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Field Trip Guide Book - D03

FIELD SIGHT NEAR RAPOLANO TERME (SIENA, TUSCANY) RELATIONSHIP BETWEEN TECTONICS AND FLUID CIRCULATION

Leaders: M. Guerra, A. Raschi

Florence - Italy
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Post-Congress **D03**

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Front Cover:
Acqua Borra spring.

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Introduction

"… terra magis quod rara tepet circum fontem quam cetera tellus multaque sunt ignis prope semina corpua aquai"
(Lucrezio De Rerum Natura, liber VI)

"…the earth about that spring is porous more than elsewhere the telluric ground, and many be the seeds of fire hard by the water"

(Lucretius, On the Natura of things, book VI, Translated by William Ellery Leonard*)*

Although it has no basis in scientific fact, Lucretius' explanation of the occurrence of hot water springs anticipates the importance of the role of the enhanced "porosity" and the "fire seeds", as understood in today's terms. In our time, these features can be associated with permeability along preferential pathways ("porous earth"), and a high geothermal gradient ("seeds of fire"). Such features deeply affect the geothermal setting of an area.

This fieldtrip, in the northernmost part of the Neogenic clay basin of Siena Radicofani, aims to provide a "glimpse" of the relationship between fluid (gas and water) and tectonics.

The results of geochemical surveys performed in this area will be shown to focus on the key-concepts of channelling, stripping, gas-lift, and gas-water partitioning.

The one-day tour starts at the Acqua Borra spring, located 15 km southeast of Siena, and includes stops at the geothermal springs and gas vents in the area of Armaiolo-Rapolano Terme (15 km from Acqua Borra).

Selected references:
Geological sheets no.s 120 (Siena) and 121 (Montepulciano), Italian Geological Survey.

Topographic map (scale 1:50000): "Siena, le Crete e le Colline Senesi" no. 661 Kompass.

Regional geologic setting

The geological evolution of the Rapolano Terme area, is related to the Post-Tortonian disjunctive phase of the Apennine orogenesis, which led to the formation, along the western margin of Italy, of many continental Miocene and marine Pliocene NW-SE trending basins (Figure 1).

The investigated area corresponds to the Neogene Siena-Radicofani basin, a graben structure bordered on its eastern edge by the master fault of Rapolano Terme. The maximum throw reaches 2000 m near Rapolano Terme, and decreases southwards. 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 (Figure back cover). The western edge, bordered by the Monticiano-Roccastrada metamorphic ridge, has a more complicated fault system with lower 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 is connected with these lineaments. During the Quaternary, the ascent of sub-crustal material to the surface, formed the volcanoes in the southern part of the area (Mt. Amiata, Radicofani, and the Vulsini Mts.). Anomalous heat flow developed as a consequence of this magmatic activity, leading to intense hydrothermal circulation throughout the region.

The most apparent hydrothermal manifestations are located along the edges of the basin (approximately along the Rapolano-S. Casciano ai Bagni line to the east, and along the Orgia-Petriolo line to the west). Discharges of gas-rich (CO_2) waters are also present in the middle of the basin along the transversal fault systems (Acqua Borra, Bagnacci, and Acquapuzzola), where the thickness of the clay marine sequence is estimated to be a few hundred meters. These structural features exercise the dominant control over local hydrothermal circulation.

The chemical features of waters discharged in the Siena-Radicofani basin have been described by many authors (e.g. Chiodini and Cioni, 1989; Duchi et al., 1992; Duchi and Minissale, 1995). Taking into account the distribution of the major elements, the waters can be split into three groups:

- Ca-HCO_3-SO_4 waters discharge along the fault systems bordering the basin (Rapolano- Mt. Cetona to the E, Orgia-Petriolo line to the west). Their chemical makeup suggests that these waters circulate in the anhydrite-carbonate Mesozoic rocks, which form the main geothermal reservoir (Figure 2).
- Na-Cl waters discharge in the middle of the basin. This composition resembles that of fluid from the deep wells at the Latera, Torre Alfina, and Piancastagnaio geothermal fields, and are thought to be the result of

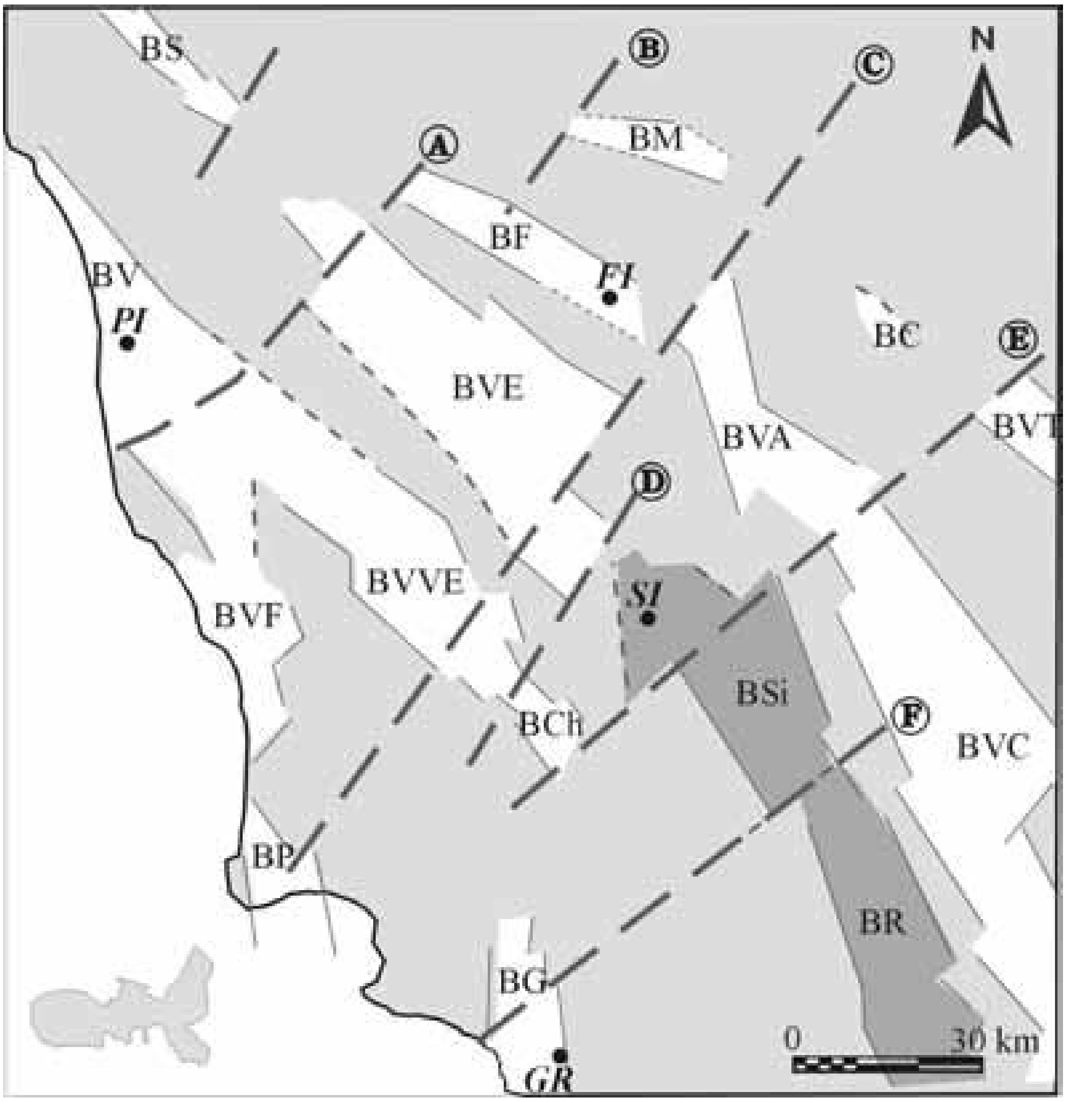

Figure 1 - Main sedimentary bains in Tuscany during Pliocene and Quaternary. NW-SE oriented normal faults formed graben structures, cut by transversal tectonic lines:
BAVM: B. dell' alta Val di Magra; BBVM: B. della bassa Val di Magra; BS: B. del Serchio; BV: B. della Versilia; BM: B. del Mugello; BF: B. di Firenze; BVE: B. della Val d' Elsa; BVVE: B. di Volterra-Val d' Era; BVF: B. della Val di Fine; BBVC: B. della Bassa Val di Cecina; BP: B. di Piombino; BC: B. del Casentino; BVA: B. della Val d' Arno; B. Ch.: B. di Chiusdino; BVT: B. della Val Tiberina: BVC: B. della Val di Chiana; BS: B. di Siena; BR: B. di Radicofani; BG: B. di Grosseto.
A) Livorno-Pistoia Line; B) Prato-Sillaro Line; C) Piombino-Faenza Line; D) Belforte-Monteriggioni Line; E) Arbia Line; F) Grosseto-Pienza Line (after Costantini et al., 1982) .

the interaction of deep fluids with the thick sequence of marine deposits overlying the reservoir. Waters from both these groups have temperatures lower than 50°C.

- Na-HCO$_3$ waters discharge from the Mt. Amiata volcanic rocks. These waters are cold, low-mineral, and gas-poor waters; the NaHCO$_3$ composition results from shallow circulation within

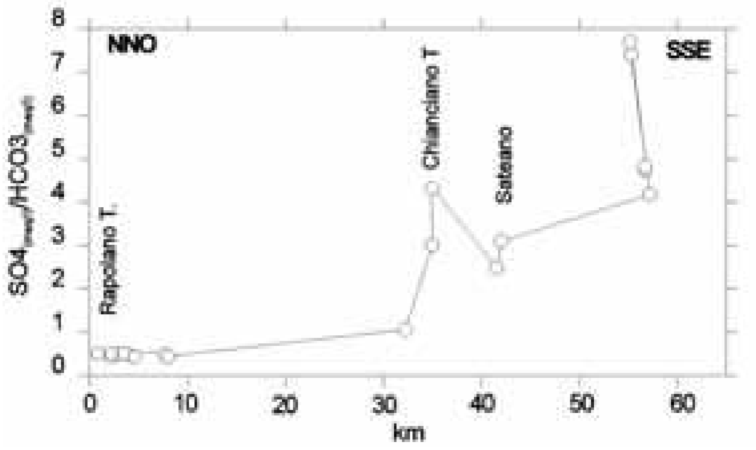

Figure 2 - SO_4/HCO_3 ratio for water discharged along the NNO-SSE Rapolano M.te Cetona ridge. Increasing values are related to the decreasing depth of anhydrites (anidriti di Burano) at the bottom of the "Tuscan Nappe" (Guerra, 1996)

the rhyodacitic rocks.

Isotopic studies (δD and $\delta^{18}O$), show that waters discharging both at the borders and the middle of the basin, have a common meteoric origin.

Duchi *et al.*, (1992), have interpreted the composition of gases discharged with waters as typical of low temperature thermal 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 content are variable, depending on the mixing with recharge waters.

In the neighbouring area, Rapolano Terme, two main regional tectonic structures are recognised: the *Rapolano fault*, that is the master fault bordering the

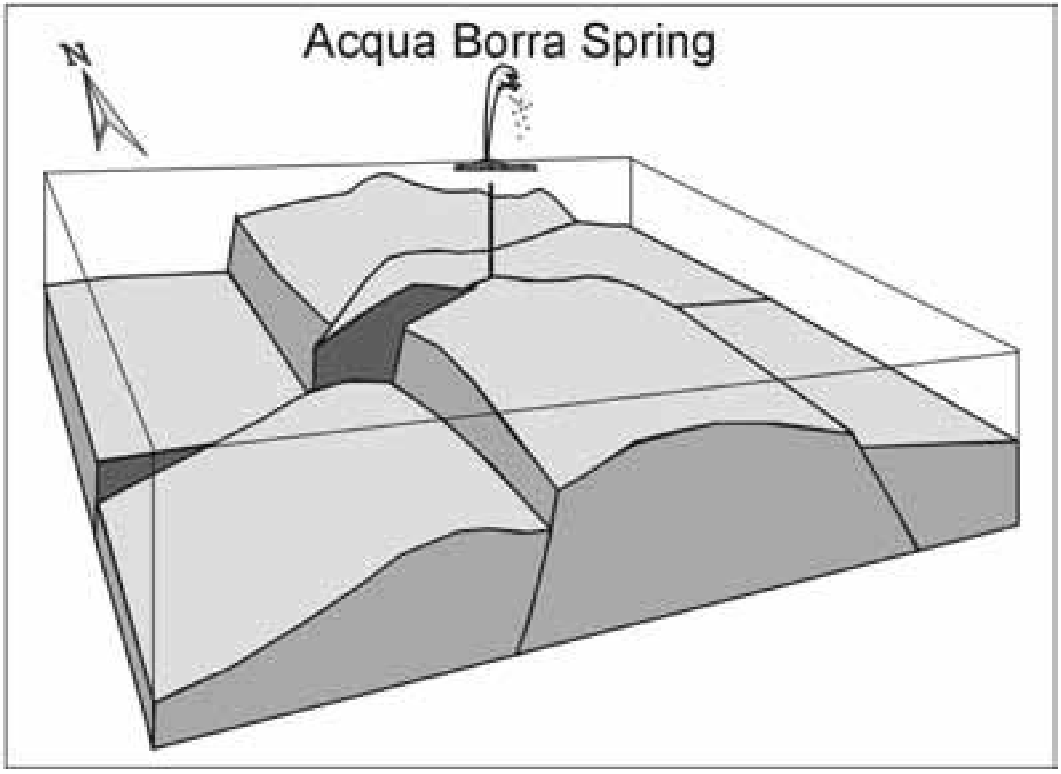

Figure 3 - Top of the carbonate geothermal reservoir in the Acqua Borra area. N-S oriented normal faults form a horst structure cut by the strike fault known as the "Linea dell'Arbia", (after Barazzuoli et al., 1987)

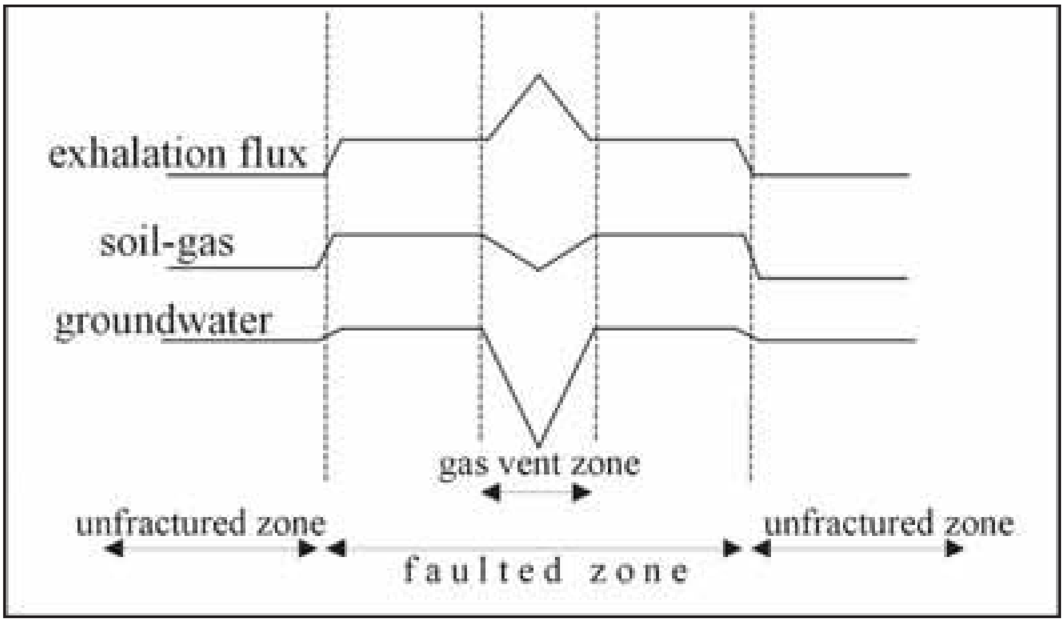

Figure 4 - Qualitative model of the observed results in different sub-systems sampled in the Siena basin. High flux of carrier gas (CO2) occurring along fault planes determines stripping of dissolved Rn and He, and suction of the gases trapped in soil pores, according to the Bernoulli effect. Accordingly, the groundwater and soil-gas in fault zones may not display anomalies of the tracer gases (after Guerra and Etiope, 1999)

Figure 5 - Hazardous CO_2 emission at Podere Castiglione gas vent

Figure 6 - Terme S. Giovanni, the travertine "ridge".

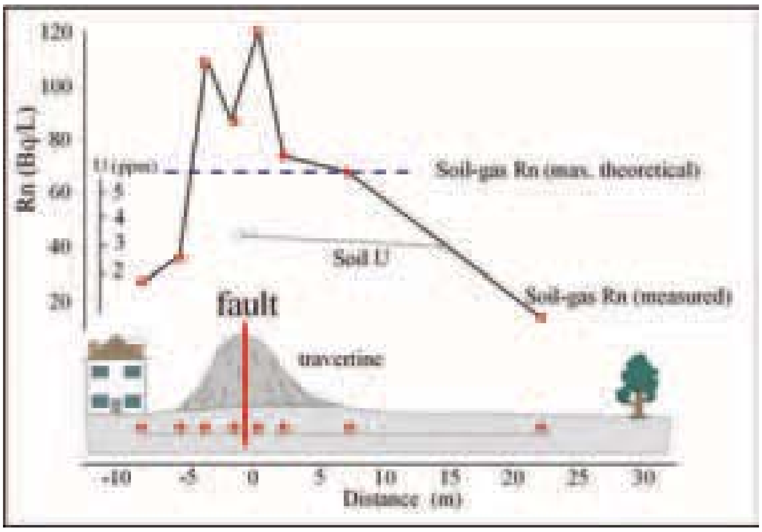

Figure 7 - Radon concentration in soil gas at Terme S. Giovanni. A profile was performed crossing the fault, which was identified by a 150 m long rectilinear travertine "ridge" formed by over-saturated CO2 waters. Rn values, significantly higher than the computed values (horizontal dashed line,) were found just in correspondence with the fault (after Guerra and Etiope, 1999)

NE side of the Siena basin, and the *Arbia line*, an anti-Apennine structure, crossing the NE part of the basin transversally. Such structural features exercise the dominant control on the local hydrothermal circulation, and make the uprising of geothermal fluids (gas and water) easier. Isotopic studies (D and ^{18}O) show that both waters discharging at the border of the basin (along the *Rapolano fault*), and waters discharging in the middle of the basin (along the *Arbia line*), have a common meteoric origin. Nevertheless, their chemical composition is quite different, being heavily affected by the rock-water interaction. In the first group, Ca-bicarbonate and Ca-

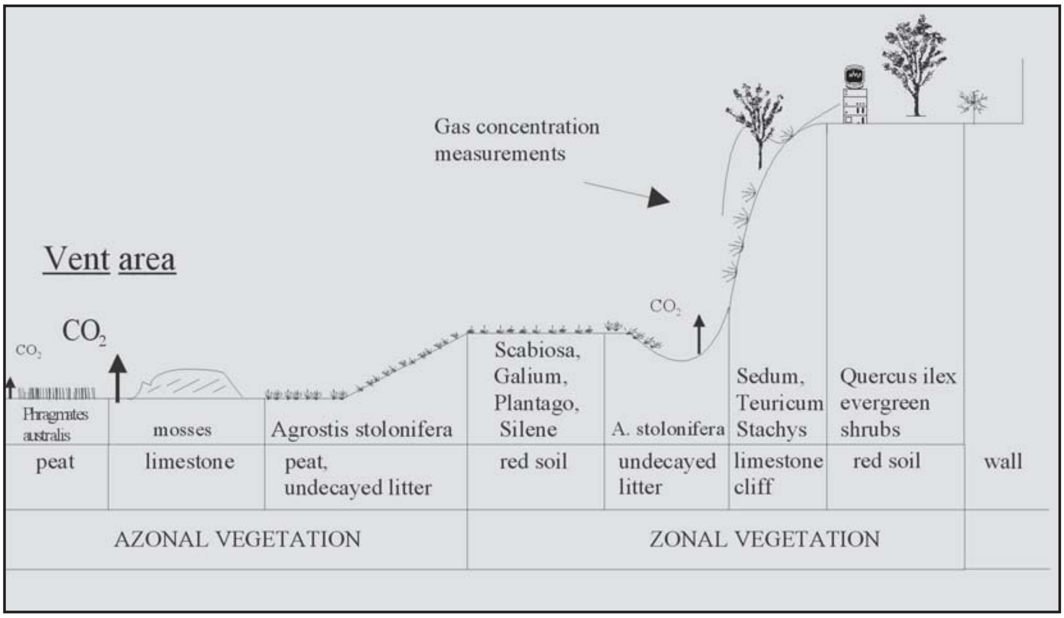

Figure 8 - Cross-sectional diagram illustrating the relationship between topography and vegetation at the Bossoleto site (modified from Miglietta et al., 1993).

sulphate waters prevail, whereas the second group is characterised by Na-cloride waters, reflecting the interaction with the marine clayey sequence.

Field itinerary

Stops are located within a radius of about 15-20 km. Field sights are all concerned with water and/or gas manifestations, and the structural setting. The itinerary will start at Acqua Borra, a few km south of Siena; the other stops are all clustered near the town of Rapolano Terme.

Stop 1:

Acqua Borra Spring

Acqua Borra is the most important spring to be found along the Arbia line; in addition, other springs or gas vent lie on this line (Ropole, Guistrigona, T. Ambra). As shown in Figure 3, this spring is located in correspondence with a "horst" recognised by geoelectrics and gravimetry. At this point, the thickness of the Pliocene clayey sequence, overlying the carbonate "basement", is about 400 m. Although Na and Cl content prevails by far, the absolute Ca-HCO_3 content is, approximately the same as that of the waters discharging along the Rapolano Fault, and supports the deposition of travertine. The temperature of the water is 37°C, and the TDS is 10,900 mg/l.

Stop 2:

Podere Castiglione

Poderese Castiglione is a dry gas vent placed at the limit between the Pliocene clay sequence filling the Siena graben, and the Cenozoic marine sediments of the Tuscan Nappe just along the Rapolano fault. CO_2 represents more than 99% of the discharged gas.

A high flux of carrier gas (CO_2) can determine stripping of dissolved Rn, He and other rare gases, as well as suction of these gases out of soil pores in which they have been trapped, according to the Bernoulli effect. Accordingly, near gas vents, the groundwater and soil-gas in fault zones may not display the anomalies of the tracer gases (Figure 4).

In some atmospheric circumstances (e.g. no ventilation), a local increase of atmospheric CO_2 can become a hazard for human and animal life (Figure 5).

Stop 3:

Terme S. Giovanni

Terme di S. Giovanni is located 2 km SW of Rapolano Terme.

The upwelling of thermal, CO_2 rich water, through a structure related to the Rapolano fault, has produced a travertine "ridge" 100 m long and several meters wide

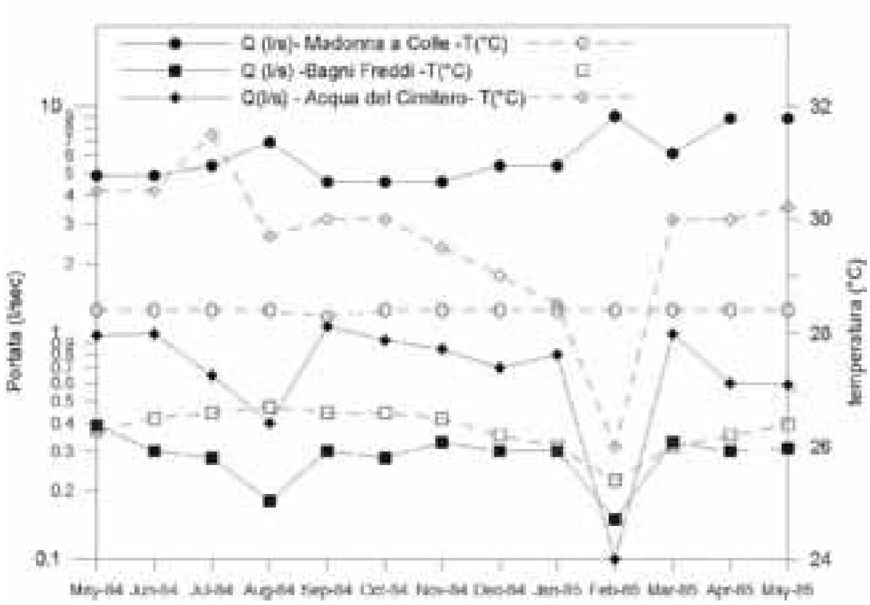

Figure 9 - Flow rates and temperature changes at "Bagni Freddi" and "Acqua del Cimitero" springs, as a response of pumping test at "Madonna a Colle" well (data from Barazzuoli et al., 1987).

(Figure 6). A fracture cuts the top of this structure longitudinally.

A 20-m-deep, artesian well, drilled in 1950, just few meters from the travertine "ridge", collected most of the discharged water. Water emerges at 37-39°C, with a flow rate of about 1 m^3/min. Historical analysis shows a slight decrease of temperature from 39° –just after the drilling– to the 37.6 measured during the 1990s, with all other parameters unchanged.

The stripping of dissolved trace gases by CO_2, and/or their leakage along the fault, were suggested by an analysis of the results of soil gas survey (Figure 7).

Stop 4:

Bossoleto

Just few dozen meters east of the travertine "ridge", there is a circular-shaped doline, known as Bossoleto (Lat. 43°17', Long. 11°35'), about 80 m in diameter and 6 m deep.

Gas emissions come out from several vents distributed on the bottom of the crater, and from a large cave located at the bottom of the bowl towards the south of the site. CO_2 emissions at this site have locally been known at least as far back as the early part of the 19th century.

	Composition(V/V)
CO_2	96.1 %
H_2S	0.02 %
CH_4	0.45 %
N_2	3.40 %
H_2	Traces
He	39 ppm
Ar	3 ppm

Table I - Chemical composition of the gas emitted at the naturally CO_2 enriched area of Bossoleto.

Gas emissions are mainly composed of CO_2 (Table I). Although traces of hydrogen suphide have been detected accompanying the CO_2 venting at the surface, this phytotoxic gas is dissolved in the water, then rapidly oxidised in contact with the air, and finally greatly diluted in the atmosphere. Chromatographic determination of H_2S concentrations made in air samples collected at Bossoleto, showed that H_2S levels in this site were below the detection threshold of 0.0001 µmol mol^{-1} when [CO_2] was about 5000 µmol mol^{-1}. This small bowl-like depression is surrounded by ancient natural walls that have reduced factors of human disturbance.

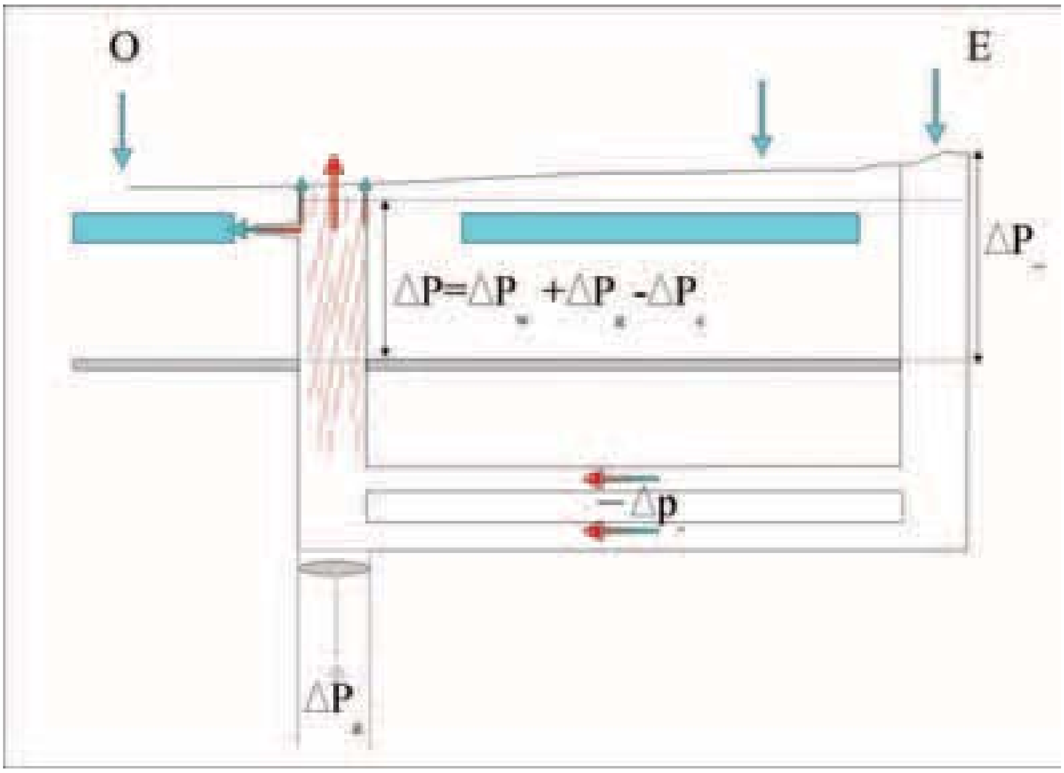

Figure 10 - Model of fluid circulation at in the Rapolano area. This model can be applied to the "Antica Querciolaia" geyser, and the Madonna al Colle and Terme S. Giovanni wells. At discharge, fluid pressure (P) is due to the balance between hydraulic head (P_w), gas pressure (P_g) and head loss (P_c). The gas pressure produces the overpressure that can lift water above ground level (Guerra, 2003).

Atmospheric CO_2 concentrations vary during the day, and partly depend on atmospheric conditions. Concentrations as high as 75% have been measured between 7 and 8 am. At this time of the day, it is possible to see the refractive boundary between the region with very high CO_2, and the more normal, less dense, air above it. The boundary tends to become unstable as soon as direct solar radiation falls on the zone at the bottom of the doline. Then the high concentration is rapidly dispersed, dropping to levels of around 2000 µmol mol-1.

Other environmental factors at Bossoleto are influenced by the combination of topography and carbon dioxide emissions; the most marked example is observed for air temperature, which shows a rapid increase in the early morning, associated with the presence of the stable atmospheric conditions at the bottom of the doline. This heating is associated with an enhanced greenhouse effect, resulting from the high CO_2 concentration at the bottom. When direct solar radiation is incident on the high CO_2 atmosphere, a sudden temperature increase takes place; temperature decreases to more "normal" values when buoyancy promotes air mixing.

Vegetation

This extreme environment has led to the establishment of a peculiar plant community, whose spatial arrangement follows the typical centrifugal model, as in the vegetation of solfataras, but has a different and more variable species composition, due to the absence of a strong acidity, because of the conflicting effect of basic salts such as calcium carbonate. The absence of "disturbing" factors, such as soil acidity and H_2S in the emitted gas, together with the higher species richness, allow this type of mineral spring to provide the most suitable biotopes for studying the effects of elevated atmospheric CO_2 on plants. A recent survey highlighted that Bossoleto's vascular flora consists of about 90 species of grasses, herbs, shrubs and trees, belonging to 39 families (Selvi 1999), along with several bryophytes and lichens. This highly diversified taxonomic range, which is subjected to different levels of CO_2 concentrations, provides valuable opportunities to study CO_2-plant relationships, also at population and community levesl. The lowest areas, characterized by very high carbon dioxide concentrations for at least part of the day, show the presence of a monospecific population of Phragmites australis, together with lichens and mosses, surrounded by a ring of Agrostis stolonifera. On the raised banks of the doline, a more varied population exists, followed by a grove of different Mediterranean tree species (Figure 8).

Stop 5:

Bagni Freddi and the geothermal well at Madonna al Colle.

These manifestations are very easy to reach from the HOTEL 2 MARI (a 5 min walk). Bagni Freddi is a thermal spring (T°C 25-26, TDS 4,500 mg/l), used for therapeutic purposes since 1750, now abandoned.. The thermal well at Madonna al Colle (depth 54 m) was drilled in 1977 for geothermal prospecting. The "artesian" character of Madonna al Colle well, the geyser at "L'Antica Querciolaia", and the well at Bagni San Giovanni, is closely related to the large amount of gas (CO_2) that is released during the upwelling of geothermal fluids. In such circumstances, water is lifted by gas pressure. Pumping tests have demonstrated the hydraulic connection between this well and the springs of "Bagni Freddi" and "Acqua del Cimitero", located a few dozen meters apart. The increase of pumping rate causes the decrease of the natural flow rate and temperature at the springs, and, as a result of this, a depletion of the input of "deep" hydrothermal waters" (Figure 9).

Stop 6:

Cava Paradiso

Cava Paradiso is a travertine quarry near Serre di Rapolano. The discharging of water begin in 1964 while the extraction of travertine was in progress. The initial flow was quite high (30 l/sec). This event forced the quarry to be abandoned. A thick cover of travertines outcrops all over the area near Serre di Rapolano. Here, the depth of the carbonate "basement" is very small, and it outcrops locally, forming the so-called *Rapolano-Mte Cetona ridge*. In this way, the important deposition of travertine is mainly due to:

- a very abundant source of $CaCO_3$ (the marine Mesozoic carbonate) placed at a shallow depth;
- a CO_2 gas-rich component in groundwater. It makes the groundwater aggressive, so the dissolution of primitive carbonate is increased. At the surface, the degassing of CO_2 produces the deposition of travertine.

Acknowledgments

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Reference cited

Barazzuoli P, Costantini A., Grassi S., Lazzarotto A., Micheluccini M., Piantelli F., Salleolini M., Sandrelli F., Squarci P., Taffi L., Veronesi G. (1987): L' energia geotermica in provincia di Siena. Amministrazione provinciale di Siena.

Chiodini e Cioni, (1989): Gasgeobarometry for hydrothermal system and its application to various Italian geothermal areas. Appl. Geochem., 4, pp 564-572.

Costantini A., Lazzarotto A., Sandrelli F. (1982): Conoscenze geologico-strutturali. In: Il graben di Siena. CNR, PFE, SPEG, R.F. 9, PEG ed. Milano.

Duchi V., Minissale A. (1995) Distribuzione delle manifestazioni gassose nel settore peritirrenico tosco-laziale e loro interazionie con gli acquiferi superficiali . Boll. Soc. Geol. It., 114, pp. 337-351.

Duchi V., Minissale A., Paolieri M., Prati F. Valori A. (1992): Chemical relationship between discharging fluids in the Siena-Radicofani graben and the deep fluids produced by the geothermal fields of M.te Amiata, Torre Alfina and Latera (Central Italy). Geothermics, vol. 21, n°3, pp 401-403.

Guerra M. (1996): *I gas disciolti nelle acque e loro significato nelle indagini strutturali ed idrogeologiche (in Italian)*. Ph.D. thesis. Dip. Scienze della Terra, Un. "La Sapienza" Roma. Depositata presso le biblioteche nazionali di Roma e Firenze.

Guerra M. ed Etiope G., (1999): *Effects Of Gas-Water*

Partitioning, Stripping And Channelling Processes On Radon And Helium Gas Distribution In Fault Areas. Geochem. J. Vol. 33, n° 3, pp. 141-151.

Guerra M., (2003): “Relazione tecnico-scientifica sulle principali emergenze termali del Comune di Rapolano Terme: variazioni pluriennali, interconnessioni e prospettive per una corretta gestione” (in Italian). Rapporto tecnico per il Comune di Rapolano Terme.
Miglietta, F., Raschi, A., Bettarini, I., Resti, R., Selvi, F. (1993). Natural CO2 springs in Italy: a resource for examining long-term response of vegetation to rising atmospheric CO2 concentrations. *Plant, Cell & Environment*, **16**, 873-878.

Selvi F. (1997): Acidophilic grass communities of CO2-springs in central Italy: composition, structure and ecology. In: Raschi A., Miglietta F., Tognetti R. & Van Gardingen P. R. (Eds.), Plant Responses to Elevated Carbon Dioxide: Evidence from Natural Springs, pp. 114-133. Cambridge University Press.

Back Cover:
field trip itinerary

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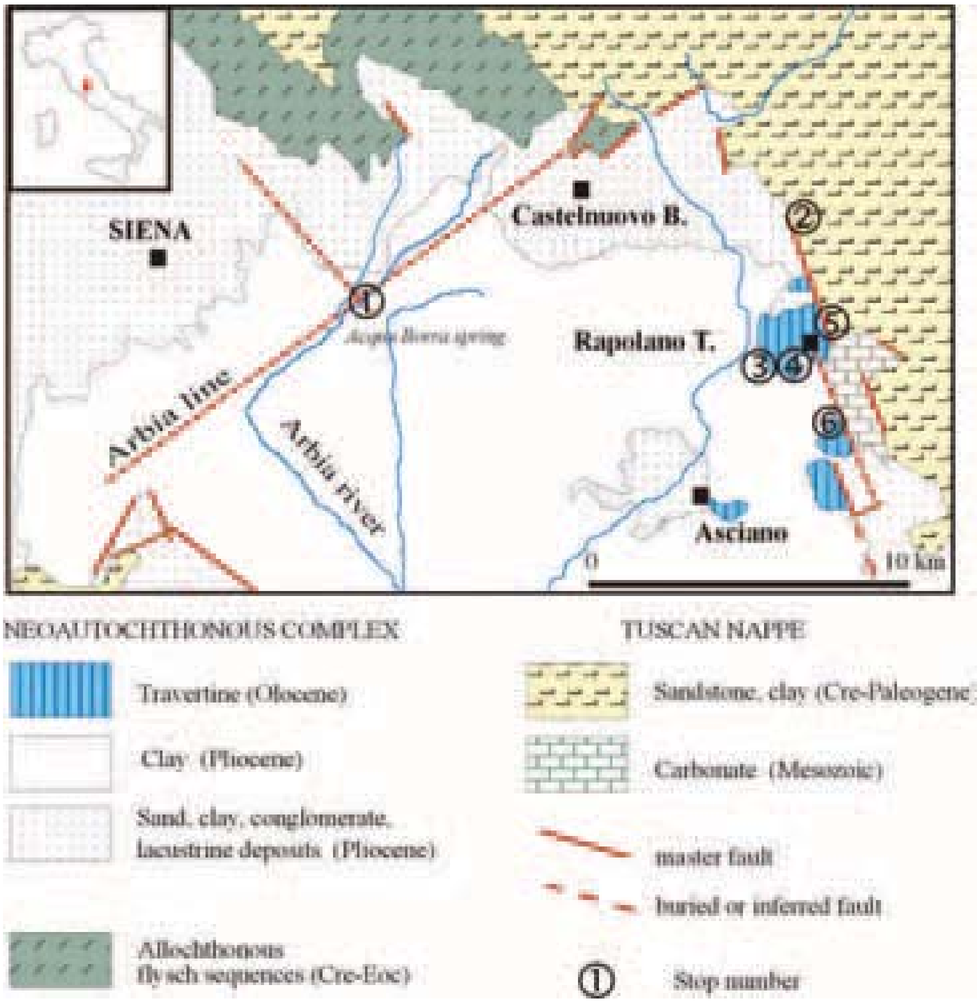
FIELD TRIP MAP



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