	2 ± 1	21 ± 12	78 ± 12
90 EP	2 ± 1	22 ± 11	75 ± 11
96 EP	20 ± 6	11 ± 10	70 ± 10
97 EP	3 ± 1	29 ± 10	68 ± 10
99 EP	4 ± 1	14 ± 14	83 ± 15
100EP	3 ± 1	12 ± 12	85 ± 12
		Vulcano Lichens	
5 VUP	37 ± 11	9 ± 9	54 ± 9
10 VUP	5 ± 1	63 ± 6	32 ± 6
13 VUP	12 ± 4	78 ± 2	10 ± 2
16 VUP	5 ± 1	39 ± 11	56 ± 11
17 VUP	10 ± 3	46 ± 9	44 ± 9
22 VUP	6 ± 2	23 ± 14	71 ± 14
23 VUP	3 ± 1	69 ± 6	28 ± 6
25 VUP	5 ± 2	34 ± 12	61 ± 12
38 VUP	10 ± 3	37 ± 11	53 ± 11
40 VUP	17 ± 5	36 ± 9	46 ± 9
43 VUP	16 ± 5	22 ± 12	62 ± 12
46 VUP	15 ± 5	48 ± 7	37 ± 7
48 VUP	5 ± 1	42 ± 11	53 ± 11
50 VUP	22 ± 7	25 ± 11	53 ± 11

[a] See text for details about calculation.

The contribution from volcanic emissions may be estimated by using the following set of equations

$$Pb_{volc} = Pb_{tot.} - (Pb_{subst} + Pb_{anthr})$$

$$Pb_{anthr} = Pb_{tot.} * [(^{206}Pb/^{207}Pb)_{lich} - (^{206}Pb/^{207}Pb)_{volc}]/ [(^{206}Pb/^{207}Pb)_{anthr} - (^{206}Pb/^{207}Pb)_{volc}]$$

where $Pb_{tot.}$ is the total lead content in each lichen sample; Pb_{volc} is the amount of lead derived from volcanic aerosols; Pb_{anthr} is the anthropogenic lead; and $(^{206}Pb/^{207}Pb)_i$ is the isotopic ratio measured in each lichen samples (lich), in the anthropogenic source (anthr), and in the local volcanic rocks and aerosols (volc).

To solve this system of equations, the $^{206}Pb/^{207}Pb$ ratio of the anthropogenic source is required. Pb content in lichens represents an integral of the exposure during the last 10−20 years and not a recent exposure. As previously described, the isotopic signature of anthropogenic lead has widely varied with time. Moreover as demonstrated by our aerosol samples, a wide range of isotopic composition can be observed at different Sicilian sites, even at the present time.

Thus the overall anthropogenic signature should fall in the range defined by the extreme values measured during the last 20 years (1.080−1.165), but these extreme values can only be recorded close to emission sources, while intermediate signatures should be observed in rural areas. That is why we can reasonably consider that the mean anthropogenic signature over the last 20 years was characterized by $^{206}Pb/^{207}Pb$ of about 1.135 ± 0.020. Such a range includes the value of 1.15, which was considered as representative of the average composition of Western Europe atmosphere during the 1980s (*38*−*40*), and it takes into account the recent addition of unradiogenic Pb in Italian gasoline.

Table 3 shows the contributions of the three potential sources: substratum, volcanic emissions, and anthropogenic in the lichens of Vulcano and Etna. They are also graphically

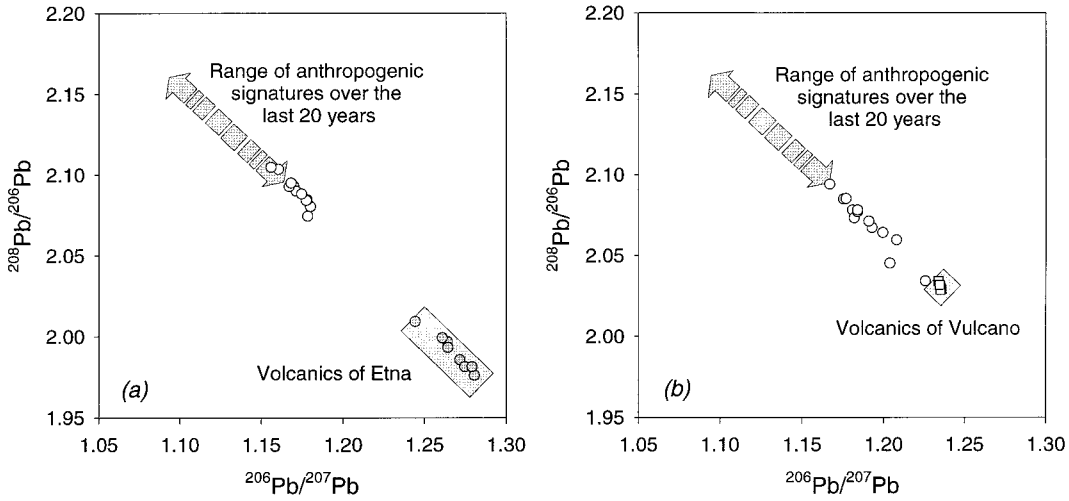

FIGURE 4. $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$ in lichens (○) from Mt. Etna (a) and Vulcano island (b). The compositional fields of the natural source and range of anthropogenic signatures over the last 20 years (dotted arrow) are also plotted for comparative purposes.

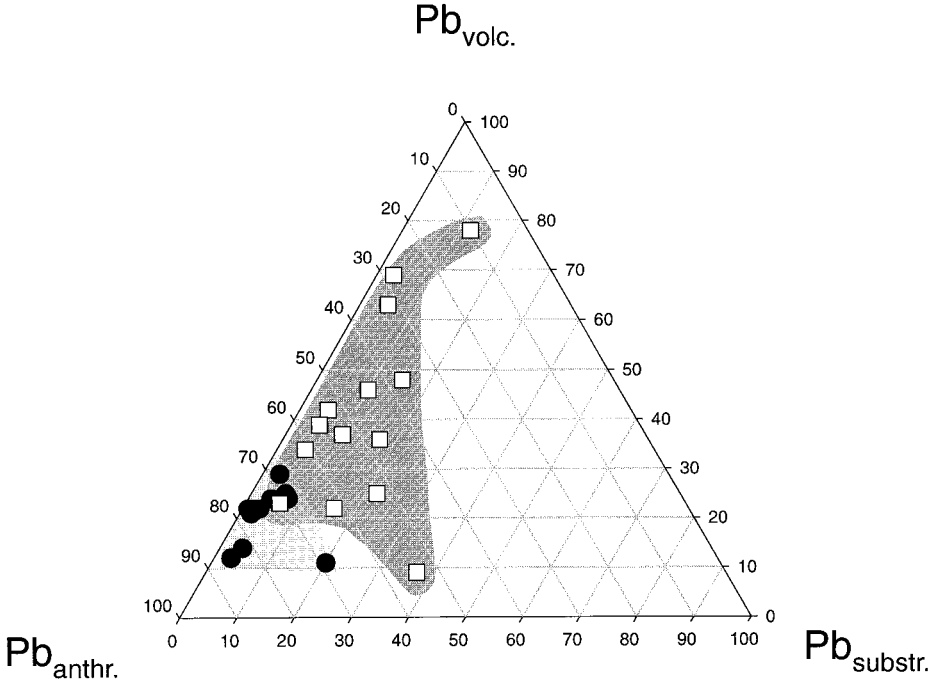

FIGURE 5. Ternary diagram representing the relative contribution of each substratum, volcanic emissions, and anthropogenic sources in lichens from Mt. Etna and Vulcano island.

expressed in the triangular plot of Figure 5. The percentages of anthropogenic lead found for lichens from Vulcano island (32−71%; av: 47%) appear lower than those from Mt. Etna (68−85%; av: 74%). This is not surprising considering the low anthropogenic activity on the island. In addition, these results reveal that volcanic activity is a significant source of lead release to the atmosphere not only during eruptive phases but also during passive (quiescent) degassing. Although Nriagu (*9*) has shown that, on a global scale, volcanoes account for less than 1% of the total emissions of lead (3300 t/y), our data strongly suggest that near volcanic areas the natural emissions are added significantly to anthropogenic activity, with the consequently increased risk level for lead accumulation in soil, grass, plants, and groundwaters.

Data presented in this paper, besides representing the first extensive series of measurements on the isotopic composition of lead in lichens and aerosols from Sicily, constitute a preliminary database for future surveys in air quality monitoring programs and in addressing decisions on remedial actions. On the basis of lead isotope composition, two anthropogenic sources are recognizable: gasoline, where lead is added as an antiknock compound, with $^{206}Pb/^{207}Pb$ ratios varying from 1.067 to 1.137 (av: 1.085), and industrial activities, releasing lead having a $^{206}Pb/^{207}Pb$ signature of about 1.14−1.16. This is consistent with the data observed in the neighboring European countries. Lichens appear to be a powerful tool for studying the complex mixing between anthropogenic and natural sources over long-term periods (up to 20 years). Finally, the ICP-MS technique, less precise than TIMS (Thermo Ionization Mass Spectrometry) but much more convenient, provides good reliability for extensive and relatively easy isotopic monitoring.

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