Atti Soc. tosc. Sci. nat., Mem., Serie A, 106 (1999)
pagg. 45-53, figg. 7, tab. 1

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ISOTOPIC AND CHEMICAL COMPOSITIONS OF SOME THERMAL GROUNDWATERS AND ASSOCIATED GASES IN THE SERCHIO RIVER VALLEY, NORTHERN TUSCANY, ITALY

Abstract - The isotopic composition of thermal water from the neighbouring localities of Torrite and Pieve Fosciana in the Serchio River valley, Northern Tuscany, was measured together with the chemical composition of associated gases and radon activity. At Torrite water nowadays outflows through an artificial tunnel: it shows high radon activity and its isotopic and chemical features suggest considerable mixing with shallow cold water. At Pieve Fosciana, water from boreholes was almost constant in stable isotope abundance during the years 1983-1998. Tritium contents also showed only very slight variations, their low values agreeing with the presence of waters older than 25 years in the Pieve Fosciana aquifers. An ephemeral spring that appeared at Pieve Fosciana in 1996, linked to an abrupt lowering of the water level in the nearby pond, was isotopically and chemically very similar to borehole water. Gases associated with this ephemeral spring had a lower radon content and a higher helium abundance than those measured at Torrite.
Water recharge elevations are calculated at about 1100 m a.s.l. for Pieve Fosciana and 900 m a.s.l. for the Torrite sample. The Torrite value is very doubtful due to the shallow contamination. Probably, two separate circulation systems, linked to the Apuan and Apennine relief systems, are involved in feeding the aquifers studied even though these two manifestations are only a few km apart. We can hypothesise that the same geological formation serves as a common reservoir, but the isotopic and chemical features of waters and gases indicate the different routes and times used to reach the surface. Longer residence and/or rising times of thermal waters appear to be associated with the Apennine side circulation system.

Key words - Tuscany, Apuan Alps, Garfagnana, thermal water, stable isotopes, tritium, helium, radon.

Riassunto - *Composizione isotopica e chimica di acque termali e dei gas associati nella valle del fiume Serchio, Toscana settentrionale, Italia.* In questo lavoro vengono riportati i risultati dello studio della composizione isotopica e chimica dei fluidi in due manifestazioni termali, poste a pochi km di distanza fra loro nella valle del fiume Serchio, Toscana nord-occidentale. Le acque termali delle antiche sorgenti di Torrite, vicino Castelnuovo Garfagnana, sono attualmente convogliate in parte all'interno del canale artificiale di scarico di una centrale idroelettrica e sono campionabili raramente e con molta difficoltà. I campioni di acqua raccolti hanno una temperatura di 20.6°C ed un residuo solido di 1940 mg/l, ma questi valori sono nettamente inferiori a quanto riportato in studi precedenti la scomparsa della sorgente naturale. I gas associati mostrano un'elevata concentrazione di ^{222}Rn. Nel complesso le composizioni isotopica e chimica delle acque suggeriscono un elevato grado di mescolamento con una componente superficiale fredda. Le acque termali di Pieve Fosciana, storicamente caratterizzate da temperature massime intorno ai 40°C e salinità oltre i 6 g/l, fuoriescono al presente in località Prà di Lama da due pozzi artificiali, che hanno causato la scomparsa delle sorgenti preesistenti, e confluiscono in un piccolo lago. Saltuariamente la formazione di sorgenti effimere si accompagna ad improvvisi svuotamenti del lago stesso; il monitoraggio dei pozzi negli anni 1983-1998 ha compreso anche l'evento di questo tipo occorso nella primavera del 1996. Nel corso degli anni non sono state osservate variazioni apprezzabili nel contenuto in isotopi stabili, nemmeno nella sorgente temporanea del 1996, ed anche il contenuto in tritio ha mostrato oscillazioni molto piccole, suggerendo età superiori ai 25 anni per le acque termali. I gas campionati alla sorgente temporanea del 1996 hanno mostrato un'attività ^{222}Rn notevolmente più bassa, ed un contenuto in elio più elevato, di quanto rispettivamente misurato in quelli associati alla manifestazione termale di Torrite.
Tutte queste acque si mineralizzano a temperature relativamente basse, senza scambio isotopico con le rocce circostanti. Le altitudini medie d'alimentazione sono stimate intorno ai 1100 m per le acque di Pieve Fosciana e di 900 m per quelle di Torrite; fermo restando che per quest'ultime l'accertata contaminazione con circuiti superficiali introduce una sensibile incertezza. Queste due manifestazioni sono localizzate a pochi chilometri di distanza l'una dall'altra, probabilmente alimentate da due diversi circuiti idrogeologici, collegati ai rilevi appenninici ed apuani. È ipotesi prevalente che la formazione geologica sede del serbatoio profondo e luogo della mineralizzazione e riscaldamento delle acque sia la stessa per tutte le acque termali dell'area, ma le caratteristiche isotopiche e chimiche dei fluidi termali testimoniano comunque l'esistenza di differenti circuiti nonché diverse modalità di risalita. Tempi di residenza e/o risalita più lunghi appaiono riferibili alla circolazione che interessa il versante appenninico.

Parole chiave - Toscana, Alpi Apuane, Garfagnana, acque termali, isotopi stabili, tritio, elio, radon.

INTRODUCTION

Tuscany is a region rich in thermal water systems, the most famous being the well-known Larderello geothermal field located in southern Tuscany (Minissale, 1991). The thermal waters studied in this work occur north of the Arno river, in the northwestern corner of Tuscany. This area is characterised by numerous thermal manifestations distributed over about 2000 km^2 bordered by the Ligurian Sea to the west, to the east by the Apennine chain and cut by the Serchio River val-

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ley. It is a mountainous region with highest elevations close to 2000 m a.s.l., which includes the Apuan Alps, known world-wide for the «Carrara» marble quarries, and site of a number of base metal ore deposits that were mined in the past. Annual rainfall values are in the range of 900 to 3200 mm, with strong inland gradients, related to the altitude and location of the two mountain chains lying roughly parallel to the coast.
The systematic isotopic study carried out in recent years on the precipitation and springs from this area (Mussi *et al.*, 1998), also includes a survey of thermal waters too (Calvi *et al.*, 1999). There are also some thermal springs on the northern border of the Apuan Alps too, but those under consideration are located in the Serchio River valley, which runs along the eastern border of the autochthonous units of the Apuan Alps (Fig. 1). The two springs studied are located at Torrite, near Castelnuovo Garfagnana, and Pieve Fosciana, in the province of Lucca. These springs are of particular importance owing their temperatures of 34 ÷ 39°C and salinity values of ~ 6 ÷ 7 g/l (De Stefani, 1904; Masini, 1957; Fancelli *et al.*, 1976; Bencini *et al.*, 1977). The data reported here concern the stable isotopes of hydrogen and oxygen, the radioactive isotopes of hydrogen and radon and some chemical parameters. They are the first isotopic and gas abundance measurements concerning the Torrite thermal waters. Conversely, the Pieve Fosciana manifestation has been studied in the past for its isotopic composition (Fancelli *et al.*, 1976 and some unpublished technical reports) but never regularly monitored for a long period. The Pieve Fosciana thermal waters are very close to a pond which undergoes an abrupt lowering of level or disappearances from time to time: a detailed series of measurements was also carried out during one of these events, in the spring of 1996.

ANALYTICAL METHODS

Isotopic and chemical analyses were performed at the laboratory of the International Institute for Geothermal Researches of C.N.R, Pisa, following well-established procedures.
The oxygen isotopic composition was measured by the water-CO_2 equilibration method at 25°C (Epstein & Mayeda, 1953). The hydrogen isotopic composition was measured following basically the procedure of Coleman *et al.* (1982), reducing water to H_2 at 460°C using metallic zinc. All the procedures were calibrated to the international standards according to the recommendations of the International Atomic Energy Agency of Vienna (IAEA). CO_2 and H_2 were analysed with a mass spectrometer for $^{18}O/^{16}O$ and $^2H/^1H$ ratios, the results expressed in δ‰ units relative to the VSMOW standard (Gonfiantini, 1984). Analytical uncertainties are ± 0,1‰ for oxygen and ± 1‰ for hydrogen. Determination of tritium content was done in a proportional counter by β^- counting in the gaseous phase of ethane obtained by reaction of hydrogen with ethylene (Cameron, 1967). Tritium contents are expressed in tritium units (TU): one tritium unit has an isotopic ratio $^3H/^1H = 10^{-18}$ (IAEA, 1983). Accuracy of the results is reported accompanying each analysis. Chemical analyses of gases were performed by standard gaschromatography procedures. ^{222}Radon activity in gases was measured in the laboratory by proportional counting of a gaseous sample, about three hours after collection.

GEOLOGICAL SETTING

In the survey area, the Apuan Alps and the Apennines are almost parallel to the coastline. Two main tectonic and stratigraphic units can be recognised in this area: the metamorphic sequence of the Apuan Alps and the comparable members of the Tuscan Nappe. The Apuan Alps are a metamorphic structure in a large tectonic window of the Northern Apennines nappe cover, overthrust during the Alpine-Apennine orogeny that caused their metamorphism (Carmignani & Kligfield, 1990). A basement of Palaeozoic to Triassic age rocks, mainly phyllites, quartzites and metavolcanics, underlies a dolomitic formation and carbonate, arenaceous and clayey formations, Triassic to Oligocene in age. The corresponding non-metamorphic or very low-grade formations of the Tuscan nappe «Falda Toscana» are Mesozoic to Tertiary sedimentary units with limestones, dolostones and siliciclastic lithologies. The basin of the Serchio River is located between the two mountain chains, in a tectonic depression bordered by numerous fault lines associated with the extensive phase of the Plio-Pleistocene. It comprises two basins in part filled by Quaternary fluvio-lacustrine deposits. There are also outcrops of arenaceous, marly and clayey terrains of the Unità Liguri and of the Tuscan Nappe. These lithologies also predominate on the Apennine side, where sporadic outcrops of carbonate rocks can be found in correspondence with the nucleus of folded structures. Carbonate formations, metamorphic or otherwise, form the highest part of the Apuan side (Dallan Nardi & Nardi, 1974). Low permeability distinguishes the Palaeozoic basement, with no fractured zones, whereas high permeability is typical of the carbonate formations, such as the «Marmi» and «Grezzoni» of the Apuan Alps, the «Calcare Cavernoso» and «Calcare Massiccio» of the Tuscan nappe cover. These carbonate rocks represent the main regional water circulation system (Baldacci *et al.*, 1993) (Fig. 1). The evaporitic glide horizon of the Norian «Cavernoso» cellular dolomitic limestone, responsible for the detachment of the Tuscan nappe, probably influenced the thermal reservoir of all the manifestations of the study area (Baldacci & Raggi, 1982).

THE STUDIED THERMAL WATERS

Torrite thermal spring

The thermal waters of Torrite were also known in ancient times: «*mille passus procul a Thermis* (of Pieve

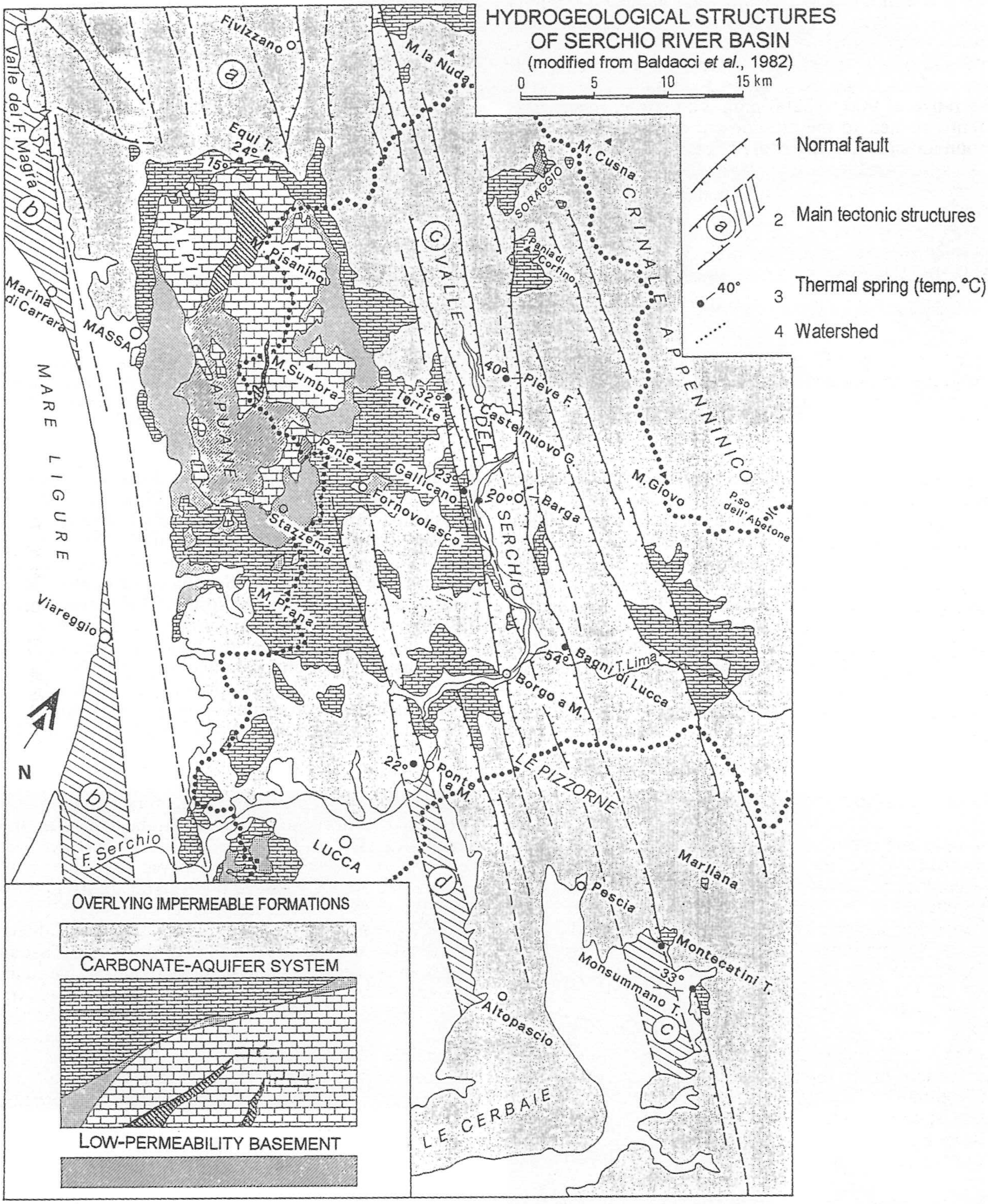

Fig. 1 - Location of the springs studied and hydrogeological structures of the Serchio river basin. (a...d, main grabens in the area; dotted lines: hidden by sedimentary cover).

Fig. 2 - Image reproduced from an old picture postcard «*Greetings from Garfagnana. View of the thermal spring of Torrite, after the earthquake of March 5 1902*».

Fosciana*), sed in opposita parte alterius montis quaedam aquae thermales nuper inventae sunt*» (Jacopo Lavelli, 1609, quoted in De Stefani, 1904). The spring disappeared after an earthquake in 1740, but appeared again after another earthquake in 1902 (Fig. 2). A detailed description of the history of these springs can be found in De Stefani (1904). During the excavation of the discharge tunnel of the nearby hydroelectric power plant, built around 1948, thermal waters were intercepted and drained into the tunnel. Therefore the ancient springs vanished.

The Torrite spring was located near Castelnuovo Garfagnana, at 290 meters a.s.l., on the Apuan side of the Serchio River valley. It was located along the Turrite Secca torrent, outflowing from the «Calcare Massiccio» limestone formation, which directly overlies the «Calcare Cavernoso» dolomitic limestone of evaporitic character. A fault joins limestone to the impermeable formation of «Scaglia e calcareniti a nummuliti», thus originating the spring. This thermal manifestation is very difficult to sample because nowadays it can only be found under the water surface and deep inside the water discharge tunnel of the hydroelectric power plant. Sampling was possible on September 5, 1994, when the hydroelectric power plant stopped for a period of maintenance. We entered the tunnel for

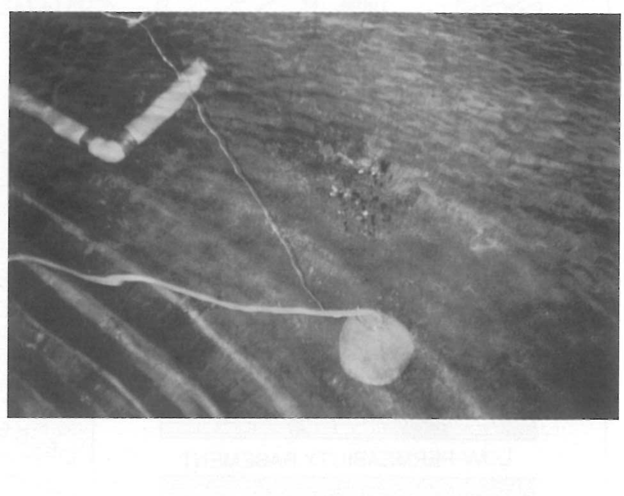

Fig. 3 - Gas bubbling from the bottom of the tunnel and sampling apparatus.

Tab. 1 - Analytical results on Torrite and Pieve Fosciana thermal waters and gases. Right, left and tunnel refer to waters from the two holes near the tunnel basement or flooding the tunnel, respectively. The Torrite gas sample was collected directly above the tunnel basement. See text for more details.

	Torrite, September 5, October 6, 1994			Pieve Fosciana, March 12÷April 24, 1996		
	right	left	tunnel	P2 borehole	P1 borehole	ephemeral spring
°C (max)	20.6	19.8	14.0	37.8 ÷ 38.3	31.7 ÷ 32.4	26.6 ÷ 37.0
Res. 180°C (mg/l)	1940	-	930	6150 ÷ 6320	5950 ÷ 6190	6100 ÷ 6180
cond. (μS)	2670	-	1270	8600 ÷ 8850	8450 ÷ 8590	8570 ÷ 8970
pH	7.1	-	7.5	6.8 ÷ 7.3	6.9 ÷ 7.3	6.9 ÷ 7.2
alc.tot.(meq/l)	3.12	-	-	3.7 ÷ 3.9	3.9 ÷ 4.0	3.3 ÷ 3.5
$\delta^{18}O$‰ (SMOW)	-7.47	-7.47	-7.40	-7.78 ÷ -7.92	-7.80 ÷ -7.93	-7.83 ÷ -7.96
$\delta^{2}H$ ‰ (SMOW)	-46.5	-46.3	-46.6	-50.3 ÷ -50.9	-48.9 ÷ -50.4	-49.1 ÷ -50.3
^{3}H (UT)	7.1 ± 0.9	5.9 ± 0.7	8.5 ± 1.0	1.3 ÷ 2.4	0.2 ÷ 1.9	0.0 ÷ 1.4
^{222}Rn (nCi/l)	-	-	38.1	-	-	1.3
He %	-	-	0.106	-	-	0.38
N_2 %	-	-	86.5	-	-	92.2
O_2 %	-	-	9.31	-	-	< 400 ppm
Ar %	-	-	1.04	-	-	1.15
CO_2 %	-	-	0.7	-	-	3.3 ÷ 4.0

some hundreds of meters by using a small boat and looked for the thermal waters. Well inside the tunnel, warm waters flowing from two artificial holes near the bottom were found. Separate samples were taken also by means of a PVC tube inserted by a scuba diver in the hole with a higher water temperature, i.e. at the right hand side of the observer. The thermal waters reached a level of 2.5 centimetres higher than the surface of the water in the channel and showed a maximum temperature of 20.6C° with a flow of about 10 l/m (Fig. 3). Temperatures of 19.8 and 20.6°C were measured where the thermal waters outflow, 2.5 m under the water level, while the water of the channel was 14.0°C; no H_2S was detected. The physical, hydrochemical and isotopic data obtained are shown in Table 1. As far as stable isotope abundances are concerned, no significant differences were found between the samples from the two outlets and the same values were found for the water flooding the tunnel. Tritium values are also similar, except in the water from the tunnel, which has a higher content of this radioactive isotope. On October 6, 1994, gas samples were collected by means of a funnel placed on the bottom of the channel near the two holes, where bubbling was evident

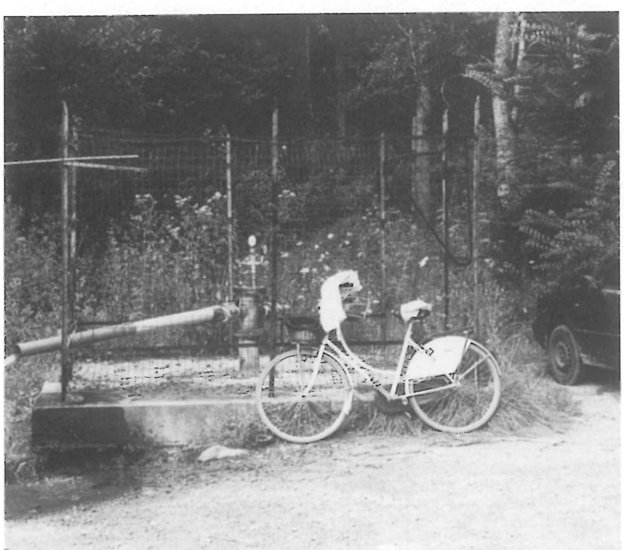

Fig. 4 - Pieve Fosciana: a) the higher temperature borehole; b) lowering of the pond level and the ephemeral spring (March, 1996).

throughout the cement floor of the tunnel. They were stored in a sealed Pyrex container by means of a polyethylene tube and immediately sent to the laboratory where they showed high radon activity. Chemical and radiometric results are shown in Table 1.

Pieve Fosciana thermal waters

Well known during the XVI° century, these thermal waters were represented by some mutable springs in the locality of Prà di Lama, very near Pieve Fosciana. They come out through Pliocene silt and clay lacustrine sediments on the Apennine side of the Serchio River, and these springs concurred to feed a small pond that now covers about 5000 m^2 at 362 m a.s.l. (De Stefani, 1879). Nowadays, the thermal waters are captured by two boreholes, P2 and P1, drilled in 1980-81 and 97 and 92 m deep, respectively. Drilling caused the disappearance of the above mentioned springs. Waters from the P2 and P1 boreholes showed at that time a temperature of 39.9 and 33.5°C, with a flow of 18 and 1.8 l/s, respectively. An ephemeral warm spring appeared in March 1996 at a distance of 200 m from the boreholes, in concomitance with the abrupt and almost total disappearance of the pond formed by thermal waters. The previous level of the waters of the pond was restored within two weeks (Fig. 4). Temperature, TDS and isotopic composition reported from the previously cited authors differ from each other more than the analytical accuracy, but only a continuous monitoring will clarify if time- dependent fluctuations actually affect these parameters.
Stable isotope composition, repeatedly monitored in the waters during the years 1983 ÷ 1998, shows no appreciable variations with values in the boreholes of $\delta^{18}O = -7.8 \pm 0.15‰$ and $\delta^2H = -49 \pm 1.0‰$. Tritium content in the lower temperature borehole P1 waters was in the years 1994 and 1996 0.7 TU with a fluctuation of ± 0.7 TU. Samples from the higher temperature borehole (P2) averages 2.1 ± 0.8 TU, with reference to the years 1992, '93, '94 and '96. Data reported in Table 1 show how the same, and almost constant, contents in stable isotopes were found in the spring that appeared in March 1996 when the pond suddenly disappeared. In this period, March 12-April 24, stable isotopes show no significative variance in the two boreholes and in the ephemeral spring while tritium content oscillates from 0 to 1.4 TU in the ephemeral spring and from 0.2 to 2.4 TU in the two boreholes. On the other hand, the small differences we observed between the two boreholes are at the limit, if not beyond, of the analytical error of ^{18}O and ^2H routine analyses; this consideration is also valid for tritium. The ephemeral spring was also analysed for ^{222}Rn and other gases, see Table 1.

Discussion

The oxygen and hydrogen isotopic compositions of the water from the two springs studied are plotted in Figure 5 together with the mean values of the 47 springs sampled in the area of interest by Mussi *et al.* (1998). Both thermal waters fit very well the «local meteoric line» obtained by Mussi *et al.* (1998), even considering that the Torrite samples refer to a single sampling. This indicates the meteoric origin of these thermal waters as well as the absence of the oxygen isotope shift caused by high temperature exchange with rocks. The comparison of the isotopic composition of waters with the $\delta^{18}O$ - altitude relationship of the pertaining slope (Mussi *et al.*, 1998), gives mean infiltration altitudes of about 900 m and 1100 m for Torrite and Pieve Fosciana thermal waters, respectively (Fig. 6).
The Pieve Fosciana waters show tritium content as low as 0 ÷ 2.5 TU, thus suggesting residence times in the

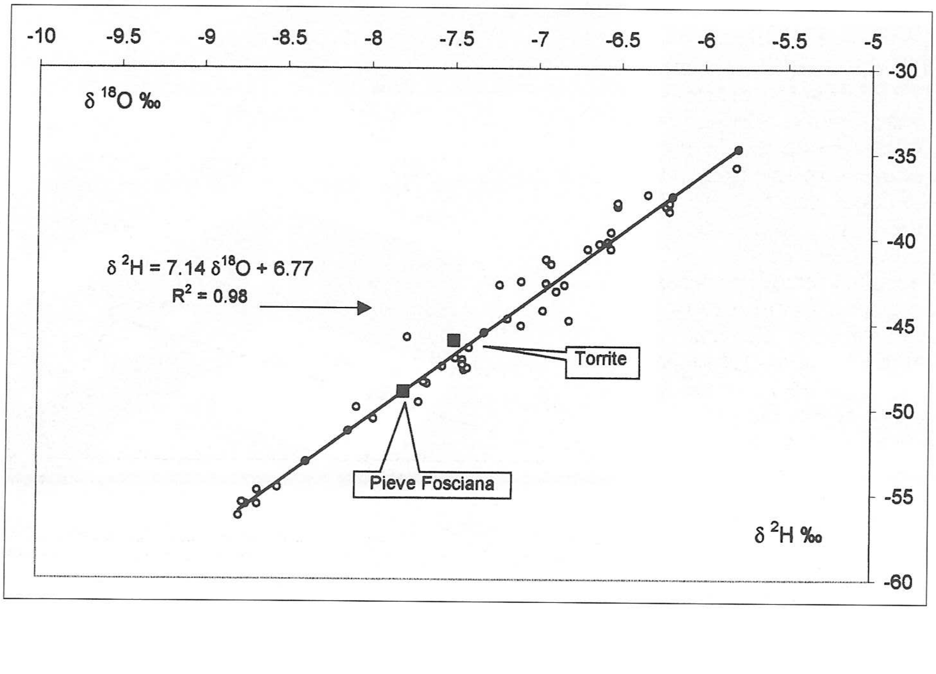

Fig. 5 - δ^2H versus $\delta^{18}O$ relationship for the Alpi Apuane-Garfagnana area spring waters (from Mussi *et al.*, 1998).

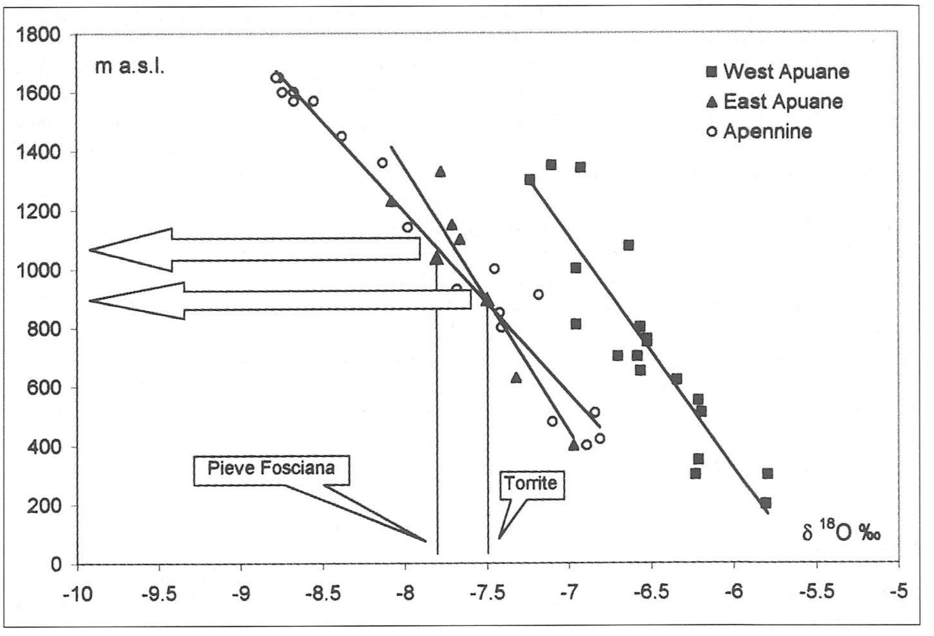

Fig. 6 - $\delta^{18}O$ of Torrite and Pieve Fosciana thermal waters and the relationships between estimated altitude for recharge and average $\delta^{18}O$ of spring waters from the three main slopes in the Alpi Apuane-Garfagnana area.

underground longer than 25 years. On the other hand, the tritium content of the Torrite waters are higher, 6 ÷ 7 TU, probably due to dilution of old water with large amounts of present-day meteoric waters, the weighted mean value of the present rainfall of Central Italy being about 7 ÷ 8 TU (Mussi *et al.*, 1998). This mixing may obviously alter the stable isotope content and the estimated recharge altitude of the Torrite thermal waters.
^{222}Rn activity in the Torrite manifestation is 30 times higher than in the gases associated with the Pieve Fosciana ephemeral spring and comparable with the highest measured values in the Larderello geothermal field (D'Amore, 1975). On the other hand, the helium content in the Torrite gas is considerably lower than at Pieve Fosciana. As regards the geochemical features of these two gases helium is composed of two stable isotopes: ^3He mainly concentrated in the mantle from the primordial planetary formation; ^4He formed by radioactive decay in the lithosphere. Radiogenic and deep-seated helium migrates along faults connected to the flow/storage system and accumulates in the thermal water. The analyses of helium isotopes can be helpful to assess groundwater residence time and/or anomalous input of the radiogenic component. Marty *et al.* (1992) analysed helium in the Equi Terme mineral spring, at about 20 km of distance, and found it mostly radiogenic, whereas samples from the Larderello geothermal field show ^3He positive anomalies (Hooker *et al.*, 1985). Also Costagliola *et al.* (1997) found a typical crustal value by analysing the $^3He/^4He$ ratio in fluid inclusion in metamorphic veins from the Apuan Alps. If we hypothesise a common source where thermal waters acquire their temperature and deep seated gases, the radiogenic helium content increases with the length of water storage. On the contrary, ^{222}Rn is a short living isotope originated by the radioactive decay of ^{226}Ra, an isotope of the ^{238}U decay series, and has a 3.8 days half-life. Rn is a very soluble gas and its noble structure prevents it from chemical reaction with rocks. High radon concentration in a groundwater suggests therefore a rapid circulation of the waters between radon acquisition and surface discharge.
The He-N_2-Ar triangular diagram (Giggenbach, 1991), (Fig. 7), allows a first classification of non-reactive gases according to their main sources. Datum on total gases from both the springs matches with a mixing model involving a deep crustal component and a mete-

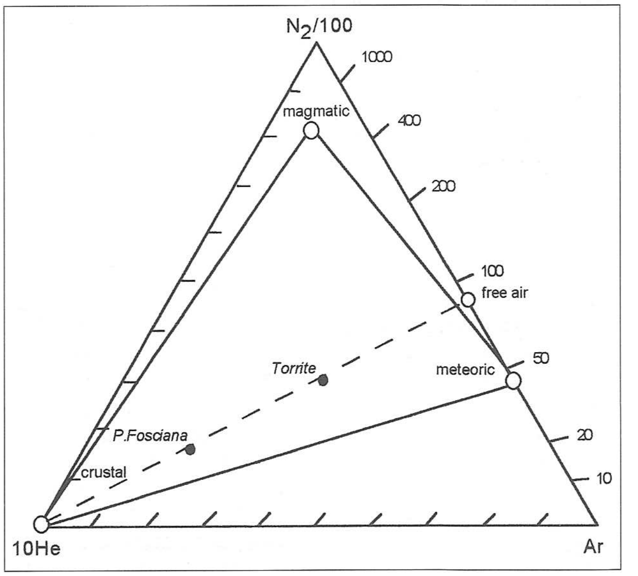

Fig. 7 - Relative N_2, He and Ar contents in gases associated with thermal manifestations plotted on the triangular diagram of Giggenbach, (1991). «Meteoric» represents air saturated groundwater.

oric one, the latter being represented by free air rather than by air saturated groundwater. The higher proportion of the air component at Torrite with respect to Pieve Fosciana is also supported by the much higher O_2 content of 9.3%. As previously mentioned, the Torrite waters are now sampled after a mixing with shallow waters, probably in the fractured rocks around the tunnel. On the other hand, the higher He content in the Pieve Fosciana gas, testified by the displacement of the point representative of the sample towards the helium corner in Figure 7, is in keeping with a longer residence time of water in the aquifer (D'Amore *et al.*, 1989).

All these observations concerning the isotopic and chemical characteristics of the two thermal manifestations are in agreement with a longer residence time in a deep aquifer and/or longer rising times for the Pieve Fosciana waters than for those of Torrite.

Conclusions

Based on their oxygen and hydrogen isotope composition, the waters studied probably acquired their salinity at a relatively low temperature, without isotopic exchange with host rocks. Mean altitudes of recharge, calculated by the isotopic vertical gradient, are at about 1100 m a.s.l. for the Pieve Fosciana thermal waters and at about 900 m a.s.l. for the Torrite sample. There is a doubt regarding the Torrite water sample due to the mixing between thermal water and cold surface waters, as testified also by the historical data showing higher temperatures and salinity than those measured today. Consideration of these data suggests the component corresponding to the «maximum cited temperature and salinity» is approximately 25% in the Torrite sample we collected. Tritium content, a little lower than present days-meteoric water, confirms this observation. The Pieve Fosciana water appears to be older than 25 years, or 40 years for the lower temperature borehole, according the tritium content compared to that in the past meteoric waters. Radon and helium abundance in the gases suggests a longer residence time at depth for the Pieve Fosciana waters than for the Torrite waters.

The Pieve Fosciana and Torrite thermal water systems are only a few km apart, but are located on the opposite sides of the Serchio River, and are probably fed by different circulation systems, related to the Apuan Alps and Apennine ridges, respectively. Baldacci and Raggi (1982) and Baldacci *et al.* (1993), suggested that a single reservoir, namely the Triassic carbonate-evaporite formation, influenced all the thermal manifestations of the area, which acquire their characteristics by deep circulation in buried carbonate-anhydrite rocks. Nevertheless, these authors recognise two main distinct circuits, connected to the Northern Apennine extensional structures, which were later influenced by the system of faults which developed within the Serchio Valley «graben». The chemical composition and temperature of these fluids probably reflects interaction processes with rocks of the same reservoir but the different sources, routes used and times required to reach the surface are reflected in their isotopic and chemical features. When considering the bordering fracture system of the Apuan Alps, longer residence times and/or rising times of waters appear to be associated with the Apennine side circulation system and with the sedimentary cover of the Pieve Fosciana type manifestation.

Acknowledgements

Authors are particularly grateful to ENEL for permission to enter the tunnel of the hydroelectric power plant and to Mr. Cappelli and co-workers for their invaluable technical support in sampling the Torrite thermal waters. The old picture postcard is by courtesy of Dr. Ilaria Nardi. Mrs. N. Gelli and Mr. R. Giorgi are acknowledged for tritium analyses, Mrs. E. Gherardi for the preparation of water samples for oxygen isotope analyses, Mr. R. Dall'Acqua for deuterium analyses.

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(ms. pres. il 17 gennaio 2000; ult. bozze il 19 dicembre 2000)