CHEMICAL AND ISOTOPIC CHARACTERISATION OF GAS AND WATER IN A SCIENTIFIC BOREHOLE AT ALBAN HILLS: NEW INSIGHTS ABOUT FLUID CIRCULATION AND NATURAL GAS HAZARD

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Abstract
In the framework of a multidisciplinary project funded by the Italian "Dipartimento della Protezione Civile", focused on the Alban Hills volcanic district (Central Italy), a 350 m deep borehole (named CA1) was drilled in order to: 1) understand the shallow crust structure beneath the volcanic complex; 2) characterize the physical properties of the rock units through on site measurements and laboratory experiments; 3) provide data on the local present-day stress field, and 4) install a broad-band seismometer at depth of about 200m.

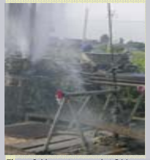

Figure 2: blow-out occurred at CA1 borehole.

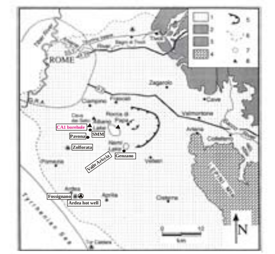

Figure 1: Alban Hills volcanic area schematic map. Legend: 1) area covered by Alban Hills volcanics; 2) Tortonian flysch (pelitic-sandy facies); 3) Meso-Cenozoic pelagic carbonate units (Sabina facies); 4) Meso-cenozoic carbonate platform units (Latium-Abruzzi facies); 5) caldera rim; 6) Alban Hills Volcanic District boundaries; 7) hot springs; 8) gas emissions.

The borehole is located near Santa Maria delle Mole village, adjacent to the western rim of the Tuscolano-Artemisio caldera, where several phenomena of unrest recently occurred (**Fig. 1**). In the period 1989-90 a seismic swarm affected this area (Amato et al., 1994) and a related uplift was recognized by geodetic investigations and satellite image analysis. In addition, this area is affected by high gas concentrations (mainly CO2 and H2S) both in aquifers and soils (Pizzino et al., 2002; Carapezza et al., 2007); gases have a deep origin (methamorphism of deep carbonates and/or magmatic degassing, as results in Chiodini and Frondini, 2001; Carapezza et al., 2007). During the phase of hydraulic fracturing tests at the CA1 borehole, in a sandy unit at a depth between 345 and 350m, a blow-out occurred (**Fig. 2**), causing the collapse of its deepest part. The over-pressured fluid column (mainly gas, with minor water) has risen up to 5m from well-head and leaked out for about one hour without changing its intensity, with pressure measured at the surface about 30 bar. The following day the leak of gas and water went on but the pressure at well-head stabilized around 13 bar. In order to emphasise the origin of the fluids issuing from the CA1 borehole, gas and water were collected and analysed for their chemical and isotopic characterisation; data are compared and discussed with new ones gathered inside the project, concerning water wells and springs (about 200 sites) and 7 natural gas manifestations located throughout the Alban Hills area. New geochemical data provided additional information about both the deep volcanic circulation of fluids and their possible connection to a deep-seated magma chamber.

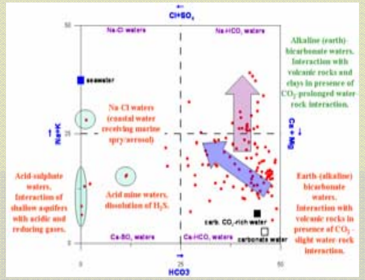

Figure 3a: Ludwig-Langelier diagram of 113 Alban Hills groundwater. For comparison, both carbonate and carbonate CO2-rich water compositions are reported. Main geochemical processes are showed. Light blue and purple arrows indicate the evolution of the Ca-HCO3 waters (i.e. enrichment in Na and K due to water-rock interaction) and interaction with clays, respectively. Both processes occur in presence of CO_2.

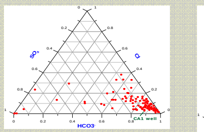

Figure 3b: Cl-HCO3-SO4 ternary plot.

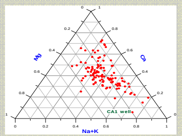

Figure 3c: Ca-Na+K-Mg ternary plot.

General outline of the Alban Hills water chemistry
The chemical composition of 113 water samples is presented in terms of relative major cation (Ca, Mg and Na + K) and anion (Cl + SO_4 and HCO_3) contents (Ludwig-Langelier and ternary diagrams, **Figs. 3a, b and c**). Earth (alkaline)-bicarbonate waters are generally cold (10 < T < 18 °C) and are characterised by positive values of redox potential, acidic to neutral pH and different salt contents (spanning between 0.15 and 1.3 mS/cm), mainly due to their different CO_2 content. Indeed, increase in the leaching power of the CO_2-rich waters, resulting in the enrichment of both alkaline-earth elements and some minor and trace ones such as silica (up to 100 ppm), strontium and iron, was observed. Waters have a relatively fast circulation in the volcanic rocks at low temperatures and are characterised by a limited fluid-rock interaction (i.e. they are "immature" as they do not reach the equilibrium with silicate minerals constituting the rocks). In some sectors of the volcano, waters receive a huge gas input from below (mainly CO_2), that contribute to the observed evolution in their chemical composition (i.e. enrichment in Na and K). Generally, waters of the Alban Hills are very rich in potassium (up to 90 ppm), reflecting the interaction with the particular potassic-bearing minerals (leucite) building up the volcanic rocks outcropping in the area. Waters with longer interaction with volcanic rocks, in presence of CO_2, evolve towards the alkaline-bicarbonate field with silicate hydrolysis and conversion of feldspar to clays, following reactions such as:

$$4KAlSi_2O_6\ (leucite) + 15H_2O + 6CO_2 \leftrightarrow 4K + 4H_4SiO_4 + Al_4Si_4O_{10}(OH)_8(kaolinite) + 6HCO_3^-$$

They discharge locally in the *Genzano, Frascati, Valle Ariccia and Pavona-Albano* sectors. These waters are warmer than the previous ones (T up to 23°C) and are characterised by an average value of electrical conductivity of 0.7-0.8 mS/cm and neutral to alkaline pH. To this group belongs the CO_2-rich water issuing from the project well (CA1) drilled in Santa Maria delle Mole village. Waters contain noteworthy amount of F (values up to 6 mg/L), Li and B, mobilised by relatively high temperatures. Samples discharging in the *Genzano*, *Frascati and Pavona-Albano* sectors deserve particular attention in the tectonic setting of the Alban Hills as they represent the only warm waters in the study area. Acid-sulphate waters are formed by dissolution of acid and reducing gases (CO_2, H_2S) into oxygen-rich shallow aquifers; H_2S is oxidised to SO_4 and huge amounts of protons (H^+) are released into solution, causing the observed very low pH values (1.2-2.5). These waters discharge at the *Zolforata Pomezia, Tor Caldara and Cava dei Selci* sites. The only Na-Cl water issues along the Tyrrhenian coast in the *Tor Caldara* area, and owes its chemistry both to the aerosols and marine spry. As results from the **Fig. 3a**, waters have no interaction with the deep Mesozoic carbonates underlying the shallow volcanic complex.

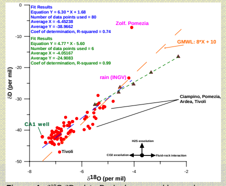

Figure 4: δ18O-δD plot. Dashed orange, blue and green segments represent the Global Meteoric Water Line, the Local Groundwater Line (with respective statistical reports) and the Evaporation Line for the Alban Hills. Main processes leading to isotopic shifts with respect to GMWL are reported.

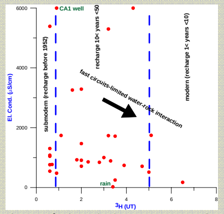

Figure 5: 3H-El. Cond. plot. Immature waters (i.e. characterised by limited water-rock interaction) show higher tritium values than mature waters, characterised by prolonged interaction with leached rocks. Black arrow shows the general trend. CA1 water shows a meteoric recharge before 1952 (pre nuclear-tests) and a high salinity.

Water chemistry at CA1 well
Hypothermal CO_2-rich water (T= 20.1°C, calculated pCO_2 -partial pressure of carbon dioxide- 0.9 bar) shows some peculiar geochemical features. Besides its Na-HCO_3 chemistry, already found in other sectors (**Figs. 3a, b and c**), water shows unusual high salinity (Total Dissolved Solids = 7 g/l, the highest in the area as a whole), very high Na, Mg and bicarbonate contents (2488, 360 and 8845 mg/l, respectively), as well as a strong enrichment in minor and trace elements such as Li, B, Si and Fe (6, 15, 31 and 55 mg/l, respectively). pH is almost neutral (6.92) and negative Eh values (-97 mV) denote reducing conditions. As for the other samples, both oxygen and hydrogen stable isotopes delineate the meteoric origin (**Figure 4**) of the issuing water, excluding any other source (juvenile and/or connate). Indeed, CA1 water lies on the Local Groundwater Line (dashed blue line), slight dissimilar from the Global Meteoric Global Line (dashed orange line) because of water-rock interaction processes. CA1 water show a depletion in 18O probably due to the CO_2 exsolution during its upraise toward the surface. Water is tritium-free (<0.6 TU, vs. a value of 3.5 TU measured in the present rain), suggesting a long residence time (> 50 years) in the aquifer (**Figure 5**); this is the general isotopic signature of the other artesian aquifers sampled in the Alban Hills area. At the CA1 well, the presence at the top of the aquifer of a thick (150 m) clay layer determines the artesian feature of the deep aquifer. The slow circulation and the prolonged water-gas-rock interaction, together with the presence of a huge amount of dissolved CO_2, favor a huge chemical attack on clay minerals; consequently, saline content of water is high.
The main gas-water-rock interaction processes occurring at depth can be pointed out by using the Phreeqc geochemical code (Parkhrust and Appello, 1999). Speciation calculations and saturation indexes of the main mineral phases indicate that CO_2-rich water dissolves minerals such as calcium and magnesium carbonate, illite, Fe-Mg chlorite, alkaline feldspars and Na-bearing minerals (smectite group). The set of the above reactions gives rise to an aqueous solution enriched in the following elements: Si, Fe, Ca, Mg, K, Na. Bicarbonate is one of the principal products of the dissolution reactions; it is the largest phase of carbon existing in the solution owing to the measured pH value. However, processes involving organic matter contained in sedimentary layers can not be completely ruled out to justify the extremely high bicarbonate contents,. The possible preferential removal of Ca than Mg from solution, via incorporation into secondary minerals (for example cation exchange with Na) can account for the unusual low Ca/Mg ratio (1:3). Moreover, Ca can precipitate as carbonate during the water ascent, because of the CO_2 loss by degassing. Boron occurs in the form of $B(OH)_3$ and it is a typical constituent of non marine highly saline waters, mainly if leaching clays; lithium is in equilibrium with the Al-silicate mineral (spodumene) that could represent its main source.

Water geothermometric applications

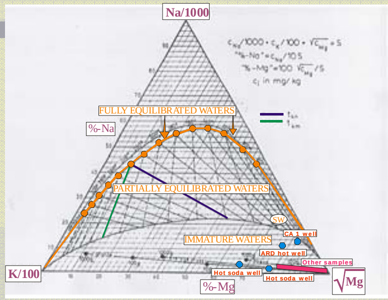

Figure 6: Na-K-Mg Giggenbach ternary plot for collected waters of the Alban Hills area. Waters fall very close to the Mg corner and far from the full equilibrium line. Samples lie on an area representing quantitative leaching of cations ranging both from a basalt-type rock and an average crust (with a progressive enrichment in Na and K "driven" by the high dissolved pCO_2), strongly suggesting that the different water chemical compositions are mainly due to isochemical dissolution of rock rather than by attainment of equilibrium with it. Four samples deviate from the above-reported trend: CA1 well, ARDH and two thermal soda waters that have outlet temperatures between 20 and 55°C. In particular, the CA1 sample falls very close to the field of the partial equilibrated waters, becoming suitable for attempting to infer deep temperature. The method proposed by Reed and Spycher (1984) was used, considering the mineralogical composition of similar clays outcropping few kilometers away from the CA1 borehole (Bozzano et al., 2006, **Table 1**): we obtained an equilibrium temperature among water and mineral assemblage of about 100-120°C (**Figure 7**), confirming the medium-low enthalpy of the geothermal system beneath the volcano, at least in its upper part. Indeed, the estimated temperature is typical of aquifers hosted in the shallower part of the sedimentary sequence (sands and clays). Unfortunately, no waters circulating in the deep sedimentary sequence (carbonate) were detected (**Fig. 3a**) not allowing to infer the temperature of the deep geothermal reservoir.

	Cc	Do	Fill	Qtz	Feld	Sm	Mi	Ill/Sm	Cl	Cl/Sm	K
N = 19	33	2	46	9	8	52	22	1	8	9	7
s	3	1	7	1	3	11	4	1	3	5	2

Table1: Average mineralogical composition (wt %) of Pliocene and Pleistocene clays (Bozzano et al., 2006). Cc = calcite, Do = dolomite, Qtz = quartz, Feld = alkaline feldspar. Phyllosilicate composition: Sm = smectite, Mi = mica like minerals, Ill/Sm = illite/smectite solid solutions, Cl = chlorite, K = kaolinite.

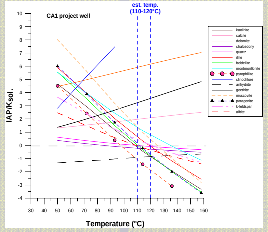

Figure 7: Temperature vs S.I. (Saturation Indexes) plot for CA1 water. Clay composition was taken from Bozzano et al., 2006 (see table 1). An equilibrium temperature of about 110-120°C was estimated by using the method proposed by Reed and Spycher (1984).

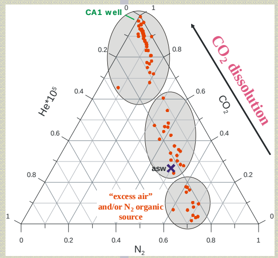

Figure 8: Dissolved CO_2-N_2-He plot. Three groups of waters are recognised, characterised by: *i)* enrichment in N_2 with respect to ASW ("excess air" phenomena and/or dissolution of soil-derived organic nitrogen); *ii)* dissolved gas composition similar to the ASW or slightly enriched in CO_2 and *iii)* remarkable enrichment in CO_2. N_2/He ratio is quite similar for all samples.

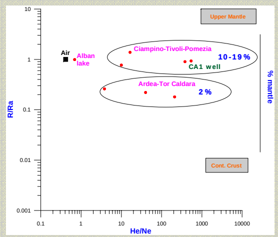

Figure 9: He/Ne vs R/Ra plot. Helium isotopic composition of CA1 issuing gas is quite similar to that measured in this sector of the Alban Hills area. We can estimate a mantle contribution of about 10-15%. R is the 3He/4He of the sample, while Ra is the same ratio in the air (1.4*10-6).

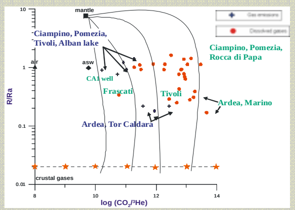

Figure 10: He/Ne vs R/Ra plot. Helium isotopic composition of CA1 issuing gas is quite similar to that measured in this sector of the Alban Hills area. We can estimate a mantle contribution of about 12%. R is the 3He/4He of the sample, while Ra is the same ratio in the air (1.4*10-6).

Gas chemistry
Gas emitted is largely dominated by CO2 (92 % v/v), with N2 as second most important component (7 % v/v), **Figure 8**. Trace gases are represented by CH4 (2570 ppm), H2 (79 ppm) and He (45 ppm). It is worthy of note that total He (3He + 4He) content is the highest found so far throughout the Alban Hills emission sites. Total He content is 10 times higher than other gas vents, indicating a larger residence time of gas in the crust (4He enrichment), as reported for the associated water, more than an anomalous flux of magmatic origin (3He enrichment), being the isotopic composition quite similar to those measured in this sector of the Alban Hills area (**Figure 9**). 3He/4He isotopic ratio is 0.9 times the atmospheric value (1.4*10-6), indicating a mix between a magmatic (about 12 %, one of the highest in the area) and a (prevalent) crustal component, as emphasised by the log CO2/3He vs R/Ra and N2-He-Ar plots (**Figures 10 and 11**). The 4He/20Ne value of about 400, remarkably higher than the atmospheric value (0.318), confirms the relevant contribution of radiogenic (crustal) 4He to the gas source and an only minor addition of near-surface atmospheric fluids. Similarly, carbon isotope of CO2 (-0.53 ‰ vs PDB) indicate a high temperature origin of this gas, probably due to decarbonatation processes (crustal contribution) caused by a cooling magma chamber hosted in the deep carbonatic series, as reported in **Figure 12**. Remarkable H2 content (one of the highest in the area) could be favoured by the: i) reducing environment, also in the shallow strata ii) presence of Fe-bearing minerals in the rocks and sediments leached by fluids, as discussed in the previous section, and iii) relatively high temperature at depth. Notwithstanding the lack of isotopic composition of carbon, we could infer a thermogenic (i.e. biogenic, as defined in Welhan J.A., 1988) origin of methane probably due to the thermocatalytic breakdown at moderate to high temperature (> 100°C) of organic compounds contained both in sand and clay layers. Indeed, this origin was generally hypothesised for the other gas-vents of the Alban Hills by analysing its 13C/12C isotopic ratio (spanning from -22 to -40‰ vs PDB, **Figures 13 and 14**). Radon was measured only as dissolved gas and it shows very low content (3 Bq/l). Low radon activity could be due mainly both to the CO2 dilution and to the slow hydraulic circuit, leading to the radon decay through time (T1/2 = 3.82 days).

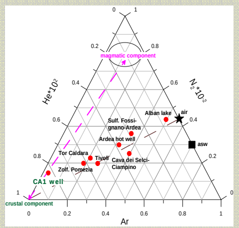

Figure 11: N_2-Ar-He plot. All gas samples represent a mixing, at various degree, between an atmospheric (N_2-rich, more evident in the Alban lake sample) and a crustal (He-rich, more evident in the Zolf. Pomezia, Tor Caldara and Tivoli samples) component. Only CA1 sample deviates from this trend, being a mix between a magmatic (about 10-15%) and a (prevalent) crustal component.

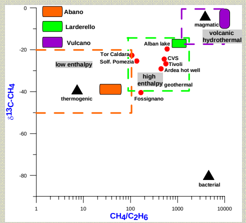

Figure 12: δ13C-CO2 vs log CO2/3He plot. Carbon dioxide has a high temperature origin: it is a mix between a mantle source (more evident for CA1 and Tivoli samples) and a crustal component (more evident in the Ardea hot well, Tor Caldara and Sulf. Fossignano-Ardea samples) that can be identified in the termometamorphism of the deep carbonate beneath the Alban Hills volcano. Low-temperature biogenic CO_2 production by shallow sediments is minimised in the Alban Hills gas manifestations. For comparison, isotopic composition of high temperature volcanic gases of Italy is also reported, as well as mantle, sediment and limestone end-members.

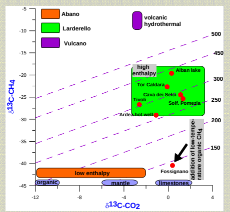

Figure 13: δ13C-CO2 vs δ13C-CH4 plot. Thermogenic origin of methane can be inferred in the Alban Hills natural manifestations. Only in the Sulf. Fossignano sample an addition of low-temperature organic CH_4 can not be ruled out. Unfortunately, isotopic carbon values of methane for CA1 sample are missing. Equilibrium temperatures between carbon of CO_2 and CH_4 give too high values, unrealistic for the studied volcano. As comparison, fields referred to low and high enthalpy, as well as volcanic hydrothermal systems are reported.

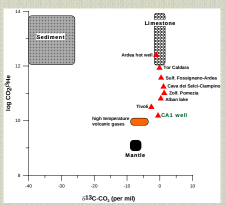

Figure 14: CH_4/C_2H_6 vs δ13C-CH_4 plot. High enthalpy thermogenic origin for methane (geothermal, with high CH_4/C_2H_6 ratio) is inferred for the Alban Hills natural manifestations. Only in the Sulf. Fossignano sample an addition of low-temperature organic CH_4 can not be ruled out. Unfortunately, isotopic carbon values of methane for CA1 sample are missing. As comparison, fields referred to low and high enthalpy, as well as volcanic hydrothermal systems are reported. Thermogenic, magmatic and bacterial end-members of methane are showed.

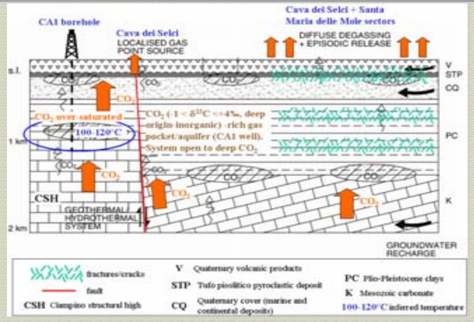

Figure 15: Hydrogeochemical-structural model for the CA1 area (Ciampino structural high, modified after Tuccimei et al., 2006).

Discussion and conclusions
CA1 borehole was a great opportunity to directly measure water and gas coming from the zone where they originate. In the Alban Hills area several blowouts were observed (Pizzino et al., 2002; Carapezza et al., 2007), and although different hypothesis were put forward to explain the origin of such eruptions, few direct geochemical samplings were performed so far in the study area (Carapezza et al., 2007). The origin of such phenomena is related to: i) the removal of the shallow impermeable fine-grained sediments that discontinuously cover the area, as occurred in the past in the Alban Hills (Funiciello et al., 2002) and ii) drilling intercepting pressurized gas pockets of deep origin, both at the top of the Mesozoic carbonatic platform and in the overlying sandy formations. Gas pockets occur mainly when lithological and structural conditions are favourable as, for instance, in presence of impervious layers, such as Plio-Pleistocene clays, or minor depth of the carbonatic platform and a more intense fracturing of the volcanic cover, as occurs in the structural highs (Pizzino et al., 2002, Tuccimei et al., 2006).
A general and schematic hydrogeochemical-structural model is proposed in **Figure 15**. It illustrates the possible locations of the pressurized gas pockets in the frame of the geo-structural setting of the Alban Hills complex. In particular, the local situation encountered at the CA1 well is emphasized. Deep CO2-rich gases rise from depth preferentially along the extensional faults bordering the Ciampino structural high. The top of the buried limestone horst (inferred at a depth of about 600-700 m by ENEL geothermal explorations, 1990) is the preferential site for gas accumulation, as suggested by the gas caps frequently found in that position by the geothermal wells drilled in other Latium volcanic areas (Chiodini et al., 2005). Gas pocket intercepted by the CA1 well was located just in the sands probably overlying the top of the carbonates, at a depth down to 350 m. Further rise of the gas can occur both through major faults and associated fracture/crack networks, also in impervious layers; gas can reach surface both as localised spot and as diffuse degassing affecting large sectors of the volcano. During their ascent, gases dissolve and accumulate into aquifers, either in the sedimentary or in the volcanic sequences up to very shallow depths (5-10 m), as in the Cava dei Selci area (Pizzino et al., 2002). Aquifers are fed both through direct vertical infiltration of rainwater in the highly permeable volcanic rocks and through lateral circulation from the karstic and fractured limestones outcropping to the NE and SE of the volcano that likely feeds permeable layers at any depths (Boni et al., 1995). Sometimes, these aquifers are oversaturated in CO2, causing the escape of carbon dioxide as "free" gas phase to the surface. Furthermore, in periods characterised by enhanced tectonic load/stress accumulation on the faults (i.e. causing modifications in the existing fracture networks and/or new opening of cracks and fractures in the different layers, modifying their porosity/permeability) soil degassing can affect wider areas with a relevant gas hazard for the local population, as happened in November 1995 (Pizzino et al., 2002). Therefore, considering all the above reported subjects, we can conclude that it is very important to identify the depth, the thickness and the spatial location, as well as to measure the permeability and porosity coefficients of both the fine-grained sediments and the impervious layers underlying the Alban Hills volcanites. These investigations are necessary pre-requisites in order to mitigate and, possibly, prevent further harmful gas escapes. The CA1 borehole provided the first and very useful geological and stratigraphical information for the Santa Maria delle Mole sector and adjacent areas.

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