Isotope Ratios in Low and High T Gases Help to Constrain Volcanic Activity: Vulcano Island.

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Introduction

Isotopé geochemistry of volcanic gases has been mainly used in recent years to better understand origin and genesis of volcanic as well natural fluids retracing and remodeling geodynamic constraint which are not clear, in some cases, using also geophysical methodologies. On the other hand, some key isotope ratios have been constantly used to try to monitor variations of volcanic activity.

So, very recently I have partly succeeded, using as a "site test" the Italian volcanic scenario, to use some isotopic parameters, namely $^3He/^4He$, $^{21}Ne/^{22}Ne$, $^{40}Ar/^{36}Ar$ and $^{13}C/^{12}C$.

The example I refer to is related to Vulcano Island [Fig.1] where volcanic gases from La Fossa crater and the Acque Calde systems were systematically collected over a period of 6 years. During this period the volcanic activity, or better to say, the thermal regime of the volcano substantially changed. Higher temperatures were observed at the crater, from 300 to 700 C, while temperature remained unchanged at the beach side (100C). At the same time chemical oscillations were also reported by different groups working on the island. So, how to use and to interpret isotopic data was our main concern in the mist of this so called "volcanic crisis".

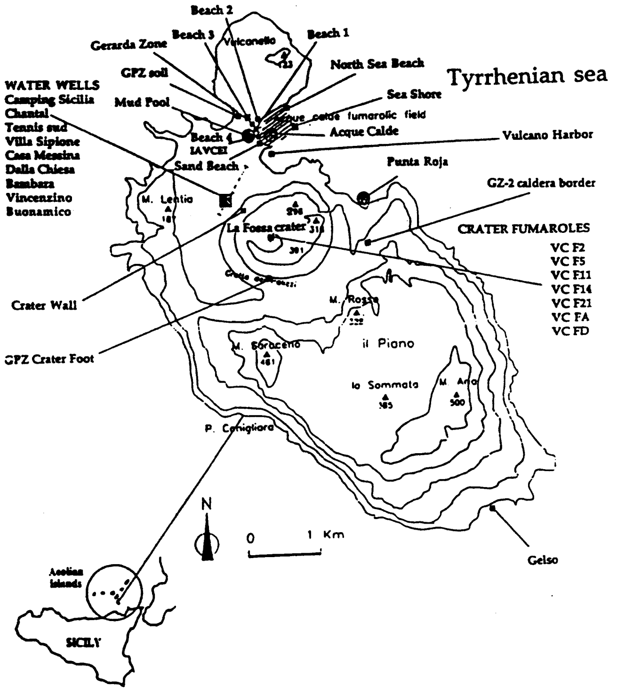

Figure 1. The 33 sites collected for this study are shown: crater, beach and submarine fumaroles, water wells, and soil gases.

The obtained results indicates with very small uncertainties: (a) origin of fluids, (b) existence of deep and more superficial reservoirs, (c) possible mixing of fluids of different origins en route to the surface, (d) constant supply from the deep reservoir(s) (e) no relation between isotopic and seismic (very low) activity and (e) no indications of a possible unrest of the volcano.

Origin.

The higher $^3He/^4He$ ratio found at Vulcano island is about 6 R/R_a. This value is 25% lower than the $^3He/^4He$ ratio of subducted-related volcanism implying that it has been probably diluted, locally, by some other crust helium (^4He). On the other hand, the $^3He/^4He$ R/R_a at Vulcano island is in the lower range of values found in mantle xenoliths from the ESCM (European Sub Continental Mantle) and close to the lowest limit of the R/R_a from island arcs. Samples were collected all over the island in order to understand how deep and superficial systems are located and related to themselves. Figure 2 shows a trend already found in Japan volcanic gases between $^3He/^4He$ and $^4He/^{20}Ne$ ratios. This figure is extremely useful because shows us (1) the sources involved in the mixing and (2) the maximum expected $^3He/^4He$ ratio from fumarolic fluids at Vulcano.

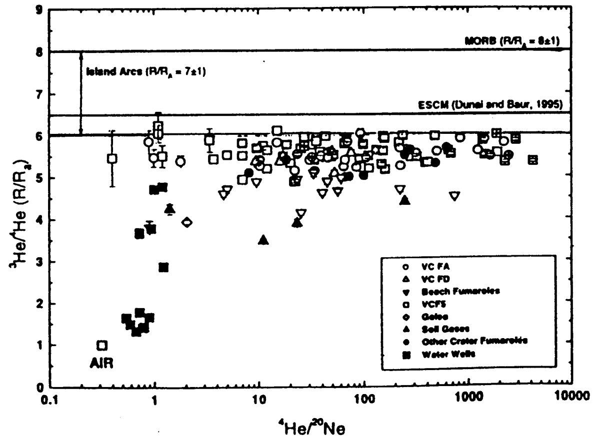

Figure 2. The $^3He/^4He$ ratio is plotted versus the $^4He/^{20}Ne$ ratio. Two end-members have been found: a surficial one, the atmosphere, with low $^4He/^{20}Ne$ and $^3He/^4He$ ratios, and a deep one, a mixing between magmatic and crustal fluids. The evolution of this trend suggests that all fumaroles are fed by a similar deep magmatic source differently contaminated by local surficial ^4He-rich sources. The error bars are often smaller than the symbol size.

Lower $^3He/^4He$ and $^4He/^{20}Ne$ ratios are related to fluids of more superficial origin; while higher ratios are related to a more magmatic, deeper or simply less diluted reservoir (a more typical ESCM or Island Arc type source), locally modified by some crust radiogenic ^4He additions.

It is reasonable to assume that the highest measured helium ratio (6.0-6.2 R_a) gives the best estimate of the $^3He/^4He$ value of Vulcano Island's source region. The heliun ratio at the crater oscillates between 4.9 and 6.2. This result means that in one case (6.2) the helium is 100%, purely magmatic, in the second case (4.9), some crust helium (^4He) should have been added to the gas rising to the surface by a ^4He-rich reservoir. The location of this reservoir must be at a depth of at least 3 km, because deep drillings have not detected crustal formations. A dyke related to the last eruption, occurred in 1888-1890, is located at about 3 Km at depth beneath the crater. This means that if any crust exists beneath Vulcano island must be at a depth lower than 3 km, probably lower than the dike itself.

The very similar $^{3}He/^{4}He$ ratios of most of the island gas emanations can be explained within a single deep magmatic source. Volcanic fluids belonging to beach and crater fumarolic systems have high to very high $^{4}He/^{20}Ne$ ratio [up to 4,000, air for comparison is 0.314], implying little or no dilution by air saturated waters. This means that the magmatic source is contaminated by a crustal, not an atmospheric, source. Figure 2 shows also that the helium ratio have attained the maximum value. In the case of volcano unrest leading to an eruptive event, it is difficult or even impossible to imagine an increase of the He ratio above the maximum ratio of 6.2 proposed in this study. Therefore the helium ratio from crater fumaroles should be carefully used as a precursors of variation of volcanic activity.

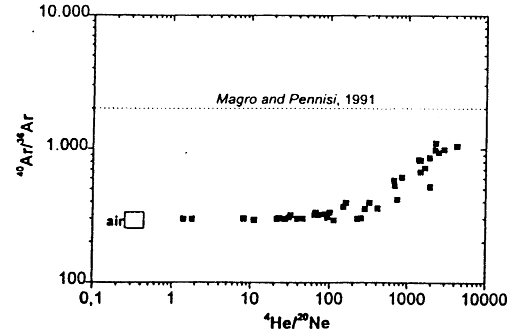

Figure 3. The $^{40}Ar/^{36}Ar$ ratio in fumarolic fluids shows a maximum of 1100. The argon ratio has been plotted together with the $^{4}He/^{20}Ne$ ratio, the maximum value found at Vulcano, 2000 [*Magro and Pennisi*, 1991]. Unfortunately, the associated $^{4}He/^{20}Ne$ ratio is not available. Lower $^{40}Ar/^{36}Ar$ratios, close to the atmospheric argon value (303 and 311), have been recently found from fluid inclusions in phenocrysts.

The $^{40}Ar/^{36}Ar$ ratio is similarly plotted with the $^{4}He/^{20}Ne$ ratio [Fig.3]. Being the argon more easily affected by air contamination, the lower values of the argon ratios should be referred to simple air contamination. The maximum value obtained 1,100-1,200 is in the range of those found from the island-arc region in Japan. If close-to-air values (300) are discarded because of collection problems during the sampling, it is possible to hypothesize that the maximum $^{40}Ar/^{36}Ar$ ratio found here at Vulcano island should be related to the least contaminated deep gas. It is still unclear if and how the $^{40}Ar/^{36}Ar$ ratio decreased from 2,000 to 300 from 1979 to 1989. On the other hand, $^{40}Ar/^{36}Ar$ ratios in fluid inclusions show air-like values (303 and 311). Air incorporation from air-rich fluids or the result of an highly degassed magma are the two possible options to explain these values. Similar to the helium ratio also the argon isotopic ratio should be used with extreme caution to forecast changes in volcanic activity.

Most of the neon isotopic ratios obtained at Vulcano island cluster close to the air value or near the mass fractionation line. There is not a likely reason why this happens, however, when not fractionated or air contaminated, our data mainly follow the trend of the crust line [Fig. 4]. Neon isotopic data from both gas and phenocrysts plotted in the lower corner of Figure 4 suggest the existence of a crustal component, responsible for high $^{21}Ne/^{22}Ne$ ratios and low $^{20}Ne/^{22}Ne$ ratios. This continental source may have different location at depth: (1) at mantle level, related to the subduction of a continental plate (the Africal plate beneath the European one) and/or (2) between the source region and the surface where crustal neon may be leaked to the fluids because of magma-crust interactions. Figure 5 shows the evolution of the $^{21}Ne/^{22}Ne$ ratio and associated $^{4}He/^{20}Ne$ ratio. The diagram shows a perfect linear correlation (0.9). It is a further evidence that samples with high $^{4}He/^{20}Ne$ ratio (up to 4,000) considered air-free are usually associated to high $^{21}Ne/^{22}Ne$ ratios. On the other hand, it is still possible that some minute air contamination at the time of the sampling cannot be ruled. In agreement with this hypothesis data obtained on fluid inclusions belonging to plagioclase and pyroxene collected at Vulcano Island, show similar, 0.039 or higher, 0.052 $^{21}Ne/^{22}Ne$ ratios.

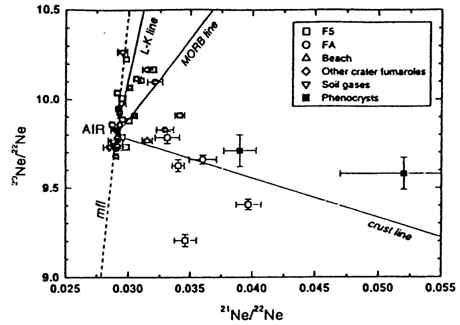

Figure 4. The three-component Ne diagram. The $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios show different trends. Most of the sample cluster close to the air value or the mass fractionation line (mfl). Three different lines have been plotted: the Kilauea-Loihi (K-L) line, the MORB line, and the crust line, in order to know which is the possible source feeding neon to this volcano. Surprisingly, part of the neon data plot near the crust line, suggesting the presence of a crustal source deeply involved in the degassing of the volcano. On the other hand, fewer neon data, if not fractionated, seem to plot between the K-L and the MORB lines. More data in the future are needed to confirm this latter trend.

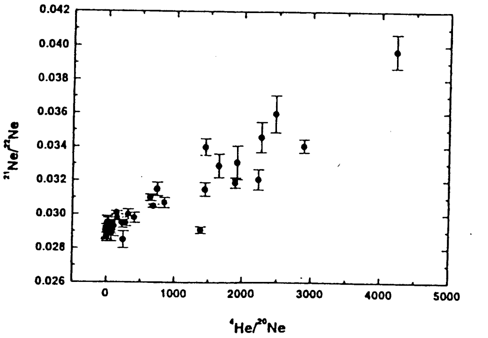

Figure 5. The $^{21}Ne/^{22}Ne$ ratio plotted versus the $^{4}He/^{20}Ne$ ratio seems to still have margin to increase, as suggested by the neon data obtained on phenocrysts. Figure 5 also clearly shows the existence of a close atmospheric end-member (lower left part) where most of the data cluster, and a deep crustal (and magmatic?) end-member (higher right part).

How the Volcano Works: Time Variations.

The continuous variation from a maximum value of 6.0-6.2 R_a to a minimum value of 4.9 R_a is likely to be due to mixing with a ^{4}He-rich source (Fig. 6). Superficial air-saturated waters seem to be excluded because of the high ^{4}He/^{20}Ne ratios. On the other hand, magma chamber aging (the dyke intrusion), roof foundering and an associated elevated geothermal gradient are expected to contribute a significant radiogenic component, partially diluting the mantle signal. It is suggested that the large oscillations derive from a magmatic pulse, a kind of *"volcano breath"*. The period between two different phases (positive or negative peaks) seems to be constant witha duration of two years. The oscillation of the He ratio has been observed at the two fumaroles (F5 and FA) collected at La Fossa crater, although not always synchronous. This differemce has vanished with time.

The existence of two different phases.

Chemical and isotopic analysis of fumaroles discharges appear to show two distinct phases of behavior, each associated to its own geochemical and isotopic signature. Phase (a) has low sulphur, CO_2, N_2 and ^{3}He/^{4}He (4.9 R_a) and a higher proportion of steam, consistent with a higher input of "surficial" materials. Phase (b) is higher in sulphur, CO_2, N_2 and ^{3}He/^{4}He (up to 6.2 R_a) and a lower proportion of steam, consistent with with high degassing of a deep, more juvenile source. The variations may be created by periodic release of fluids from a gas vapor accumulation zone somewhere beneath the crater region. Such a mechanism has been proposed to explain transients in the gas chemistry of fumaroles at Nevado del Ruiz. At Vulcano, variations in the ^{3}He/^{4}He may be caused by a periodic breach of a gas accumulation chamber when the pressure of deep fluids (P_{df}) exceeds that of the pore fluid in the roof zone (P_r). This would result in transport of ^{3}He/^{4}He-rich gas to surficial ^{4}He-rich material. So it is likely that the observed increase of ^{3}He/^{4}He ratio may reflect an increasing proportion of the deep gas relative to the ^{4}He-rich surficial component.. With time this proportion would decrease as the deep chamber is slowly emptied, causing a return to a surface-dominated ^{4}He-rich character to the fumaroles. However, this is not the only possible way of changes in the amount of surface versus deep gas. Sudden events such the seismic crisis of August 1988 at Vulcano and/or sustained periods of seismicity as were observed at Long Valley.

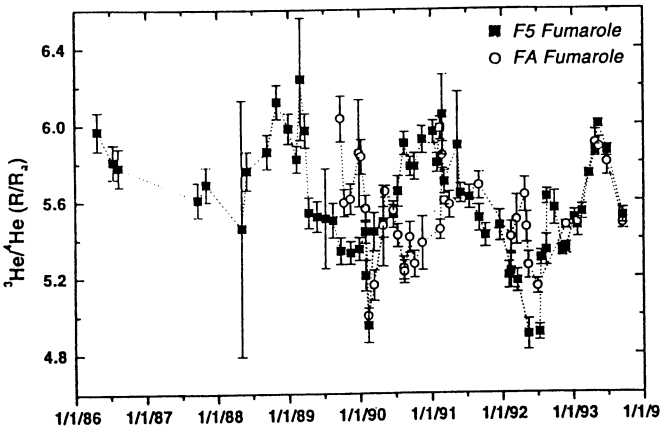

Figure 6a. The periodic oscillation of the helium ratio is shown. The F5 fumarole is the reference crater fumarole sampled by all researchers working on Vulcano Island since 1960s, and the FA fumarole is a new-born fumarole inside the crater with the highest outlet temperature. The similar oscillation occurs despite the difference in temperature of both fumaroles, 315°C at F5 and T_{max} of 700°C at FA. The oscillation suggests a mixing between two sources, (1) ^{3}He-rich source related to a deeper and less contaminated magmatic source and (2) a ^{3}He-poor, more surficial source. Associated ^{4}He/^{20}Ne ratios discard the presence of an atmospheric component. The same kind of variations for both rim (F5) and inside crater (FA) fumaroles suggests that the same phenomenon is recorded at all crater fumaroles. The oscillation is explained with the release of a ^{3}He-rich gas phase from a deep gas reservoir (accumulation chamber), which periodically occurs beneath the volcano. The gas pulses belong to the normal life of the volcano, related to the emptying and recharging of a deep gas reservoir due to pressure rise.

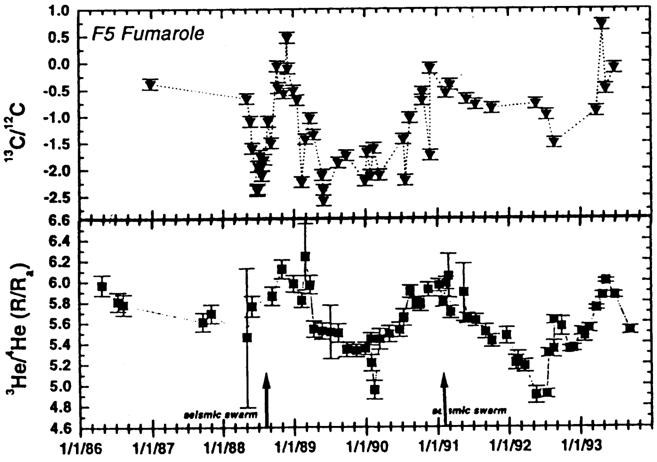

Figure 7. The helium and carbon isotopic ratios show a synchronous but antithetic oscillation. When the helium becomes more magmatic, the carbon shifts to more positive values, more crustal, while when the radiogenic helium increases, the crustal carbon decreases and the juvenile carbon appears. This "anomalous" variation led us to suggest two hypotheses (1) that the heavier carbon is extracted from crustal formations, located between the deep magma chamber and the surface, anytime the gas pulses occur and/or (2) that the source region has a carbon similar to those of carbonates (0‰) because of the assimilitation of carbonatic-rich sediments.

In our case the arrival at the surface of deep fluids is a long, steady and gradual phenomenon, as can be inferred by our data, and not an impulsive, violent magmatic gas release. The slow emptying of the deep gas reservoir takes 1 year. This is the time needed for the $^3He/^4He$ to pass from a maximum to a minimum value, when the content of crustal and surficial fluids increases compared to the juvenile ones. Another year is required to complete the full cycle.

The recorded oscillation is not related to any geophysical activity, either seismicity or ground deformations.

The C isotopic ratio varies similarly, going from phase (a) to phase (b), but in contrast to chemical species and to the helium isotopic ratio, instead of becoming lighter and more magmatic, it becomes, as shown by the antithetic correlation between He and C in Figure (7), heavier with a very pronounced sedimentary/crust $\delta^{13}C$ signature from -2/-3 per mil **(a)** to 0 per mil **(b)**. One hypothesis is that during phase (b) the flux of heat towards the surface increases. If this is so, according to this model, heavier carbon is released from rocks surrounding the magmatic reservoir located somewhere between the source-region and the intermediate dyke intrusion, so that anytime the pulse occurs, the wall rock will release a certain amount of crustal carbon. The heavier carbon should be interpreted in terms of continuous extraction of crustal sedimentary carbon when the activity switch from **(a)** to **(b)**.