

# Nitrogen and Argon in Volcanic and Hydrothermal Fluids. Implications for the Volatile Budget in Subduction Zones

Yuri Taran

Institute of Geophysics, UNAM, 04510, Mexico

Nitrogen, argon and other air components are inevitably recycled from the subducted oceanic lithosphere to the surface by magmatism and accompanying volcanic and hydrothermal activity. A part of N and Ar are of the “old” atmosphere origin, and a significant fraction of N can be derived from the subducted organic-rich sediments, appearing as “excess nitrogen” in volcanic and geothermal gases. However, excess nitrogen can be released also from the continental sedimentary organics or metamorphic rocks, with the same isotopic characteristics ( $\delta^{15}\text{N} \geq +5\text{‰}$ ) and the same high  $\text{N}_2/\text{Ar}$  ratio in the gas discharge. On the other hand, gas with the  $\text{N}_2/\text{Ar}$  ratio close to the ASW (air-saturated water) values (40-80),  $\delta^{15}\text{N} \sim 0$  and  $^{40}\text{Ar}/^{36}\text{Ar} \sim 296$  can be released also from altered basalts of the subducted oceanic plate, poor in pelagic sediments. A complex interplay between  $\delta^{15}\text{N}$ ,  $^{40}\text{Ar}/^{36}\text{Ar}$ ,  $\text{N}_2/\text{Ar}$  and absolute concentration of  $\text{N}_2$  in a surface thermal manifestation has different issues for the volcanic and hydrothermal vents within different subduction zones. The excess nitrogen in volcanic fumaroles may have magmatic origin. In that case its amount should correlate with fraction of magmatic water. “Magmatic” in this context means “derived from the magma generation zone”. The total nitrogen in a volcanic gas is a mixture of air (analytical errors, bad sampling or permeable fumarolic roots), ASW, crustal  $\text{N}_2$  (metamorphic, sedimentary) and magmatic, which is in turn is a mixture between nitrogen from the “old” recycled air (subducted air-saturated seawater – ASSW), subducted oceanic sediments, altered basalts, and the MORB-like nitrogen from the mantle wedge. Argon with very high  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios can be produced in the crust, as well as by the mantle-wedge-MORB-like material. Argon

in volcanic gases with the air-like 40/36 ratio of 296 could be supplied by ASW, ASSW and air contamination. The lower is a real “magmatic”  $\text{N}_2$  and Ar content in a volcanic gas, the higher probability to contaminate a sample by any sort of air-derived gases.

There are not too many good sets of volcanic and hydrothermal gas data with  $\text{N}_2/\text{Ar}$ . The first is by Magro&Pennisi (1991) for Vulcano, the second is by Mizutani for Showa-Shinzan (from Symonds et al. 1996). Good, partially published data of Chiodini and co-workers exist for Campi Flegrei, Vesuvius (Italy) and Nisyros (Greece). The three last are typical hydrothermal gases in spite of their location inside volcano craters. The two first are arc-magmatic + hydrothermal. All five show similar “weird” patterns on the  $\text{N}_2$ &Ar vs  $\text{N}_2/\text{Ar}$  plots: relatively constant  $\text{N}_2$  concentration, much higher than that for the completely evaporated ASW, and decreasing Ar from high concentrations at close to the air  $\text{N}_2/\text{Ar}$  to low Ar, close to its ASW content at high  $\text{N}_2/\text{Ar}$  ratios (see Figure 1). Our data from El Chichon volcano-hydrothermal system show same trends.

The excess nitrogen in “meteoric-hydrothermal” systems as a rule has crustal origin and correlates positively with the methane content.

Volatile outputs from volcanoes and geothermal systems of a subduction zone are comparable. ( $3.1 \cdot 10^{10}$  mol/a of  $\text{CO}_2$  by volcanoes vs  $2.3 \cdot 10^{10}$  mol/a by geothermal systems in Kamchatka without diffusion soil flux). In order to estimate the gas output from a hydrothermal system one needs to measure the total water discharge and gas/water ratio. However, direct estimations of the gas discharge from a bubbling thermal spring sometimes impossible. A simple expression based on the phase equilibrium is derived for the calculation of the total gas content using exclusively the gas analysis:

$$X_g = 78.1 p_r / [(\%) \text{N}_2 \beta(r)] - 1/\beta(st),$$

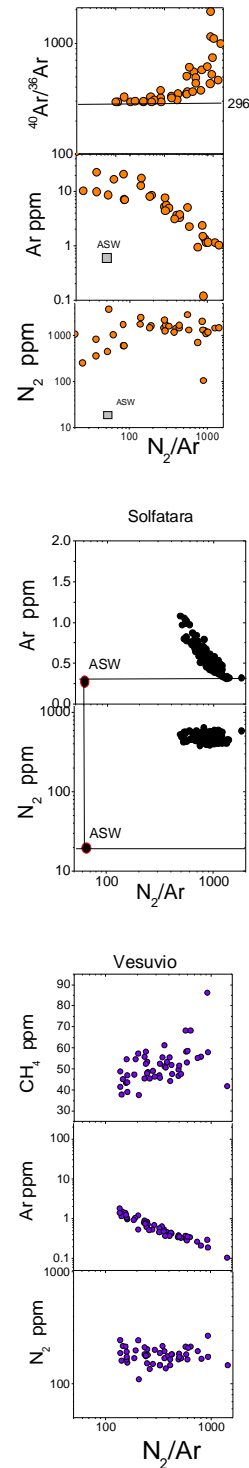
where  $X_g$  in mol/kg of water,  $(\%)N_2$  is mol % of  $N_2$  in dry gas,  $p_r$  is atmospheric pressure at the altitude of the recharge area and  $\beta$  are solubility coefficients for  $N_2$  at recharge and discharge temperatures, respectively. Nitrogen in this equation can be replaced by Ar or Ne with their corresponding solubility coefficients and concentrations in air (See Taran, 2005 for details).

Different mechanisms of the ASW degassing (open, closed, multi-step, continuous, partial, etc.) result in different  $N_2/Ar$  ratios, but all are in the range of 36-84. The  $N_2/Ar < 30$  can be realized only by Rayleigh-type degassing of a limited water body, without any supply from an external source of ASW. Another, but little probable cause of low  $N_2/Ar$  is a contribution of radiogenic  $^{40}Ar$  from the rock matrix.

Such approach and mixing relationships help to constrain ranges of absolute concentrations of  $N_2$  and Ar in a free gas phase of thermal ASW with an external source of  $CO_2$  and to discriminate the “net” excess nitrogen in thermal manifestations. The method is applied to the estimation of the output of subducted nitrogen and argon from the Kamchatka-Kurile volcanic arc.

## References

- Magro G, Pennisi M. (1991) JVGR,  
 Symonds R.B., et al (1996) JVGR,  
 Taran Y.A. (2005) GRL,



**Figure 1.**  $N_2$  and Ar in gases from Vesuvius and Solfatara (Chiodini, unpublished) and Vulcano (Magro&Pennisi, 1991). Concentrations in ppm in the total discharge (water + gases).

