CHEMICAL AND ISOTOPIC CHARACTERIZATION OF ISCHIA HYDROTHERMAL SYSTEM: AN INTERPRETATIVE MODEL OF FLUIDS CIRCULATION

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Ischia Island is an active volcanic area in the Campanian Magmatic Province (CMP). Although currently quiescent, Ischia volcano has been active in historic time, most recently in 1302 A.D.. The present activity is characterised by the widespread occurrence of surface hydrothermal manifestations, such as hot water discharges from wells and springs, steam and gas emissions (fumaroles), and diffuse soil degassing.

High thermal fluxes and the intense hydrothermal circulation at Ischia Island have been a matter of interest since the ‘50s (Ippolito, 1942; Penta, 1949, 1954; Penta & Conforto, 1951a,b). Thermal manifestations on the island have been interpreted as reflecting the surface discharge of a complex and multi-reservoir hydrothermal system, where fluids of formerly meteoric and/or seawater origin get-heated and chemically modified by the interaction with magmatic volatiles (Panichi *et al.*, 1992; Caliro *et al.*, 1999; Inguaggiato *et al.*, 2000; Chiodini *et al.*, 2004).

Chemical and isotopic features of 120 thermal groundwater samples (collected from wells and springs) concentrated along the coastal areas of the island, and of 5 free gas emissions, located in the major fumarolic areas of the island, are here discussed. Data have been acquired during a series of hydrogeochemical surveys, performed between 2006 to 2007, and are here integrated with previous measurements performed by Istituto Nazionale di Geofisica e Vulcanologia (INGV), Sezione di Palermo, in the attempt to provide a comprehensive model of hydrothermal circulation on Ischia.

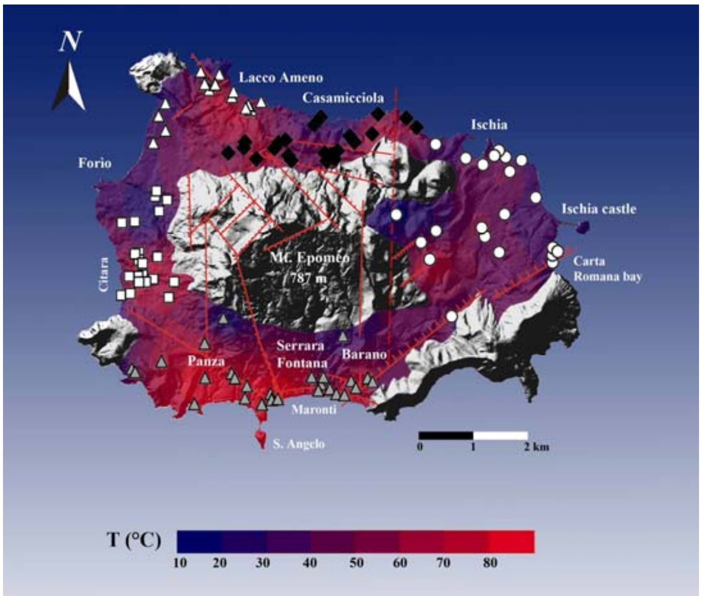

Fig. 1 - Spatial distribution map of discharge temperature of Ischia groundwaters. Samples are distinguished as according to their position: the Eastern-sector (white circles), the Northern-sector (black diamonds), the North-North-Western-sector (white triangles), the Western-sector (white squares) and the Southern-sector waters (grey triangles).

One of the most prominent characteristics of Ischia groundwaters is a remarkable heterogeneity in their chemical composition and physical-chemical parameters. Discharge temperatures measured both in springs and well waters vary in a wide range from 13 to 90°C. Their spatial distribution (Fig. 1) indicates that the north-western (Casamicciola - Lacco Ameno) and the southern-western sectors (Panza - Serrara Fontana - Barano) are the main thermal areas of Ischia Island, characterised by groundwaters emerging with T > 70°C. In term of temperature, the eastern slope of Mt. Epomeo, a lowland in which volcanism connected with the resurgence phenomenon has been concentrated in the past 10 ka B.P. (Orsi *et al.*, 1991; 2003), is apparently marked by a minor hydrothermal circulation. Indeed, springs and well waters are generally cooler (T ≤ 60°C) than in other areas.

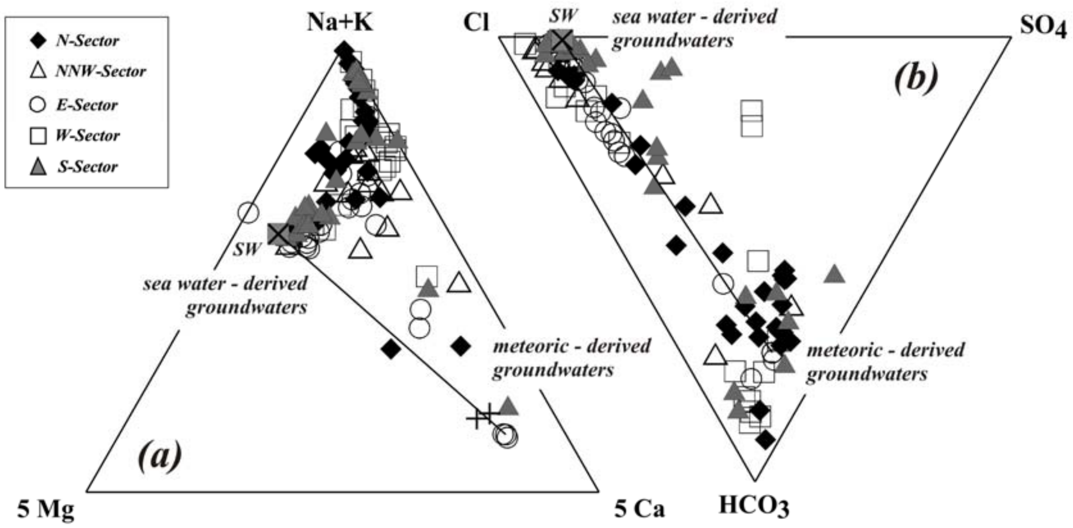

Fig. 2 - In terms of their major dissolved ions, (a) cations and (b) anions, Ischia samples range from calcium-bicarbonate to alkali-chloride groundwaters. Crosses representing rain waters from Vesuvius are from Madonia & Liotta (pers. comm.). The triangular diagrams are drawn from concentrations in mg/l.

The significant heterogeneity of Ischia hydrothermal system is also reflected by total dissolved solids (TDS), which typically increase from inland areas (where more diluted waters with TDS < 1 g/l are recognised) towards coastal areas (where saline waters with TDS > 16 g/l are identified). This trend is an evidence of a multiple recharge of the Ischia hydrothermal system from both sea water and meteoric water, a fact also that fit with major dissolved ion compositions (Fig. 2). For instance, several waters show a clear meteoric signature, having a prevalent bicarbonate composition (Fig. 2b), and being characterised by low TDS, and discharge temperatures (< 25°C) very close to the average annual air temperature. However, only a few data points in Fig. 2 cluster along the meteoric-sea water mixing line. A group of samples plot far below the meteoric-sea water mixing line in Fig. 2b, near the HCO_3 corner: such an enrichment in HCO_3 is also paralleled by higher temperatures (up to 45°C), likely reflecting longer residence time and deeper infiltration in the hydrothermal envelop, where interaction with a CO_2-rich gas phase may occur. On the contrary, saline waters with sea water-like composition have Cl as the prevalent dissolved anion (Fig. 2b), and show enrichments in sodium and potassium and depletion in Mg with respect to sea water composition (Fig. 2a). They likely reflect water-rock interaction processes at high temperatures, which cause leaching of alkali from the reservoir rocks and precipitation of new mineral phases (Mg-bearing) from supersaturated solutions.

The large dataset on the chemical and isotopic composition of groundwater discharges and gas

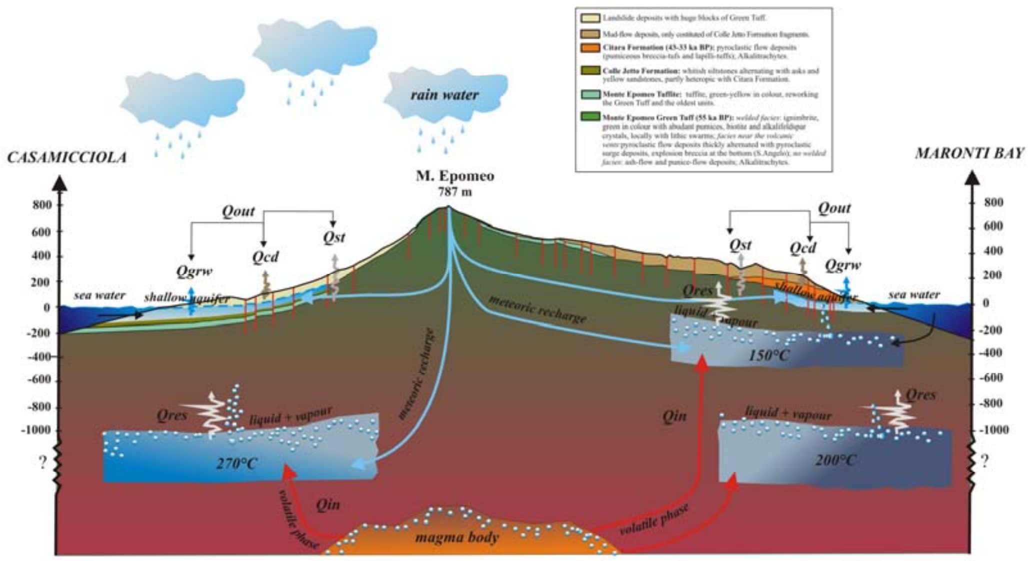

Fig. 3 - Geochemical conceptual model of Ischia geothermal system in a N-S section (from Casamicciola village to Maronti bay).

emissions from Ischia hydrothermal system, presented in this work, has been used to drawn a geochemical model of fluid circulation at depth (Fig. 3), revealing the existence of a complex hydrothermal system composed of at least two superimposed deep reservoirs. As simplified in Fig. 3, the Ischia hydrothermal system is recharged by both meteoric water and sea water. However, groundwater discharges have major and minor ion compositions which can only be partially reproduced by mixing between meteoric and sea water (Fig. 2) requiring that other components (hydrothermal end-members) take part to the mixing processes. Three compositional end-members are identified in this work (Fig. 4), using Mg-depletion in hydrothermal solutions as an index of their maturation, namely an expression of degree of water-rock interaction at high temperature in the deep reservoir. Using this line of reasoning, the chemistry of superficial manifestations suggests, as for the southern Ischia sector, the existence of an hydrothermal end-member (represented by *hydrothermal end-member* "B" in Fig. 4) characterised by low TDS (Cl ~ 1921 mg/l) and isotopically negative ($\delta^{18}O$ ~ -4.98‰) composition. Accepting that this hydrothermal end-member is the surface expression of a deep thermal reservoir, the latter must be thus prevalently recharged by meteoric fluids. On the contrary, *hydrothermal end-member* "C" (Fig. 4), highly saline (Cl ~ 13000 mg/l) and isotopically more positive ($\delta^{18}O$ ~ -0.28‰) than the previous, and thus of likely marine derivation, feeds thermal waters in the western sector of the island (Fig. 3). The chemical dissimilarity between hydrothermal end-members "B" and "C" could seemingly suggests the existence of two distinct reservoirs in the southern and western Ischia sectors. However, this is in conflict with the estimated depths of the thermal reservoirs in the two areas, being remarkably similar. In fact, the deep equilibrium temperatures of *hydrothermal end-members* "B" and "C" (estimated by using classical solute geo-thermometers; Giggenbach, 1983), combined with geothermal gradient data deduced from SAFEN's explorative wells, point to the existence, both at south and west, of a main reservoir located at about ~ 300 m of depth, with equilibrium T ~ 150°C (Fig. 5a,b). In addition, several thermal groundwaters collected in the S-W sector have compositions consistent with the mixing trend between hydrothermal end-members "B" and "C" (see Fig. 4). As such, it is proposed that the same ~ 300 m deep reservoir

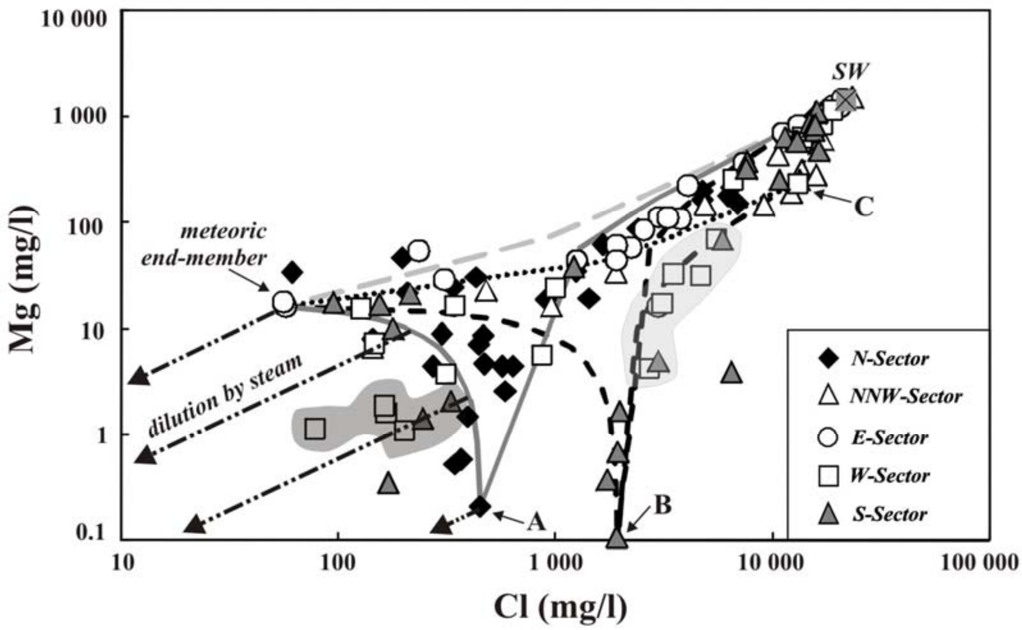

Fig. 4 - Magnesium versus chlorine concentrations. The plot suggests that the compositional range of thermal manifestations on the island reflects the mixing of at least 5 component, namely: i) sea water, infiltrating on coastal areas along the margins of the thermal field; ii) meteoric water; iii) end-member A, iv) B and v) end-member C, Grey dashed line represents the meteoric-sea water mixing, while mixing between meteoric and sea water and the end-members A, B and C are indicated by dark grey solid line, black dashed line, and dotted line, respectively. Some samples collected in the western and southern sectors of the island (plotting within the light grey shaded area) do not follow the trends displayed in this figure, and cluster along a line connecting B and C end-members. The scattering of samples from the above mentioned mixing trends towards Mg and Cl poor compositions (samples into the dark grey shaded area) can be interpreted as resulting from dilution by steam which causes heating of the samples and a general depletion in the dissolved ions.

supplies surface hydrothermal manifestations at S and W (Fig. 3). This relatively shallow reservoir is mainly fed by sea waters in the western Ischia sector, and by meteoric water in the southern portion of the island. In addition, both in the southern and western sectors, the existence of second deeper (> 1000 m) reservoir is supported by thermal waters with equilibrium T > 150°C (Figs. 3 and 5a,b); this hot (~ 200°C) reservoir having been captured by the deepest of the SAFEN drillings in the area. Knowledge about the hydrothermal setting in the northern sector of Ischia is poorer, because of the lack of direct depth-T information from deep drillings. Assuming however that the same geothermal gradient observed in the S and W sectors holds true also at N (see Fig. 5c), the very high equilibrium temperatures (up to ~ 270°C) calculated for thermal waters of the latter area suggest that the reservoir is very deep (>> 1000 m) (Fig. 5c). A shallower depth (350-550 m) for this reservoir (but still deeper than at S and W) can be calculated accepting coexistence of liquid and vapour at depth (as it seems indeed to be suggested by several point overlapping the boiling curves in Fig. 5c). Independently from its location, the composition of the *hydrothermal end-member* "A" in Fig. 4 (Cl ~ 450 mg/l and $\delta^{18}O$ ~ -5.29‰) suggests that meteoric waters feed the thermal reservoir in the northern part of Ischia Island. Again, mixing of "A" with both meteoric and sea water in the shallow thermal groundwater system gives rise to the chemical heterogeneity of surface manifestations at Casamicciola and Lacco Ameno. (Fig. 4)

The significant hydrothermal circulation observed at Ischia requires the existence of a large heat source in the subsurface, which is likely represented by a cooling and degassing magmatic body at depth. The existence of such a degassing magma is also consistent with the observation of widespread interactions of the hydrothermal system with a deep-originated gas phase, indicated as DGC (deep gas component) and being characterised by CO_2 ~ 97% (on a water-free basis), $\delta^{13}C$ = -3.5‰ and R/Ra = 3.5. It must be noted, however, that the composition of such DGC does not univocally supports its magmatic derivation, since an at least partial crustal or mantle origin cannot be ruled out. It is also clear that the composition of the deep-rising gas phase is strongly modified by interaction with (and fractional dissolution in) hydrothermal aquifers, making interpretation of the chemical and isotopic composition of the DGC more questionable. Contrasting dissolved CO_2 content in groundwaters (expressed as molar fraction) against the corresponding isotopic compositions (see Fig. 6), it can be inferred that the ^{13}C-depleted isotopic compositions of CO_2-poor (low X_{CO2}) samples reflect a prevalent contribution from soil-CO_2 ($\delta^{13}C_{CO2}$ = -25‰ *vs.* PDB) and/or atmospheric-CO_2 ($\delta^{13}C_{CO2}$ = -7.9‰). Instead the more positive isotopic compositions observed on increasing dissolved CO_2 contents converge towards the range of isotopic compositions displayed by free gas samples ($\delta^{13}C_{CO2}$ from

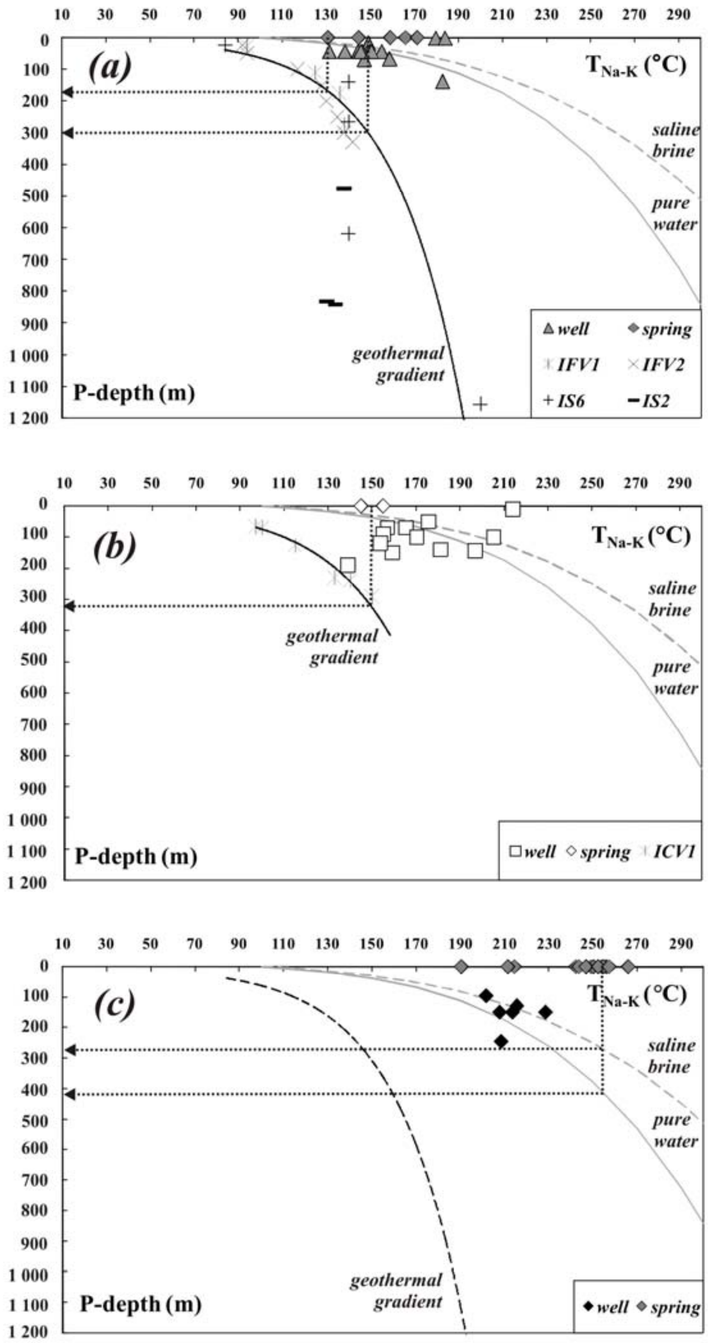

Fig. 5 - Deep equilibrium temperatures for a selection of sampled fluids, calculated from the Na-K geothermometer, are contrasted against the depth of groundwaters below the ground level (0 m for springs). (a) S-sector, (b) W-sector and (c) N-sector. Boiling curves (for pure water and 5% NaCl brine) are drawn to reference. In plots (a) and (b) SAFEN's wells relative to the examined sector are also reported (data from Ippolito, 1942; Penta, 1949, 1954; Penta & Conforto, 1951a,b). See text for explanation.

-6.65 to -2‰). Accepting that the averaged composition of Ischia fumaroles ($\delta^{13}C_{CO2}$ and X_{CO2} of -3.5‰ and 0.97 mol/mol, respectively), computed from samples most enriched in CO_2 (and thus likely near to the features of the deep gas), is representative of the ^{13}C-rich deep-gas component (DGC), the soil-DGC and air-DGC mixing curves have been calculated (dashed grey and solid black lines in Fig. 6). These cover only partially the observed compositional variability in Fig. 6, however, since a significant number of samples have compositions unaccounted for by the above mixing processes. In particular, several samples have $\delta^{13}C_{CO2}$ values far more negative that the model curves could explain. In line with what previously introduced by Caliro *et al.* (1999) and Inguaggiato *et al.* (2000), it can thus be proposed that these ^{13}C-depleted compositions likely reflect the occurrence of isotopic fractionation processes involving the DGC upon its interaction (dissolution) with the aquifer(s). The processes potentially taking place during $CO_{2(g)}$-groundwater interaction have been modelled by using the Rayleigh-type fractionation. Model curves in Fig. 6 were calculated in a range of *p*H (6-8) and temperatures (25 and 100°C) relevant to the system under investigation. In such conditions, model calculations indicate that ^{13}C is preferentially partitioned to the aqueous phase, leading to net ^{13}C-decrease in the residual $CO_{2(g)}$ with a decreasing of residual gas fraction (F) (Capasso *et al.*, 1997). The largest fractionations, and the best agreement between modelled and natural compositions, are observed at neutral to basic conditions and at low temperatures (25°C).

In the assumption that magma degassing at depth is currently the driving force for hydrothermal circulation, a simplified thermal budget has been carried to get a first tentative assessment of the volume

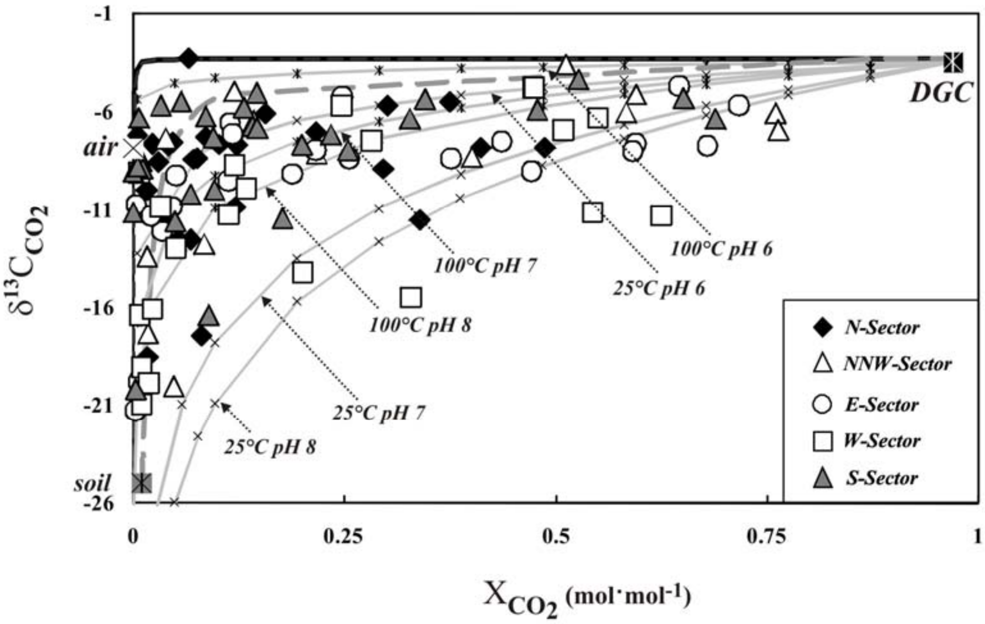

Fig. 6 - Isotopic composition of dissolved CO_2 in equilibrium with groundwaters, plotted versus dissolved CO_2 contents. The isotopic composition of the CO_2-richest waters is consistent with isotopic signature of the hypothesized local magmatic end-member (DGC = deep gas component, with $\delta^{13}C_{CO2}$ of -3.5‰ and X_{CO2} = 0.97 mol/mol). More negative isotopic values reflect mixing between magmatic gases (DGC) and air (black solid line) and/or a soil component (grey dashed line) for soil with CO_2 = 1% in vol.. Departures of samples from the above mixing trends are ascribed to isotopic fractionations involving the rising magmatic CO_2-rich gas phase upon partial dissolution into the shallow aquifer. Solid grey lines, drawn in this plot, model this phenomenon, and represent Rayleigh's fractionation curves calculated at the T and *p*H conditions indicated.

of such a source. At this aim, I have here evaluated the thermal energy dissipated by the shallow hydrothermal system (Q_{out} in Fig. 3) at Ischia at $4.8\text{-}6.9 \cdot 10^{12}$ kJ/yr. This is calculated summing three different amounts:

- Q_{grw} (in Fig. 3), the heat required to warm the infiltrating waters (meteoric and sea water), feeding the shallow aquifer at an average temperature of ~ 15°C, up to the high temperatures observed in surface discharges;

- Q_{cd} (in Fig. 3), the amount of heat lost from the shallow thermal groundwater system by conduction to the overlying rocks;

- Q_{st} (in Fig. 3), the amount of heat dissipated through steam transport and condensation in the very near-surface (in the soil system) of active fumarolic fields over the island

In a steady-state condition, it is reasonable to hypothesise that the amount of thermal energy dissipated by the shallow thermal groundwater system (which is referred as Q_{out} in Fig. 3) is perfectly balanced by the energy supply from the deep hydrothermal reservoirs (Q_{res} in Fig. 3) through the ascent of a liquid+vapour phase. In turn, heat is supposed to be persistently supplied to deep reservoirs from a degassing and cooling deep magmatic system (Q_{in} in Fig. 3). Thus, the above-calculated surface energy release (Q_{out}) provides a first (though indirect) assessment of the amount of heat Q_{in} (in Fig. 3) convectively transferred from the cooling magmatic body (which is thought to lie at depth in the subsurface of the volcano, but which location and volume are unknown). In addition, the estimated Q_{in} potentially offers a viable pathway for estimating the volume of magma currently feeding heat and volatiles to the hydrothermal system. Making the simplified assumption that this heat is provided to the hydrothermal system in convective form (*e.g.* through the ascent of a water vapour-dominated gas phase released from the degassing magma), it can be estimated that the complete degassing of $2.2\text{-}3.2 \cdot 10^7$ m^3 of trachytic magma (with an average value of 2.1 wt.% dissolved H_2O content; Sbrana, 2007) is required every years to account for the release of $1.2\text{-}1.7 \cdot 10^6$ tons of magmatic water. Once extrapolated to entire period of quiescence lasting since the last Ischia eruption in 1302 A.D., this volume corresponds to $1.5\text{-}2.2 \cdot 10^{10}$ m^3 of magma degassed in about 700 years of quiescent activity.

Finally, data presented in this work also contribute to set a baseline for the (minor, non-volcanogenic) temporal changes in the chemistry of Ischia’s thermal manifestations; and give indications on the kind of chemical variations which might herald a volcanic unrest in this densely populated area. Accepting that renewal of volcanic activity at Ischia requires replenishment of the volatile-poor alkali-trachytic stored magma with more primitive volatile-rich basaltic magma (Civetta *et al.*, 1991), I suggest that this event might be captured as an increase in the release of magma-derived CO_2 (and possibly He) in the shallow hydrothermal system, here evaluated at ~ $1 \cdot 10^4$ to ~ $7 \cdot 10^5$ tons/yr; a process which should also lead to a shift towards ever more CO_2-rich and ^{13}C-rich compositions in the sampled surface manifestations of the hydrothermal system. An alteration of the mixing relations between the different components (meteoric water, sea water and hydrothermal end-members) could also be anticipated to occur, in response to magma-induced modifications in the structural regime of the island.

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