Effects of gas-water partitioning, stripping and channelling processes on radon and helium gas distribution in fault areas

M. GUERRA and G. ETIOPE

ING - Istituto Nazionale di Geofisica, via di Vigna Murata 605, 00143 Roma, Italy

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Gas samples for analysis of CO₂, Rn and He were collected simultaneously in different types of natural occurrence, i.e., soil-air, groundwater, gas vent and soil-atmosphere exhalation flux, in the Siena-Rapolano geothermal area (central Italy). The results showed differential enrichment and depletion of Rn and He within small areas as an effect of gas-water partitioning and gas channelling in CO₂-rich faulted subsoil. In the same site low concentrations of Rn or He in water co-exist with high concentrations in the ground; low Rn in soil-air occurs in correspondence with Rn-rich gas vents; soil-gas Rn may be higher than the level induced by U decay in the ground or outcropping rocks. These results suggest that the analysis of a single "sub-system" of the geological environment (e.g., groundwater analysis only) may not provide data representative of gas occurrence and abundance at the investigated site. This must be taken into account in natural resource exploration, earthquake precursor studies and radiation protection zoning based on gas geochemistry.

INTRODUCTION

Geochemical analyses of gases in ground and groundwater are increasingly recognised as a fundamental task for geological and environmental characterisation, including natural resource prospecting (McCarthy and Reimer, 1986; Klusman, 1993), seismic forecasting (Notsu *et al.*, 1991; Bella *et al.*, 1995; Igarashi *et al.*, 1995), waste repository assessment (Gascoyne and Wuschke, 1990; Lombardi *et al.*, 1996) and identification of buried faults (Duddridge *et al.*, 1991; King *et al.*, 1996). In these studies the determination of tracer gases in a phase of the system investigated is rarely accompanied by a robust analysis of partition phenomena or gas exchange between phases occurring in the system, especially when fluid approaches the surface.

Gas-water partitioning either above the groundwater table (governed by Henry's Law), or within a bubbling water column (stripping and transport of trace gas by carrier gas; Etiope, 1998) is basically induced by pressure variations in the unsaturated zone and in the aquifers. These pro-

cesses are usually enhanced in fault zones where gas may be channelled, i.e., collected and conducted upward along, even narrow, pathways of lower resistance to gas motion (Etiope, 1995) and when large amounts of carrier gas occur. As a result, the distribution of rare gases at surface is not homogenous even at scale of metres. Accordingly, the analysis of gas concentration within a single sub-system (soil air, groundwater, gas-vent) may be not representative of the gas occurrence in the whole system (i.e., area or geologic environment investigated). For example, low concentrations of dissolved Rn and He in a spring water do not necessarily indicate that the spring area is deficient in these gases. Similarly, low U outcropping rocks may be associated with high Rn soil-gas, as a result of gas migration from deeper layers.

The main objective of this work is to discuss experimental data showing the important role played by: (i) gas-water partitioning processes involving Rn and He in a CO₂-rich environment and (ii) faults as channelling pathways for gas escape. This study was based on an integrated approach

Fig. 1. Sketch of the different types of gas occurrence (sub-systems) considered in this work: (a) soil gas, (b) groundwater, (c) gas vents and (d) exhalation flux to the atmosphere. Gas samples for analyses of Rn, He, and CO₂ were collected simultaneously in the different sub-systems within a few square metres.

encompassing the simultaneous sampling of Rn, He, and CO₂ concentrations from the following types of natural occurrences, hereafter referred as *sub-systems* (Fig. 1): (a) soil gas, (b) groundwater, (c) gas vents and (d) soil-atmosphere flux, within areas of a few tens of square metres.

The data here presented are selected from gas surveys undertaken from 1993 to 1995 within the framework of the PEGASUS (Project on the Effects of GAS in Underground Storage facilities for radioactive wastes) European project (Lombardi *et al.*, 1996). The surveys were performed in the northern sector of the Siena basin, (Tuscany, Central Italy), in correspondence with two important faults, Arbia Line (AL) and Rapolano Fault (RF), along which many discharges of CO₂-rich waters from a low-enthalpy geothermal reservoir occur. Owing to the presence of pressurised sources, permeable faults and gas discharges, the investigated area provided an excellent opportunity to study gas migration and behaviour both at local and regional scales. Complete regional and local survey data are reported in Etiope (1995), Etiope and Lombardi, (1995b), Lombardi *et al.* (1996), Guerra, (1996), Etiope and Lombardi, (1997).

GEOLOGICAL SETTING

The investigated area corresponds to the Neogene Siena-Radicofani basin, in central Italy (Fig. 2). It has been defined as a graben structure formed during the post-Tortonian extensional phase of the Apennine orogenesis. A main fault borders the graben on its eastern edge; its throw reaches 2000 m near Rapolano Terme and decreases southward. In correspondence with this lineament, the Mesozoic carbonate formations of the Tuscan nappe dip to the SW below the Pliocene marine clays and sands that fill the basin. The western edge, bordered by the Monticiano-Roccastrada metamorphic ridge, presents a more complicated faulting, with smaller individual throws. The basin is cut by two transversal fault systems: the Arbia Line and the Grosseto-Pienza line which have been interpreted as long, deep fracture zones of regional importance. A series of minor faults are connected with these lineaments. Quaternary volcanic activity developed in the southern part of the area (Mt. Amiata, Radicofani, Vulsini Mts.) inducing anomalous heat flow and hydrothermal circulation throughout the region.

Fig. 2. Geological sketch map of the northernmost area of the Siena Basin and location of the sampling points. All sub-systems were sampled at the points 1 to 7 and 14. Legend: a) travertine (Holocene); b) clay (Pliocene); c) sand, clay, conglomerate and lacustrine deposits (Pliocene); d) allocthonous flysch sequences (Cre-Eoc); e) sandstone and clay (Cre-Paleogene); f) carbonate (Mesozoic); g) master fault; dashed if buried or inferred; h) soil samples for U determinations.

The most apparent hydrothermal manifestations are located along the edges of the basin. Discharges of gas-rich (CO_2) waters are also present in the middle of the basin along the transversal Arbia fault system (Acqua Borra, Bagnacci, Acquapuzzola), where the thickness of the clay marine sequence is estimated to be a few hundreds of metres. These structural features exercise the dominant control over local hydrothermal circulation (Barazzuoli *et al.*, 1987; Liotta, 1991). The hydrological and hydrochemical features of sampled discharges have already been described by previous works (e.g., Fancelli and Nuti, 1975; Barazzuoli and Micheluccini, 1982; Barazzuoli *et al.*, 1986). Duchi *et al.* (1992) have interpreted the composition of gases discharged with waters as typical of low enthalpy geothermal systems; H_2 and H_2S are generally below the detection limit, CO_2 represents the most abundant gas (up to 99%) and the N_2 and O_2 contents vary depending on the mixing with recharge waters. He isotopic data of gas samples along the Arbia Line reveal a signifi-

cant mantle signal ($^3\text{He}/^4\text{He} = 0.15\text{--}2 \text{ Ra}$) and ^{13}C data are close to those for mantle-derived magmas (-4 to -6‰ ; Minissale *et al.*, 1997).

METHODOLOGY

The surveyed area and locations of 14 sampling sites are shown in Fig. 2. All sub-systems (soil-gas, exhalation flux, gas vents, groundwater) were analysed at sites 1 to 7 and 14; the other sites have not gas vents. In each site, the sub-systems were all sampled within a few square metres area (about 10 m^2). The average of duplicate sampling and analysis of soil-gas, gas vents and dissolved gas was considered. Sampling was focused over the two main tectonic discontinuities crossing the graben. For comparison, samples were also collected within the basin, far from tectonized areas. The Rn and CO_2 fluxes were measured in 35 sites homogeneously distributed in these three sectors. Moreover, in the sampling point 1 (Rapolano

Fault) a Rn soil-gas profile (8 points) was performed crossing a fault close to a 150 m long rectilinear travertine "ridge" formed by oversaturated CO₂ waters. Soil-gas was sampled at 0.7 m below the ground surface by portable hollow steel probes (Lombardi and Reimer, 1990). The exhalation flux was measured following a closed chamber method (Etiope and Lombardi, 1997). Free gases from vents and bubbling pools were collected through an inverted funnel and driven into gas-tight vessels. In all gas samples, ²²²Rn was determined in the field using an α scintillation counter (EDA RDA 200). Dissolved Rn was previously extracted by air stripping. Samples for dissolved He and CO₂ analyses were collected from springs (sites 1, 3, 6, 7, 10, 11) and wells (2, 5, 8, 9, 12, 13, 14) by admitting water into a gas-tight 500 cm³ glass vessel equipped with vacuum stopcocks. The stopcocks were closed after flushing with several volumes of fluid to purge the sampling system from atmospheric air.

The determination of He and CO₂ was performed in the laboratory within 10 days after sampling by quadrupole mass spectrometry. Dissolved gas was previously separated from the water phase in a vacuum line. Analyses of standards

indicate that the analytical uncertainty is within 10% for samples collected in the gaseous phase whereas it reaches 15% for dissolved gas analyses, including also the extraction procedure. In addition, 4 soil samples were analysed for ²³⁸U by gamma spectrometry, density, porosity and moisture. Further details of field and laboratory procedures are reported elsewhere (Etiope, 1995; Guerra, 1996).

RESULTS AND DISCUSSION

The results, summarised in Table 1, are discussed by comparing data from the analysed subsystems. The wide range of values (e.g., 3 orders of magnitude for dissolved CO₂), between samples collected along the faults and those collected in the inner, non-faulted basin well reflects the control of geological and tectonic setting, at large scale, upon gas leakage to the surface. The values of soil-gas and groundwater collected in the inner basin, taken as reference, are consistent with those from other non-fractured areas of Italian sedimentary basins (Etiope and Lombardi, 1995a; Guerra, 1996).

Table 1. Data set of CO₂, Rn and He in soil-gas, soil-atmosphere flux, gas vent and groundwater

Site*	Soil-gas		Flux		Gas vent			Groundwater		
	CO ₂ (%)	Rn (Bq/L)	CO ₂ (10 ⁻⁸ m ³ m ⁻² s ⁻¹)	Rn (Bq m ⁻² s ⁻¹)	CO ₂ (%)	Rn (Bq/L)	He (ppmv)	CO ₂ (mmol/L)	Rn (Bq/L)	He (10 ⁻⁸ mol/L)
1RF	17.7	97.7	19.5	65.0	86.5	10	3.4	31.8	0.33	4.04
2RF	12.2	33.7	42.9	80.2	92.8	18	5.0	32.3	1.93	2.40
3RF	55.3	21.1	166.0	53.1	80.8	16	8.9	32.9	0.29	0.70
4RF	66.7	3.3	1318.0	1495.0	97.0	27	48.8	—	—	—
5AL	64.3	8.5	730.0	92.4	94.0	39	6.2	52.2	0.18	0.32
6AL	6.1	11.4	550.0	47.8	78.3	25	5.8	36.7	0.47	1.61
7RF	1.3	42.5	4.1	128.0	—	13	4.9	16.4	0.44	4.33
8IB	2.2	24.4	3.0	42.0	—	—	—	0.076	5.62	0.54
9IB	0.4	1.5	0	52.2	—	—	—	0.055	0.76	0.65
10AL	1.7	10.9	5.4	70.8	—	—	—	33.0	8.78	1.69
11RF	2.0	—	—	—	—	—	—	36.2	—	0.04
12AL	0.3	—	—	—	—	—	—	0.23	—	9.52
13AL	2.8	3.1	—	—	—	—	—	0.04	—	1.21
14RF	43.0	4.1	1070.0	105.0	98.1	33.0	19.1	46.5	0.30	0.10

*RF: Rapolano Fault; AL: Arbia Line; IB: Inner Basin.

Radon and uranium

In fault areas, a disequilibrium between the concentration of Rn in soil pores and the U content in soil is often found (e.g., Ball *et al.*, 1991; Akerblom, 1993). The theoretical maximum value of Rn produced *in situ* by its Ra parent, can be computed according to the equation:

$$\text{Rn (soil, Bq / L)} = [\text{Ra}] \varepsilon \rho n^{-1} \quad (1)$$

where [Ra] is the radium concentration in soil (Bq/kg), ε is the emanation power (%), ρ is the bulk density of soil (kg/m³) and n is the effective porosity (%). Table 2 reports the soil properties and the computed and measured soil-gas Rn values from unfaulted (inner basin, sites 8 a-b in Fig. 2) and faulted (Rapolano Fault, site 1 in Fig. 2) areas of the Siena basin. In order to set a generous upper limit of the calculated Rn, no adsorption of Rn on soil grain surface is considered and an high emanation coefficient, $\varepsilon = 0.3$, is assumed. This value is three times the mean attributed to the type of soil collected ($\varepsilon = 0.1$ Porstendorfer, 1993) and represents an upper limit for a sandy soil with 18% of moisture (e.g., Nazaroff, 1992; and references therein). Considering the homogeneous tex-

ture and moisture of the soil investigated, an emanating power higher than 0.3 would be an exception (Akerblom and Durrance, private communications). Computations suggest that in the inner basin, far from faults and geothermal springs (sites 8 a-b), the measured mean Rn value in soil is within the theoretical value computed; this is consistent with a production *in situ* of Rn by decay of Ra in the outcropping rocks. On the contrary, in the Rapolano Fault area (site 1) the mean measured Rn is about 50% higher than the computed one. One month later, a detailed soil-gas traverse across the Rapolano fault (Fig. 3), confirmed that in correspondence with the fault plane, Rn is well above the upper theoretical limit. This result suggests the occurrence of a Rn component migrating from subsoil, in addition to that produced within the soil by Ra decay. Indeed, the ascent of CO₂-rich gas is evidenced by some vents occurring few tens metres southward along the fault plane.

CO₂ concentration in groundwater and in soil-air

Evidence for CO₂ degassing from groundwater is given by the relationship between CO₂ in soil and in groundwater within faulted areas. The direction of mass transport of CO₂ between the unsaturated zone and groundwater can be evaluated by comparing the soil-CO₂ and water-CO₂ partial pressures considering the dissolved inorganic carbon, temperature, pH (reported in Guerra, 1996) and published equilibrium constants (Butler, 1982). Accordingly, Fig. 4 highlights that groundwater in the unfaulted areas (sites 8 and 9) or far from gassy springs (sites 12 and 13) have CO₂ concentrations close to that of air saturated water and are not far from equilibrium with the gas phase above the water table. On the contrary, in faulted aquifers CO₂ partial pressure is significantly greater than that in unsaturated-zone resulting in water-to-soil transport. This occurs also near the water discharges, when the water table is expected to be near the surface (and near the sampling depth). The resulting CO₂ pressure gradient induces an upward flux of CO₂ escaping from water to the unsaturated zone, that may involve also rare gases.

Table 2. Soil properties and comparison between computed (Rn_c) and measured (Rn_m) Rn concentrations in soil gases. The former is computed according to the formula (1) (range in bracket). For each area, ρ (bulk density), n (effective porosity), w (soil moisture), U_m and Ra (uranium and radium contents) are the mean of two measurements at different points; Rn_m is the mean of four soil-gas analyses performed exactly where soil is collected. The emanation coefficient (ε) assumed is an upper limit for a sandy soil with 18% of moisture (see text).

	Inner Basin	Rapolano fault
ρ (kg/m ³)	1380 $\pm$ 10	1360 $\pm$ 10
n (%)	0.25 $\pm$ 0.02	0.26 $\pm$ 0.01
w (%)	19.3	17.9
ε (%)	0.3	0.3
U_m (ppm)	1.4 $\pm$ 0.3	3.31 $\pm$ 0.3
Ra (Bq/kg)	17.2 $\pm$ 3.7	40.7 $\pm$ 3.7
Rn_c (Bq/L)	28.5 (20.5–37.9)	63.9 (55.5–73.0)
Rn_m (Bq/L)	15.4 $\pm$ 3.6	97.0 $\pm$ 6.8

Fig. 3. Radon concentration in soil gas from Terme S. Giovanni site (sampling site 1, Fig. 2) located along the RF. A profile was performed crossing the fault identified by a 150 m long rectilinear travertine "ridge" formed by over-saturated CO_2 waters. Rn values significantly higher than the computed values (horizontal dashed line) were found just in correspondence with the fault.

Fig. 4. Disequilibrium between CO_2 partial pressure in soil pores and groundwater (derived using equilibrium constants, dissolved inorganic carbon and pH). Numbers refer to sample locations reported in Table 1 and Fig. 2.

Rn and CO_2 : soil-gas concentration and soil-atmosphere flux

In Fig. 5, the CO_2 and Rn exhalation fluxes are compared with their concentrations in soil-air. These results (not located in Fig. 2) are from a survey of 35 flux measurements undertaken within

faulted and non-faulted areas of the Siena basin (Etiope and Lombardi, 1997). Direct correlation between CO_2 flux and its concentration in soil pores is apparent for all samples, including those collected near gas vent manifestations (Fig. 5(a)). When considering Rn flux and its concentration in soil-air, a clear inverse correlation arises near the gas vent sites (Fig. 5(b)). This can be interpreted as an effect of the high flux of carrier gas (CO_2) along the fault plane producing a suction of the nearby "static" gases trapped in soil pores, according to the Bernoulli effect. The rapid transport of trace gas into the channel prevents any accumulation of rare gas in the soil pores nearby the channel. A more detailed-semi-quantitative-picture of the progressive depletion of Rn in soil pores in correspondence with sites characterised by high flux of CO_2 is shown in Fig. 6(a).

Gas concentration in vents, groundwater and soil-atmosphere flux

The depletion of rare gas in soil gas pores is balanced by their enrichment in the composition of the vent gas. From the plots of Figs. 6(b) and

Fig. 5. Soil gas concentration and soil-atmosphere flux measurements of CO₂ (a) and Rn (b). Data were collected at 35 sites throughout the northern Siena basin, not reported in Fig. 2. The horizontal scale represents random locations and the line between dots does not imply continuity. A clear inverse relationship between Rn flux and Rn concentration in soil pores arises in correspondence with gas vent manifestations (marked by arrows).

6(c) it can be seen that the enrichment of trace gas in the channel/vent is more effective as much as the flux of the carrier (CO₂) increases, in spite of the large amount of discharged CO₂ that should dilute and minimise the rare gas signal.

In Fig. 6(d), CO₂ exhalation is compared with Rn content in groundwater at the gas vent sites. An apparent inverse relationship arises, although the small range of the Rn values can suffer from measurement error. This result suggests that the "suction" effect induced by the ascending gas column, as seen in the previous paragraph, is effective also below the water level. In this case microbubbles of CO₂ produce stripping of rare gas in solution that are transported rapidly upward. The same mechanism operates for He as depicted

by the relationship between He dissolved in groundwater and He concentration in vents (Fig. 6(e)).

This microbubble behaviour is consistent with the model of Varhegyi *et al.* (1986) and the laboratory experiments of Varhegyi *et al.* (1992) and Etiope and Lombardi (1996). It was then discussed by Etiope and Zhang (1998) for implication in the seismic precursor studies.

CONCLUSIVE REMARKS

The data set discussed in the present work included simultaneous measurements of gas in four sub-systems: soil-air, soil-atmosphere flux, gas vents and groundwater. Notwithstanding it was not

Fig. 6. a) Scatterplot of CO₂ exhalation vs. Rn concentration in soil gas collected in correspondence with gas vents. A logarithmic inverse dependence highlights the depletion of Rn in soil pores within the CO₂ vent area. b) Helium concentration in gaseous phase discharged at vents. A direct dependence with CO₂ flux is consistent with the channelling effect. c) Radon concentration in gaseous phase discharged at vents. A direct dependence with CO₂ flux is consistent with the channelling effect. d) Scatterplot of CO₂ exhalation vs. Rn concentration in groundwater. A quasi-logarithmic inverse dependence highlights the depletion of Rn in groundwater where the CO₂ discharge is maximum (or nearby the most powerful CO₂ discharges). e) Inverse relationship between He in groundwater and He concentration in the free phase of vents, as further evidence of the channel-induced partitioning effects.

possible to acquire a larger data set due to the uncommon site requirements (i.e., occurrence within a few square metres of a gas vent, a spring or well and soil B horizon), the results demonstrate qualitatively the importance of gas-water partitioning, gas stripping and channelling processes

in determining differential enrichment and depletion of rare gases within small areas.

Basically, our experience suggests that more attention should be paid in data interpretation for gas geochemical characterisation of a given area: in the same site low concentrations of Rn or He

Fig. 7. Qualitative model of the observed results in different sub-systems sampled in the Siena basin. High flux of carrier gas (CO_2) occurring along fault planes determines stripping of dissolved Rn and He, and suction of the gases trapped in soil pores, according to the Bernoulli effect. Accordingly, groundwater and soil-gas in fault zones may not display anomalies of the tracer gases.

in water can co-exist with high concentrations in the ground; low Rn in soil-air can occur in correspondence with Rn-rich gas vents; soil-gas Rn may be higher than the level induced by U decay in the ground or outcropping rocks. A qualitative model of the observed results is sketched in Fig. 7. The main implication is that in correspondence with faults bearing high flux of a carrier gas, either soil-gas or groundwater may not display Rn or He anomalies related to endogenous sources (e.g., geothermal activity, seismic precursor signals). The ultimate distribution at surface of rare gas is controlled not only by large scale geological factors such as lithology (radioactive decay in the shallow rocks) and faulting (permeability allowing gas migration), as generally assumed in geochemical exploration (e.g., Klusman, 1993), but also by physical gas-water interactions at local scale within fractured media. In some circumstances these processes may add to soil-atmosphere disequilibria (soil-air flushing, dilution, etc.) leading to more heterogeneous situations. An example may be the negative He anomalies in soil gas (i.e., He values lower than the atmospheric reference level) observed also along faulted zones, whose interpretation differs among some soil-gas researchers (e.g.,

Gregory and Durrance, 1985; Reimer, 1990; Lombardi *et al.*, 1993; Etiope, 1995).

In conclusion, in order to evaluate correctly the abundance of gases in a given area and for a reliable use of gas geochemistry in any application (natural resource exploration, earthquake precursor studies or radiation protection zoning) a comprehensive gas analysis, including as far as possible all types of sub-systems in the studied area, is recommended.

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