"RADIOACTIVITY OF MT. ETNA VOLCANO AND RADIONUCLIDES TRANSFER TO GROUNDWATER ,,

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ABSTRACT

The paper presents the results of a radiometric survey carried out on the eastern flank of Mt. Etna over an area of approximately 120 km^2. Activity concentrations of ^{238,234}U, ^{232,230,228}Th, ^{226,228}Ra, from ^{238}U and ^{232}Th decay chains, and potassium ^{40}K were determined using α- and γ- spectrometry techniques. All rock samples presented activity concentrations of U, Th and Ra isotopes ranging from 20 Bq kg^{-1} to about 90 Bq kg^{-1}, and they showed no particular compositional variations over the investigated area. Based on their respective elemental concentrations, the isotopic ratios of different elements were studied to check the presence of radioactive equilibrium, or disequilibrium, in the decay chains. Moreover, an attempt to calculate radionuclide transfer factors from soil to water was made, and the radiological risk resulting from ingestion of these isotopes contained in drinking water was calculated. The results were compared with current regulations on the quality of drinking water.

1. INTRODUCTION

The area under investigation is located in the eastern flank of Mt. Etna volcano (Sicily, Italy) (Figure 1). Mt. Etna was built up during the last 540.000 years by the alternate superimposition of lava flows and pyroclastic deposits [Romano, 1982; Chester et al., 1985; Branca et al., 2011] and its edifice grew over a sedimentary substratum whose thickness is greater than 15 km [Cristofolini et al., 1979]. The source of Mt. Etna magmatism is presumably connected with voluminous mantle melting, likely resulting from the suction of asthenosphere material induced by backward rolling of the subducting Ionian crustal slab [Gvirtzman and Nur, 1999]. The structure of Mt. Etna is constituted by several nested strato-volcanoes [Condomines et al., 1995; Branca et al., 2011] that, as well as many other coeval small eruptive centers, grew on a lava plateau of tholeiitic/transitional composition produced by fissural eruptions some 0.5 Ma ago [Gillot et al., 1994; Corsaro & Cristofolini, 1997]. The
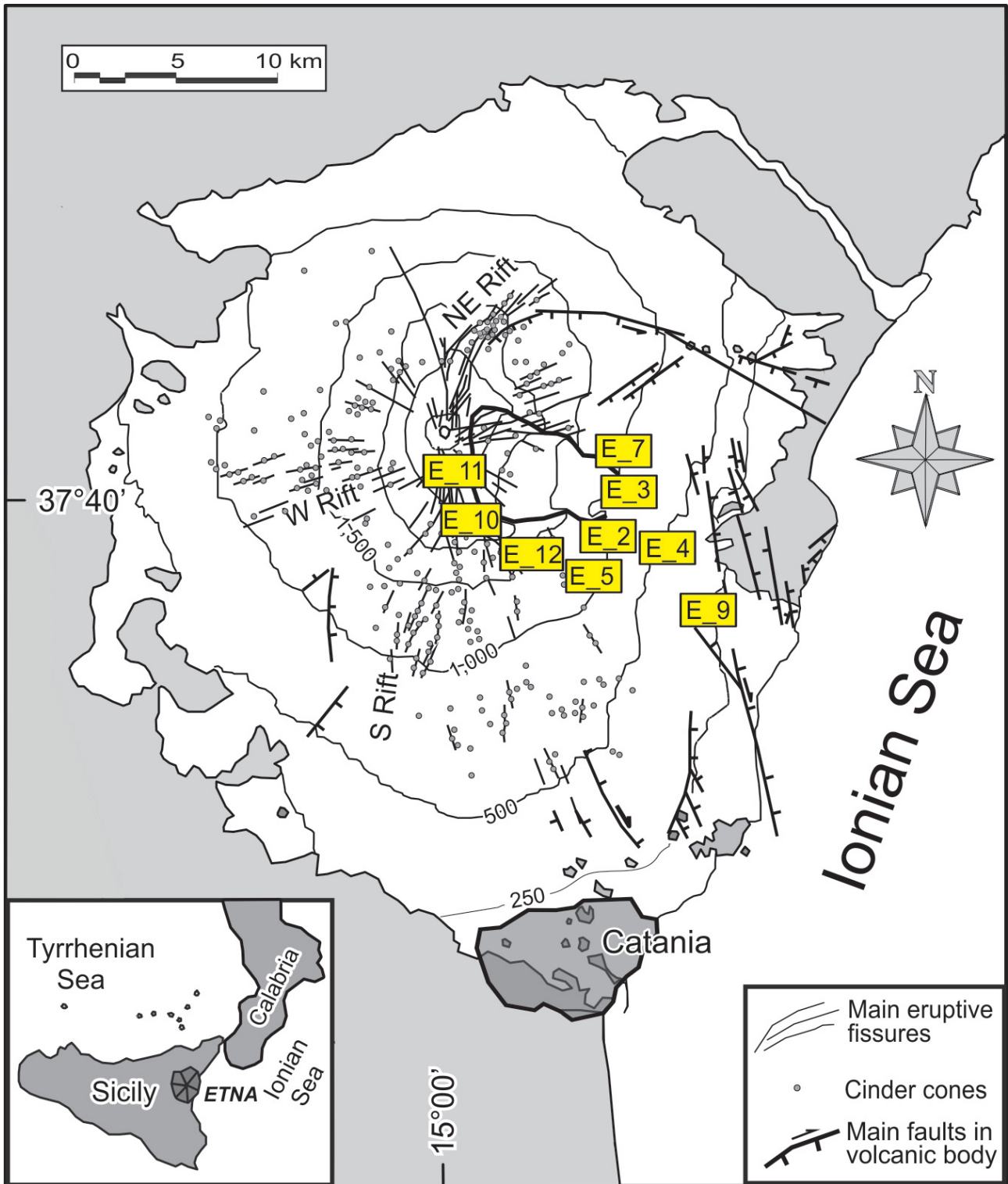
FIGURE 1. Study area and sampling sites (sites names as in Kozłowska et al., 2009). The white area delimits the outcrops of vol-canic products of Mt. Etna. The three main rift zones (NE Rift, W Rift and S Rift, correspondingly) are also shown. Volcano–tectonic data of Mt. Etna modified from Acocella and Neri (2003). Altitudes in meters above sea level.

post-plateau volcanic products, emitted through an al-most continuous eruptive activity, show a composition ranging from picritic and alkali basalt to trachytes, with mugearites and hawaiites as dominant products [Cristo-folini and Romano, 1982; D'Orazio, 1995]. The predom-inance of hawaiitic rocks in the recent activity of Mt. Etna can be explained mainly as a result of fractiona-tion/mixing processes affecting a primary picritic

magma in a relatively deep magma reservoir [Armienti et al., 1996]. Both the existence and the location of this reservoir beneath Etna are derived largely from seismological data [Sharp et al., 1980; Aloisi et al., 2002].

Magmatic activity in southern Italy has produced huge volumes of volcanic rocks with large concentrations of radioelements that often are characterized by high levels of environmental radioactivity. This was clearly evidenced by specific measurements carried out in the southern Tyrrhenian Sea and, [Chiozzi et al., 2001; 2003] in terms of the radioactive elements content the erupted lavas of Mt. Etna are instead different from the other Tyrrhenian volcanoes, with the exception of Stromboli Island [Capaldi et al., 1976], indicating that the magmas erupted by the two volcanoes share similar pre-eruption histories.

On Mt. Etna, the area that we investigated in this paper showed a rather uniform chemical composition of the outcropping volcanic products. As expected, the lavas found there were mostly alkali-basalts and hawaiites [Le Maitre, 1989].

The radioactive content in the Mt. Etna rocks has been little investigated so far, with only a few studies concerning U/Th contents [Capaldi et al., 1976; Condomines et al., 1982, 1987, 1995; Villemant et al., 1993]. In a previous work [Kozłowska et al., 2016], we determined γ background levels coming from radium isotopes in the rocks surrounding some water intakes. In this paper, we present the results of α– and γ–spectrometry measurements in the rock samples collected near water samplings sites. We focused on the activity concentrations of uranium and thorium and their daughter radium isotopes. In order to carry out our measurements, we applied two different nuclear spectrometry techniques.

2. SAMPLING SITES AND MEASUREMENT TECHNIQUES

Our investigation consisted in collecting samples of volcanic rocks from the eastern flank of Mt. Etna, over a surface of approximately 120 km^2. The geology of this area is composed exclusively of Etna's volcanic rocks, essentially represented by lava flows belonging to the so-called Stratovolcano Supersynthem [57 ka to present, according to Branca et al., 2011]. Nevertheless, some minor volcanic outcrops belong to the Timpe Supersynthem, which began to develop some 220 ka ago [Branca et al., 2011]. It should be noted that all our collected samples of volcanic rocks belong to the former.

Eight rock samples were collected and analyses of radioactivity were carried out. Fig. 1 presents the area

under investigation and the sampling sites. The first five samples were collected in proximity of the water intakes from which water samples were taken for a radioactivity performed in earlier studies [Kozłowska et al., 2016]. The samples are representative of the average rock type of the aquifers. Rock samples E_2, E_7 and in particular E_11 were collected from some of the oldest lavas outcropping in the eastern flank of the volcano [86 ka to 3.9 ka, Branca et al., 2011].

The collected rock samples were transferred to the laboratory, where they were characterized, then dried, crushed and reduced to fractions smaller than 0.2 mm for homogenization. From each sample of about 1 kg of dry mass prepared for γ-spectrometry, two separate sub-samples of 5 g each were additionally selected and sent for α-spectrometric measurements.

γ-spectrometry measurements were carried out in two laboratories, in Catania and in Katowice, in Marinelli geometry, using 0.6 dm^3 containers, where the rock samples were sealed for 30 days in order to allow for secular equilibrium in the uranium series. Activity concentrations of ^{226}Ra, ^{232}Th(^{228}Ac) and additionally ^{40}K in the collected samples were determined using HPGe gamma spectrometers (ORTEC Company) and NORM (Naturally Occurring Radioactive Materials) standards prepared by the Central Laboratory for Radiological Protection from Warsaw, Poland, with known activities of the same isotopes. The details concerning the data acquisition programs and the choice of spectral lines for ^{226,228}Ra and ^{40}K analyses are given by [Kozłowska et al., 2016]. Additionally, using γ-spectrometry technique, the ^{234}Th isotope content was determined based on the low energy 63.41 keV spectral line. Efficiency calibrations and analyses of spectra were performed based on the reference material IAEA-RGU-1 [IAEA, 2002]. This material was prepared by means of dilution of a uranium ore (7.09% U) and a thorium ore (2.89% Th, 219 µg U/g) with floated silica powder of similar grain size distribution, respectively. Uranium, ^{226}Ra and ^{210}Pb standard is in radioactive equilibrium. Measurements of the samples lasted from two to nine days due to low thorium ^{234}Th gamma line absolute emission probability (3.75%). The measurement time was strictly dependent on the activity of each sample.

The determination of ^{234,238}U and ^{232,230,228}Th was performed with the use of α – spectrometer 7401VR (Canberra – Packard, USA). The spectrometer was equipped with the Passivated Implanted Planar Silicon (PIPS) detector with a surface area of 300 mm^2. For uranium and thorium analyses, a standard of known ^{232}U and ^{229}Th activity was added to 5 g samples selected at

the beginning of each analysis. The wet mineralization of the samples was performed with the use of hot acids: HF, HNO_3, HCl with H_3BO_3. Uranium and thorium were pre-concentrated with iron and co-precipitated with ammonia at pH 9. In order to complete the uranium determination, the precipitate was dissolved in 8M HCl and then transferred to the anion exchange resin Dowex 1×8 (Cl⁻ type, 200-400 mesh) conditioned with 8M HCl. The separation of uranium from other α – radionuclides which could be present in the investigated samples was performed based on a procedure developed by Soumela (1993). Uranium was eluted with 0.5 M HCl. In order to determine the thorium content, the precipitate was dissolved in 8M HNO_3 and then transferred to the anion exchange resin Dowex 1×8 (Cl⁻ type, 200-400 mesh) conditioned with the same acid. The thorium fraction was eluted with 10M HCl. Thin α sources were prepared from uranium and thorium fractions by co-precipitation with NdF_3 (Sill, 1987). The sources were measured over a period of 1 – 2 days. Minimum Detectable Activity (MDA) was equal to 0.5 mBq L^{-1} for all uranium and thorium isotopes. The chemical recoveries varied from 50% to 80%. The method for uranium determination was tested during an inter-calibration experiment organized by IAEA in 2010. The applied methods for uranium and thorium determination in soil/rock samples were tested using IAEA-434 and IAEA-375 reference materials (IAEA, 2002).

It can be noted that the isotopes of interest are the major source of terrestrial NORM. Starting from uranium ^{238}U decay chain, measurements of ^{214}Bi, ^{214}Pb involve γ analysis and provide information on the ^{226}Ra content, taking account of the fact that radioactive equilibrium is established in this part of the chain after about one month. The parent nuclide ^{238}U cannot be determined with this type of spectrometry, although it is a common practice to assume radioactive equilibrium in the chain in order to assess its content. However, some authors acknowledge that significant disequilibrium in the ^{238}U series is common in rocks younger than 1 million years and results mainly from the relative mobility of ^{238}U itself and its decay products ^{234}U, ^{226}Ra, and ^{222}Rn [Chiozzi, 2001]. Performing measurements using separate α-semi-conductor spectrometry of the solid samples may produce precise information on these α-radioactive elements.

On the other hand, thorium is an element scarcely soluble in water, thus the ^{232}Th series may be with high probability considered in radioactive equilibrium in most geological environments. Its daughter ^{228}Ra can be evaluated using γ spectrometry by measuring, for instance, the lines of ^{228}Ac or ^{212}Pb in γ–spectrum.

3. RESULTS AND DISCUSSION

3.1 RADIOACTIVITY CONTENT IN VOLCANIC ROCKS

The results of the analyses of the volcanic rocks collected in the present survey for the detection of radionuclides are shown in Table 1. The symbols in parenthesis, (α) or (γ), indicate the type of nuclear spectrometry technique adopted to obtain the results. The values of the activity concentrations of all measured radionuclides, except ^{40}K, were in a range from 24±4 Bq kg^{-1} (for ^{238}U) to 91±9 Bq kg^{-1} (for ^{232}Th). None of them exceeded 100 Bq kg^{-1}. Conversely, ^{40}K values ranged from 331±15 Bq kg^{-1} to 725±35 Bq kg^{-1}.

The results in Table 1 are presented in order of appearance of elements in the two radioactive decay chains (i.e. thorium and uranium-radium), respectively. The first three columns present the results for the thorium chain ^{232}Th – ^{228}Ra(^{228}Ac) – ^{228}Th, whereas columns 4 – 8 show the results for the uranium-radium chain ^{238}U – ^{234}Th – ^{234}U – ^{230}Th – ^{226}Ra.

The specific activity of ^{232}Th ranges from 37±6 to 91±9 Bq kg^{-1}, while ^{228}Ra ranges from 26±2 to 75±2 Bq kg^{-1} and ^{228}Th from 37±5 to 85±4 Bq kg^{-1}. The results show lower radioactivity than that in the Aelian Islands rocks investigated by Brai et al. [2002], by Chiozzi et al. [2001; 2003] and Brai [1995].

The concentrations of nuclides of the ^{238}U decay series range from 24±4 to 66±8 Bq kg^{-1} (^{238}U), 20±15 to 51±11 Bq kg^{-1} (^{234}Th), 26±4 to 63±8 Bq kg^{-1} (^{234}U), 24±6 to 83±4 Bq kg^{-1} (^{230}Th) and 45±2 to 85±4 Bq kg^{-1} (^{226}Ra). Higher uncertainties in the ^{234}Th results obtained for some of the samples were due not only to the small masses of samples available for low-energy γ-spectrometric measurements, but also to the low activity concentrations of the investigated thorium isotope. Both uranium and other thorium isotopes were analyzed with the use of α-spectrometry, since in this case 5 g samples were enough to obtain low uncertainty levels even for low-activity samples. Radium isotopes analyses were carried out in a previous investigation [Kozłowska et al., 2016]. The study revealed that the activity concentrations of ^{226}Ra and ^{228}Ra (^{228}Ac) found in the rocks of the eastern flank of Mt. Etna were of the same order of magnitude as the European average values found in bedrock, i.e. between 10 and 50 Bq kg^{-1} [IARC, 1988]. Moreover, all activity concentrations obtained for the studied isotopes from the uranium-radium chain also point to lower concentrations alkali-basaltic rocks.

Table 2 presents activity concentration ratios calculated for selected isotopes. In the first column, the ^{232}Th/^{238}U ratios of the protoplasts of two radioactive

Sample code	Sample characteristics	^{232}Th (α) [Bq kg^{-1}]	^{228}Ra (γ) [Bq kg^{-1}]	^{228}Th (α) [Bq kg^{-1}]	^{238}U (α) [Bq kg^{-1}]	^{234}Th (γ) [Bq kg^{-1}]	^{234}U (α) [Bq kg^{-1}]	^{230}Th (α) [Bq kg^{-1}]	^{226}Ra (γ) [Bq kg^{-1}]	^{40}K (γ) [Bq kg^{-1}]
		1	2	3	4	5	6	7	8	9
E_2	Rocks from the vicinity of Valle S. Giacomo intake (age = 86 ka)	75±5	74±2	77±3	66±8	41±5	63±8	69±2	62±3	617±20
E_4	Lava and soil close to Primoti well (700 AD)	91±9	75±2	85±4	37±4	51±11	36±4	83±4	76±4	716±20
E_5	Rocks from the vicinity of Ilice well (1634 AD)	49±8	41±2	54±5	26±4	27±5	27±4	48±5	57±4	360±20
E_7	Rocks from the vicinity of Fornazzo well (age = 15 ka-3.9 ka)	37±6	45±2	37±4	27±4	24±4	26±4	36±4	61±4	445±20
E_9	Rocks from the vicinity of Guardia well (age = 3.9 ka-2ka)	48±5	68±3	61±3	35±5	28±4	36±6	53±3	85±4	725±35
E_10	Lava from La Montagnola crater (1763 AD)	41±13	29±1	58±10	25±3	25±5	27±4	24±6	45±2	331±15
E_11	Lava from Piano del Lago (age = 15 ka-3.9 ka)	48±5	48±2	61±3	40±6	28±5	41±6	52±3	46±3	421±15
E_12	1792 AD lava flow	41±8	26±2	37±5	24±4	20±15	27±4	46±5	62±4	558±20

TABLE 1. Activity concentrations, in [Bq/kg], of radioisotopes representing the beginning of two radioactive decay chains: thorium ^{232}Th – ^{228}Ra(^{228}Ac) – ^{228}Th and uranium–radium ^{238}U – ^{234}Th – ^{234}U – ^{230}Th – ^{226}Ra and ^{40}K in the investigated rock/soil samples. The type of spectrometry used is presented in parenthesis. The nomenclature of sampling sites is consistent with that of Kozłowska et al. [2016]. The age of the samples is also indicated next to the sample name.

series are presented. The obtained values were in the range from 1.1±0.2 (E_2 sample) up to 2.5±0.3 (E_4 sample), with a mean value of 1.5 and median of 1.2.

In normal radioactivity magmatic rocks, the Th/U ratio varies in a range between 2.5 and 4.5 [Plewa and Plewa, 1992]. Like Th/U, the obtained variability of ^{232}Th/^{238}U ratios indicate low radioactivity rocks. Invariability of Th/U ratio is usually related to the similarity of the characteristics of both elements in magmatic environments, i.e. under conditions of high pressure, high temperature and absence of oxygen. Under these conditions, both elements are in IV-valence state, have similar ion radius and may replace each other in minerals. Conversely, under other environmental conditions, the physical-chemical properties

of thorium and uranium are quite different. Furthermore, given that the analyzed samples are mainly from rocks that act as groundwater reservoir, the obtained ^{232}Th/^{238}U ratios may also indicate that uranium was leached by water, so the equilibrium conditions would be unsettled in the magmatic rocks. However, since different isotopes of both elements are present in the uranium-radium decay series, one may carefully assume that the isotopes in this chain may exist in a disequilibrium state.

The results in the ^{232}Th decay series are relatively easy to interpret. The values of the activity ratio ^{228}Th/^{232}Th, ranging from 0.9±0.1 to 1.4±0.5 denote secular equilibrium established between the isotopes. Thorium in the lava erupted from the volcano stays in

Sample code	^{232}Th (α)/^{238}U (α)	^{228}Th (α)/^{232}Th (α)	^{226}Ra (γ)/^{238}U (α)	^{234}U (α)/^{238}U (α)	^{230}Th (α)/^{234}Th (γ)	^{226}Ra (γ)/^{230}Th (γ)
	2	3	4	5	6	7
E_2	1.1±0.2	1.0±0.1	0.9±0.1	1.0±0.2	1.7±0.2	0.9±0.1
E_4	2.5±0.4	0.9±0.1	2.1±0.3	1.0±0.2	1.6±0.4	0.9±0.1
E_5	1.9±0.4	1.1±0.2	2.2±0.3	1.0±0.2	1.8±0.4	1.2±0.2
E_7	1.4±0.3	1.0±0.2	2.3±0.4	1.0±0.2	1.5±0.3	1.7±0.2
E_9	1.4±0.3	1.3±0.2	2.4±0.4	1.0±0.2	1.9±0.3	1.6±0.1
E_10	1.6±0.6	1.4±0.5	1.8±0.3	1.1±0.2	1.0±0.3	1.9±0.5
E_11	1.2±0.2	1.3±0.2	1.2±0.2	1.1±0.2	1.9±0.4	0.9±0.1
E_12	1.7±0.4	0.9±0.2	2.6±0.4	1.1±0.2	2.3±1.7	1.3±0.2

TABLE 2. Activity ratios in the investigated rock samples (the nomenclature of sampling sites is consistent with that of Kozłowska et al., [2016].

the rock and is not leached by water flowing through the ground or on the surface. Any ^{228}Ra isotope present in this chain does not change the equilibrium state. These results confirm the presence of equilibrium in the thorium series in magmatic rocks noted also by other authors [Condomines et al., 1995].

The ^{238}U decay series is, instead, more difficult to interpret. In most cases, the order of abundance of radionuclides is as follows: ^{226}Ra>^{230}Th>^{234}U=^{234}Th=^{238}U. The values of the isotopic ratio ^{226}Ra/^{238}U (Table 2, column 4) were in the range from 0.9±0.1 (E_2 sample) to 2.6±0.4 (E_12), with mean of 1.93 and median equal to 2.1. Considering the isotopes of the radioactive chain one by one, we observed that the ^{226}Ra content was slightly higher than that of ^{230}Th (mean value of 1.3), and that ^{230}Th was on average 1.5 times higher than ^{234}U and ^{238}U. Both uranium isotopes were in a state of equilibrium, with isotopic ratio equal to 1 for all samples. Moreover, the ^{230}Th content was on average 1.7 (median of 1.9) times higher than that of the ^{234}Th isotope present in between two uranium isotopes (Table 2).

Based both on previous studies [Kozłowska et al., 2016] and the results of the present investigation, it can be concluded that the magmatic rocks of Mt. Etna have favorable conditions for uranium leaching by water, whereas thorium and radium act as immobile el-

ements, and thus remain in the host rocks of the aquifer. This is in part supported by the general low radium activity in the ground water of Mt. Etna observed in the previous studies [D'Alessandro and Vita, 2003; Kozłowska et al., 2009]. Regrettably, this hypothesis is difficult to test given the fact that MDA for ^{226}Ra in water determined with the use of liquid scintillation technique in our previous studies was as high as 10 mBq L^{-1} (or, for smaller sample volumes, even 40 mBq L^{-1}), whereas for ^{234,238}U (analyzed with alpha spectrometry in the present studies) MDA was equal to 0.5 mBq L^{-1}. However, one previously analyzed ground water sample from site E_6 seems to support this hypothesis. The radium content in this water sample was <10 mBq L^{-1} [Kozłowska et al. 2016], whereas that of ^{238}U was equal to 70 mBq L^{-1} (^{234}U = 78 mBq L^{-1}), which may prove the main hypothesis.

This assumption is supported by the fact that the ^{232}Th/^{238}U ratio in our samples was on average equal to 1.5 (Table 2), and in all samples it was higher than the pristine ratio in the magmatic rocks at their formation (which is equal to 1, due to the similarity in the radius of Th and U atoms). By considering that the magmatic formation of those elements precede eruption processes, the deficit of uranium in the erupted rocks is likely caused by its removal from the rocks due
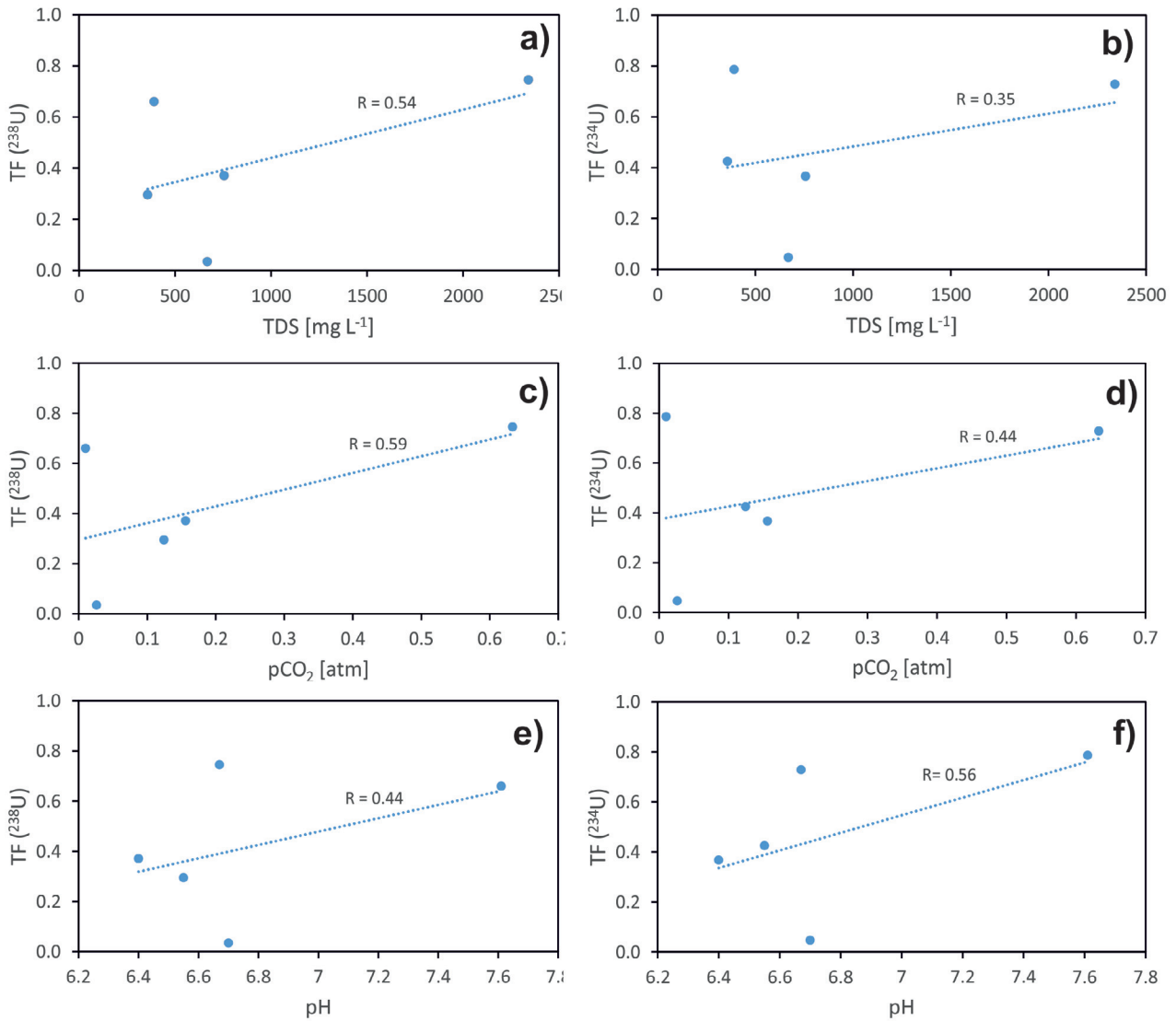
FIGURE 3. Correlation between ^{238,234}U TF values and a,b) TDS, c,d) pCO$_2$, e,f) pH in the sampled waters of Mt. Etna. The best-fit lines for each pair of parameters and the respective values of Pearson correlation coefficients (R) are also shown.

to its leaching by water. The low radium activity in the groundwater of Mt. Etna was explained by the low affinity of this element for the aqueous environment, as radium tends instead to remain in the host rocks of the aquifers [Kozłowska et al., 2016].

These investigations show that the isotopic ratios in the considered radioactive decay chains are often different than 1, and hence the equilibrium state cannot be assumed in our samples from Mt. Etna. The samples that are several hundred thousand years old show radioactive isotopes compositions that cannot be interpreted without taking into account environmental factors. Therefore, the assumption of isotopic equilibrium for old lavas does not hold true and the calculation of the pristine uranium or thorium contents via γ

spectrometry based on the radionuclides at the end of the decay chains (i.e., bismuth, polonium or lead isotopes) is not correct. Isotopic fractionation could be investigated in young lava samples, which would clearly cause experimental difficulties.

3.2 RADIONUCLIDES TRANSFER FROM ROCKS TO GROUNDWATER

The assessment of radionuclides transfer from rocks to ground water was performed based on the present investigation and on the results of groundwater analyses presented in previous studies.

Radioactivity of groundwater is mainly influenced by the physical and chemical characteristics of the reservoir rocks. A higher radioactivity level of water

may reflect a higher abundance of radioactive minerals.

A Transfer Factor (TF) can be introduced as a parameter that quantitatively describes radionuclides penetration into the environment, like, for example, from soil to plants, or from soil – through plants – to animals. A large research literature exists on the transfer of radionuclides between different elements of an ecosystem. Most often, nonetheless, it refers to radionuclides transfer from soil to plants, mainly regarding ^{137}Cs and ^{90}Sr, or sometimes transuranium elements [Wang et al.l 1996, Koehler et al., 2000, Uchida et al., 2000, Mietelski 2003, Baeza & Guillen, 2006].

The penetration of cesium and strontium to plants was discussed in detail in a publication of the International Atomic Energy Agency [IAEA, 2001]. The quoted TFs obtained for cultivated plants by different laboratories worldwide vary in the range from 10^{-1} to 10^{-4}, although larger values (up to TF = 22) were also obtained on some occasions [IAEA, 2001]. Moreover, TF may also be defined as the ratio between the activity concentration in dry mass of crop and the activity concentration of the corresponding dry soil collected from its top (10-20 cm) layer, both activities being likewise expressed in [Bq kg^{-1}].

In the studied case, TF measures the penetration of a certain radionuclide from aquifer rocks to ground water. Thus, TF may be defined as the ratio between the specific activity of a given isotope in water, A_{wat}, and its activity in the reservoir rocks, $A_{rock.}$. TF is dimensionless, as both the activity concentrations are expressed in [Bq kg^{-1}]. A_{wat} can be expressed as the activity per kg of total dissolved solids (TDS), i.e. the activity of the solid mass of material dissolved in one liter of water.

So far, data of TFs from aquifer rocks to groundwater were never published. This is presumably due to the fact that in this case TF is not so easy to determine as in the case of soil-to-plant nuclide transfer. The results of the rock-to-water TF values for ^{238,234}U uranium in the investigated area are presented in Table 3. Activity concentrations of water samples expressed in [Bq L^{-1}] were converted into [Bq kg^{-1}] of TDS dissolved in 1L of water. The values of TFs are from 0.03$\pm$0.01 to 0.75$\pm$0.10 for ^{238}U and from 0.05$\pm$0.02 to 0.79$\pm$0.19 for ^{234}U. All TF values obtained were in the order of 10^{-1} to 10^{-2}, which implies either strong binding of the radioactive elements to the rock minerals, or alternatively, that water is not actively dissolving the material. It can be noted that the reservoir rocks are all volcanic with relatively homogenous elemental content. Since the previous studies emphasized that the type of soil is one of the dominant factors influencing soil-to-plant radionuclide movement [Twining, 2004], one can apply that conclusion to water as well. Evidently, Etna's volcanic rocks provide

the soil environment with radioactive elements which seem relatively unaffected by leaching from local ground water.

Table 3 also presents activity concentrations of ^{238,234}U in five rock types surrounding five water intakes, i.e. E_2, E_4, E_5, E_7, E_9. It can be observed that the results of the analyses of our rock samples present radioactive levels in a similar order of magnitude, implying that the types of volcanic rocks in the water reservoirs are not very diverse in their radioactive content. The same observation also applies to water samples whose analytical results are close to each other. The mean ^{238}U activity concentration of five rocks is 38.2$\pm$7.3 Bq kg^{-1} while for five water samples it is 13.7$\pm$4.3 Bq kg^{-1}, with a mean TF value of 0.36$\pm$0.13. The average TF value calculated from the TF values of each sample is 0.42$\pm$0.13. Concerning ^{234}U, the mean activity concentration is 37.6$\pm$6.7 Bq kg^{-1}, whereas in water samples it is 14.9$\pm$4.0 Bq kg^{-1}; the mean TF is, therefore, equal to 0.40$\pm$0.13 and the average TF value calculated from the single TF values for each sample was equal to 0.47$\pm$0.13. These overlapping values indicate the relatively homogenous elemental content of the reservoir rocks.

Among the factors that may affect the rock-to-water TF, the most important were found to be TDS, partial pressure of dissolved CO_2 (pCO_2) and pH values of ground water. The relationship between the obtained TF values in some of the sites in the study area (i.e., only those located in the east flank of Mt. Etna) and the above chemical factors measured in the ground water collected near the same sites [data from Kozłowska et al., 2016] is apparent when computing the Pearson correlation coefficient (R) among them. Figure 2 shows the correlations that we have found in the studied sites, considering either ^{238}U or ^{234}U for the computation of TF. All correlations were positive, with 0.3>R>0.6. In some cases, such as TF(^{238}U) vs. TDS, TF(^{238}U) vs. pCO_2 and TF(^{234}U) vs. pH, the correlations were much higher (0.5>R>0.6). The correlations between TDS or pCO_2 and TFs show that the lower values of those chemical factors correspond to smaller TFs. In the case of the pH - TF correlation, lower pH values, that is more acidic water, correspond to a weaker transfer of uranium isotopes from rock to water. Although uranium is generally soluble in water more preferably at low pH values, it was found that in the Mt. Etna ground water this element can be scavenged, for example, by iron oxyhydroxides [Aiuppa et al., 2000]. Actually, in the pH range between 5 and 8 the uranyl ion (UO_2^{2+}), which is the most common U(VI) species, is strongly adsorbed by iron minerals such as hematite, goethite and amorphous

Rock sample	Water intake	TDS* [mg/L]	pCO_2*	pH*	Awat [mBq L^{-1}] ^{238}U*	Awat [Bq kg^{-1}] ^{238}U*	Arock [Bq kg^{-1}] ^{238}U	TF ^{238}U	Awat [mBq L^{-1}] ^{234}U*	Awat [Bq kg^{-1}] ^{234}U*	Arock [Bq kg^{-1}] ^{234}U	TF ^{234}U
E_2	S. Giacomo intake	668	0.026	6.7	1.5±0.5	2.3±0.7	66±8	0.03±0.01	2.0±0.6	3.0±0.9	63±8	0.05±0.02
E_4	Primoti well	2340	0.633	6.67	64.5±5.1	27.6±2.2	37±4	0.75±0.10	61.4±4.9	26.2±2.1	36±4	0.73±0.10
E_5	Ilice well	357	0.1244	6.55	2.8±0.6	7.8±1.7	26±4	0.30±0.08	4.1±0.8	11.5±2.2	27±4	0.43±0.10
E_7	Fornazzo well	391	0.01	7.61	6.9±1.3	17.7±3.3	27±4	0.66±0.16	8.0±1.5	20.5±3.8	26±4	0.79±0.19
E_9	Guardia well	756	0.156	6.4	9.8±0.8	13.0±1.1	35±5	0.37±0.06	10.0±0.8	13.2±1.1	36±6	0.37±0.07

*Data from [Kozłowska et al., 2016]

TABLE 3. Rock–to–water TF values for ^{238}U and ^{234}U uranium isotopes in the eastern flank of Mt. Etna. The nomenclature of the sampling sites is consistent with that of Kozłowska et al. [2016].

ferric oxyhydroxide [Langmuir, 1978; Hsi and Langmuir, 1985]. This process is promoted particularly under reducing water conditions, which are typical of many aquifers of the eastern flank of the volcano [Giammanco et al., 1998; Aiuppa et al., 2003, 2004].

3.3 EFFECTIVE DOSE

Activity concentrations of water samples collected from intakes around the whole Mt. Etna volcano were analyzed in the last ten years [Kozłowska et al., 2009; Kozłowska et al., 2016]. In summary, results for 20 water intakes, some of them re-sampled several times are available from previous studies. Only one, collected near our rock sample E_2, exhibits activity concentration of radium isotopes slightly above MDA, but that water is not used for human consumption. The activity of ^{226}Ra in this water sample is 12±1 mBq L^{-1} and that of ^{228}Ra is 22±9 mBq L^{-1}. The same sample shows also the lowest ^{234}U and ^{238}U isotopes, the lowest values (2.0±0.4 mBq L^{-1} and 1.6±0.3 mBq L^{-1}, respectively). All the other samples showed activity concentrations below MDA (10 mBq L^{-1} for ^{226}Ra and 20 mBq L^{-1} for ^{228}Ra). The highest values were obtained at a public water intake on the NE flank of Mt. Etna (San Paolo well): 78.6±5.7 mBq L^{-1} and 70.1±5.1 mBq L^{-1} for ^{234}U and ^{238}U, respectively.

The average value of ^{234}U, calculated from all the results, is 24.0±5.1 mBq L^{-1}, whereas the median value was equal to 12.9 mBq L^{-1}. For ^{238}U, the results were 23.0±5.0 mBqL^{-1} and 11.0 mBq L^{-1}, respectively. The rather homogenous elemental content of the studied isotopes both in the water samples and reservoir rocks as well as the consequent stable TF values lead to conclude that this level of radioactivity can be expected all around the Mt. Etna volcano. Both the World Health Organization and the Environmental Protection Agency estimated a consumption of 2 L of water per day per capita [WHO, 2004], which corresponds to 730 L per year. Since the main contribution to the effective radioactive dose comes from uranium isotopes and the mean activity concentration of ^{234}U and ^{238}U in the Mt. Etna groundwater is 24.0±5.1 mBq L^{-1} and 23.0±5.0 mBq L^{-1}, respectively, we can infer the annual total effective dose. If we use dose conversion factors of 4.9·10^{-8} Sv Bq^{-1} and of 4.5·10^{-8} Sv Bq^{-1} for ^{234}U and ^{238}U, respectively (WHO, 2004], the effective doses from ^{234}U and ^{238}U are equal to 0.86 and 0.76 μSv/y, respectively, that is well below the limit prescribed by WHO Guidelines (WHO, 2017) and by the Italian legislation (Decreto Legislativo del Governo del 17 Marzo 1995, n. 230: https://www.gazzettaufficiale.it/atto/serie_generale/caricaDettaglioAtto/originario?atto.dataPubblicazioneGazzetta=1995-06-13&atto.codiceRedazionale=095G0234&elenco30giorni=false).

Even considering the worst possible case - the San Paolo well - with values of 78.6 mBq L^{-1} and 70.1 mBq L^{-1} for ^{234,238}U, respectively, the corresponding calculated dose is equal to 2.8 and 2.3 μSv/y, respectively.

4. CONCLUSIONS

Radionuclides from two radioactive decay series were studied in some selected volcanic rocks of Mt. Etna. The activity ratios among radionuclides in the ^{232}Th decay series denoted the attainment of secular equilibrium, whereas in the ^{238}U chain, we observed the following order of abundance: ^{226}Ra>^{230}Th>^{234}U=^{234}Th=^{238}U, thus pointing to isotopic disequilibrium.

Long – lived isotopes of uranium and thorium decay series are mainly responsible for natural radioactivity content. We also measured ^{40}K activity in the rocks of Mt. Etna and the resulting values are on the same levels as the average European values found in bedrock.

The Transfer Factor, describing the radionuclides transfer from rocks to ground water, ranges from 0.03±0.01 to 0.75±0.10 for ^{238}U, from 0.05±0.02 to 0.79±0.19 for ^{234}U. As a whole, values varied between 10^{-1} to 10^{-2}, implying either strong binding of the radioactive elements to the rock minerals or that ground water is not efficiently leaching out the investigated elements from the volcanic rocks of the local aquifers. Mean TF values prove the assumption that the reservoir rocks are all volcanic with the relatively homogenous elemental content. Finally, the effective radiation doses due to radionuclides ingestion with drinking water were significantly below the limit of 100 μSv/year set by WHO [2017] and the limit of 1 mSv/year set by the Italian legislation.

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