Fluid mixing in carbonate aquifers near Rapolano (central Italy): chemical and isotopic constraints

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Abstract

Chemical (major and trace elements) and isotopic compositions (δD and $\delta^{18}O$ in waters and $\delta^{13}C$ in CO_2 and $^3He/^4He$ in gases) of natural thermal (11) and cold (39) fluids (spring waters and gases) discharging from a tectonic window of Mesozoic limestones in central Italy, have proved to be the result of mixing processes inside the limestone formations. The limestones provide a preferential route for subsurface fluid migration and they gather both descending cold, Ca-HCO$_3$, B-depleted groundwaters and rising convective Ca-SO$_4$(HCO$_3$), CO_2-saturated, B-rich thermal waters. Atmospherically-derived descending gas components (N_2, Ne, He), dissolved in rainfall that infiltrates the limestone system mix with N_2, Ne, He-depleted hot rising waters. Boron in the liquid phase and N_2 and Ne in the gas phase are the most useful elements to trace the mixing process. The deeper gas samples recognised in the area are associated with the hotter waters emerging in the area. In spite of being depleted in Ne and He and light hydrocarbons they have the higher measured $^3He/^4He$ ratios, suggesting a contribution of mantle ^3He to the gas phase. This contrasts with deep circulation in the crust which would lead to increased concentration of ^4He in the deeper gases. Paradoxically, there is more relative concentration of ^4He in the more air-contaminated gas samples than in the deeper gas samples. A similar paradox exists when the $\delta^{13}C$ of CO_2 in the deeper gas samples is considered. The shallower air-contaminated gas samples, although they should be affected by the addition of soil-^{13}C depleted organic C, have $\delta^{13}C$ in CO_2 more positive than the deeper gas samples recognized. Since any deep hydrothermal source of CO_2 should generate CO_2 with more positive values of $\delta^{13}C$ than those measured at surface, a multiple (single) calcite precipitation process from hydrothermal solutions, with C isotopic fractionation along the rising path inside the Mesozoic limestone formations, is proposed. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

1.1. Background

Italy is characterised by the presence of a large number of thermal springs, especially along the central-western, peri-Tyrrhenian, pre-Apennine sector (Minis-sale, 1991). The main reason for these thermal discharges is the anomalous heat-flow generated by the presence of magmatic intrusions in a laminated back-arc crust. The litho-stratigraphic features of the shallow crust also play an important role in generating convection of deep fluids towards the surface. A quasi-continuous regional aquifer hosted in buried Mesozoic limestone sequences ("Tuscan-Umbrian" sequences), allows the "lateral" circulation of thermal water reservoirs as well as their discharge to the surface. After long circulation such waters emerge, mainly at the edges of their outcrop areas, in the several tectonic windows of

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the Mesozoic limestones present in the topographically low areas of the peri-Tyrrhenian pre-Apennine belt of Italy (Minissale, 1991).

The main chemical composition of such thermal springs can be summarised, as follows: (i) Ca-SO$_4$, mainly related to the dissolution of the Triassic anhydrite layers underlying the carbonate sequence (Lotti, 1910), (ii) Ca-HCO$_3$(SO$_4$), where a strong flux of free CO$_2$ is associated with the water flow (generally close to areas hosting hot geothermal fluids, Minissale et al., 1997a), (iii) Na-Cl(HCO$_3$), when leaching or mixing of either deep geothermal brines (Gianelli and Scandiffio, 1989) or shallow Miocene-Pliocene connate marine waters from post-orogenic sediments (Duchi et al., 1992) occurs, locally, inside the carbonate aquifer. Calcium-sulphate springs are sometimes associated with a N$_2$-rich gas phase of meteoric origin, whereas Ca-HCO$_3$(SO$_4$) and Na-Cl springs quite frequently show strong CO$_2$ emissions. The latter are associated with both thermal and cold springs, although they may also emerge as dry gas vents (Minissale et al., 1997b).

The easternmost outcrops of the carbonate formations in the main Apennine Chain, i.e. the main backbone of Italy, are generally high in elevation (up to 2915 m), poorly vegetated, intensely fractured and characterised by heavy rainfall. Thus, they represent efficient collectors for both meteoric and for shallow groundwaters. According to such hydrogeological features, they may favour the discharge of different types of springs fed by at least 3 different sources: (i) shallow cold water directly infiltrating from the carbonate outcrops, (ii) waters forced into the carbonate layers from adjacent formations and (iii) deep rising hydrothermal waters (brines). Springs belonging to either one or all these 3 types and/or springs with mixed characters can simultaneously be present in one of the many emergence areas of central Italy. This is particularly evident around active geothermal areas (e.g. Duchi et al., 1987).

In the present study a typical thermal springs-rich area in a tectonic window of the Mesozoic limestones near Rapolano (70 km SE of Florence, Tuscany, central Italy), has carefully been investigated. This site is marginal to the well known active geothermal areas of Tuscany (80 km east of Larderello and 40 km north of Mt. Amiata volcano) but it displays as well a large variety of fluid manifestations at the surface. All thermal and many cold springs and associated gas phases have been sampled and analysed for physical, chemical and isotopic parameters. The main purpose is to investigate mixing processes among fluids from different sources flowing into the carbonate formations and to describe how the chemical composition of the gas phases associated with the spring waters can help to evaluate shallow versus deep processes. In addition, because CO$_2$ and travertine are exploited for commercial purposes, the origin of CO$_2$ in Rapolano, situated at some distance from the known active geothermal areas, is discussed.

1.2. Hydrogeology and thermal features

Apart from small outcrops of Paleozoic metamorphic crystalline formations, mainly known through deep drilling, a thick (1000–2000 m), high-permeability, sometimes laminated Mesozoic limestone sequence ("Tuscan-Umbrian" nappe) is the lowermost stratigraphic unit in central-northern Apennine. This sequence starts with Triassic evaporites ("Burano" anhydritic formation), with a central massive Liassic platform member ("Calcare Massiccio" formation) ending with an Upper Cretaceous pelagic cherty limestone sequence ("Maiolica" formation). This Mesozoic sequence has scattered outcrops in tectonic windows in the pre-Apennine, peri-Tyrrhenian sector of Italy and, in the study area (Fig. 1), is laterally bounded by allochthonous low-permeability flysch sequences and/or post-orogenic Pliocene clay-rich sediments, the latter filling the Apenninic NW–SE trending Siena basin. The limestone formations are sometimes overlain by transgressive medium permeability Oligocene sandstones ("Macigno" formation).

The carbonate outcrop of Rapolano is the northernmost outcrop of the NW–SE trending "Rapolano-Trequanda-Piazza di Siena" ridge. This ridge hosts several thermal spring discharges bordering the eastern part of the Siena basin (Duchi et al., 1992) and emerging in association with CO$_2$ and travertine deposits. CO$_2$ dry vents and CO$_2$ bubbling pools, gathering water in the rainy periods, are also present. Travertines at Rapolano are still precipitating from thermal springs at the present day and have been quarried since the Middle Ages as building stones. In the past, they have been studied from a petrographical and geochemical point of view by Cipriani et al. (1972), while more recently Guo and Riding (1998) provided a careful description of their sedimentological and depositional features. The Siena basin, formed after the Tortonian compressive phase that led to the building up of the main Apennine chain, hosts a > 1000 m thick marine clay-dominated Miocene-Pliocene sedimentary sequence. In the study area, the Siena basin is crossed by a regional NW–SE anti-Apennine fault (the Follonica–Rimini line in Fig. 1), a tectonic lineament that cuts the entire Apennine Chain from the Tyrrhenian Sea to the Adriatic Sea.

The Rapolano area has several thermal springs (some used for public spas) which have been well studied from a geochemical (Panichi, 1982; Duchi et al., 1992) and hydrological (Barazzuoli et al., 1991) point of view. Some dry gas mofettes (i.e. S. Cecilia in Fig. 1) are exploited through wells for industrial CO$_2$ production. Along the Follonica–Rimini line two isolated CO$_2$-rich thermal springs emerge in the centre of the basin (Acqua Borra in Fig. 1) and one more cold mofette, present in the NW boundary of the Siena basin (Ambra in Fig. 1), is exploited for CO$_2$ industrial production.

2. Methodology

Sample locations are schematically shown in Fig. 1. Eleven thermal springs or wells ($T > 20$ °C) and, for comparison, 39 cold groundwaters from springs and shallow wells, and the Ombrone river before and after the town of Rapolano have been collected.

Temperature, pH and electrical conductivity together with alkalinity (titration with 0.01M HCl), SiO_2 and NH_4 (both analyzed using portable Hanna colorimeters) were determined in the field, whereas the remaining elements in solution were determined in the laboratory with methods described in Duchi et al. (1986). A Dionex DX100 ionic chromatograph and a Perkin-Elmer AAnalyst 100 were used in the laboratory for the determination of anion and cation concentrations, respectively. $^{18}O/^{16}O$ and D/H isotopic ratios in the water samples were determined using a Finningan MAT 250 DeltaS mass spectrometer using standard procedures.

Gas emissions were sampled with a plastic funnel and stored in two-way glass tubes for CO_2, H_2S, N_2 and $^3He/^4He$ isotopic ratio determinations and in pre-evacuated one-way glass tubes filled with 50 ml 4N NaOH solution for the determination of non-condensable low-concentrated gas compounds. Gas bulk composition and light hydrocarbons were determined with a Shimadzu 15A gas-chromatograph equipped with a TCD detector and a Shimadzu 14A equipped with a FID detector, respectively. After purifying the sample in a vacuum line, the isotopic composition of He was determined using a MAP 215-50 mass spectrometer.

Chemical and isotopic ($\delta^{18}O$ and δD) compositions of water samples are reported in Table 1. Chemical and isotopic ($\delta^{13}C$ in CO_2 and $^3He/^4He$) compositions of associated gas phases are reported in Table 2.

3. Results

3.1. Hydrochemistry

Spring and well samples have been classified in Fig. 2 using the percentage of HCO_3 ions (in meq/L) in total anion concentration plotted versus total salinity (in mg/
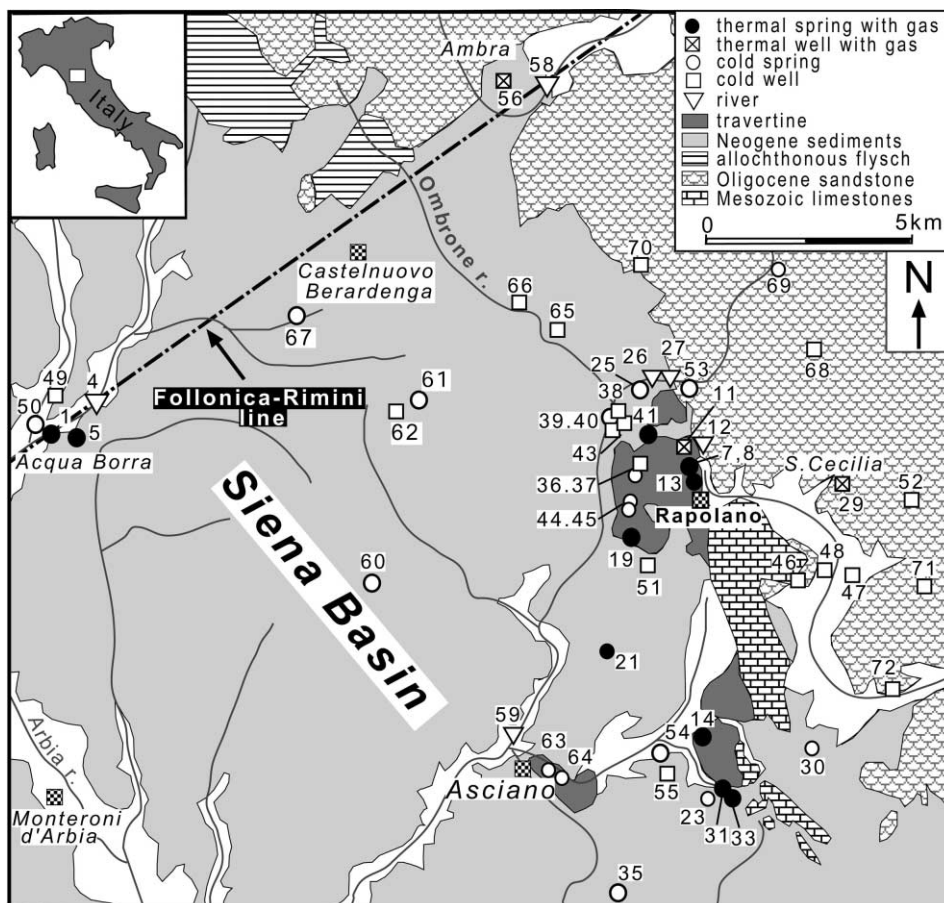

Fig. 1. Schematic geological map of the Rapolano area and location of water and gas samples.

Table 1
Chemical and isotopic composition of water samples from Rapolano area

No.	Name	Type[a]	T°C	Elev.[b]	pH	Cond.[c]	TDS	Ca	Mg	Na	K	HCO$_3$	SO$_4$	Cl	SiO$_2$	Br	NO$_3$	Li	F	NH$_4$	B	pCO$_2$	δD	δ^{18}O
1	Acqua Borra	tsg	37.9	185	6.95	18.6	14994	723	114	3972	238.3	3459	1300	4807	25.8	7.00	5.4	11.25	1.75	9.29	57.07	−0.55	−40.1	−5.4
4	Fiume Malena	r	5	185	6.76	1.3	772	140	22	45	2.6	384	114	47	6.5	0.23	7.5	0.02	0.95	0.41	0.17	n.c.	n.d.	n.d.
5	Acqua Borra Fer.	tsg	20	185	6.63	18.26	15088	689	110	4080	233.2	3508	1125	4932	27.0	7.25	1.8	10.50	0.55	31.31	58.76	−0.41	−43.5	−5.4
7	Bagni Freddi 1	tsg	25.4	290	6.33	4.42	4093	651	144	237	29.6	1989	780	198	21.5	0.35	0.2	0.67	1.45	1.81	6.68	−0.37	−44.1	−7.51
8	Bagni Freddi 2	sg	10.4	290	6.46	4.28	4616	788	158	272	35.5	1488	1556	230	36.5	0.30	0.7	0.68	0.75	0.32	8.21	−0.68	n.d.	n.d.
11	Cemetery Well	twg	30.1	295	6.4	5.32	6011	806	218	410	46.0	2830	1320	268	31.5	0.60	0.2	1.03	0.80	2.83	12.70	−0.23	−44.3	−7.05
12	Torrente sopra P.d.C.	r	6.6	297	8.27	0.4	333	50	14	16	0.6	220	17	6	7.6	0.05	0.5	<0.01	0.11	0.07	0.32	n.c.	n.d.	n.d.
13	Terme Querciolaie	tsg	35	301	6.43	2.91	3111	464	165	131	17.2	1623	566	94	25.8	0.03	3.0	0.35	1.90	0.84	3.09	−0.42	−44.0	−6.96
14	Serre di Rap 24/2/99	tsg	21.5	310	6.29	3.38	3620	504	156	157	20.3	1861	710	145	28.0	0.50	15.0	0.42	1.40	0.46	3.64	−0.40	n.d.	n.d.
14B	Serre di Rap 2/11/99	tsg	29	310	6.12	3.5	3527	549	144	159	20.9	1739	722	154	18.0	0.35	17.0	0.51	1.87	0.84	n.d.	n.c.	−42.9	−7.18
19	Terme S. Giovanni	tsg	39.9	280	6.73	6.5	5901	720	224	415	51.5	2867	1280	226	27.3	0.45	0.2	1.22	0.90	3.07	14.40	−0.38	−45.3	−6.97
21	Puzzola	tsg	20.5	212	6.39	3.3	3987	643	156	172	24.6	2123	700	122	13.3	0.35	2.5	0.47	1.40	1.04	4.66	−0.42	n.d.	n.d.
23	Montalceto	tsg	29.4	306	6.52	3.2	3096	486	130	134	18.3	1739	505	38	23.0	0.18	0.2	0.37	2.05	0.40	3.52	−0.51	−41.8	−7.87
25	Podere Casalino	s	13.5	243	6.99	1.53	1370	268	36	37	3.9	653	225	47	22.0	0.13	72.4	0.08	0.83	0.15	0.77	−1.38	−41.7	−6.63
26	Fiume Chiusella	r	8.4	245	8.1	0.46	338	51	14	14	1.2	201	32	12	9.3	0.03	0.3	<0.01	0.15	0.05	0.59	n.c.	n.d.	n.d.
27	Affluente Chiusella	r	9.4	245	7.45	0.62	606	101	21	23	1.7	354	75	16	9.1	0.03	1.5	0.02	0.16	0.07	0.66	n.c.	n.d.	n.d.
29	Poggio S. Cecilia	wg	9.3	380	6.59	2.0	2647	528	93	25	7.8	1397	563	13	16.8	0.04	0.1	0.01	0.10	n.d.	0.50	n.c.	−41.7	−8.86
30	S. Gemignanello	s	9.5	332	7.48	0.92	804	157	13	51	1.1	439	35	71	16.8	0.05	16.5	0.03	0.75	0.03	0.53	−2.00	−45.7	−7.14
31	Bogliole1	sg	14.3	330	6.25	1.55	1569	208	116	45	4.0	915	241	23	10.5	0.23	1.3	0.06	0.82	0.32	0.61	−0.75	n.d.	n.d.
33	Bogliole2	sg	14.2	331	6.19	1.37	1110	238	56	49	3.9	512	211	26	8.0	0.15	0.4	0.05	0.88	0.41	0.62	−0.98	n.d.	n.d.
35	Acqua Purgativa	s	10	275	7.92	3.36	3940	380	301	305	29.3	500	2240	93	13.3	0.25	74.5	0.14	1.15	0.38	0.30	−2.43	−41.9	−6.67
36	Podere Casarotta	s	15	290	7.04	1.26	1298	189	39	73	10.3	641	218	84	20.8	0.20	12.0	0.14	0.90	0.13	1.55	−1.42	n.d.	−6.75
37	Podere Casarotta	w	17	290	6.93	1.38	1372	215	38	74	10.1	653	232	88	9.3	0.20	41.0	0.13	0.80	0.58	1.51	−1.31	n.d.	n.d.
38	Torricella	w	18	202	7.19	1.23	1273	195	49	68	11.3	549	210	90	11.3	0.60	80.0	0.11	0.70	0.19	1.27	−1.60	n.d.	−6.52
39	Capannacce	s	14	206	7.03	1.17	1209	204	27	61	2.6	580	202	82	16.5	0.20	26.0	0.08	0.60	0.01	1.19	−1.46	n.d.	−6.5
40	Capannacce pozzo	w	17	206	7.16	1.04	1008	164	24	52	3.5	482	166	62	10.8	0.20	36.0	0.07	0.60	0.01	1.04	−1.63	n.d.	n.d.
43	Podere S. Giuseppe	w	13.5	206	7.07	1.69	1652	220	64	116	8.2	695	384	116	16.8	0.20	21.0	0.11	0.40	0.01	1.55	−1.43	n.d.	−6.52
44	Fontepietra	s	16	295	7.32	1.29	1177	203	15	65	18.2	500	122	110	13.8	0.20	125.0	0.02	0.40	0.21	0.62	−1.76	−42.0	−6.53
45	Fontepietra 2	s	17	295	7.07	1.26	1188	208	15	72	16.3	506	132	114	13.8	0.20	105.0	0.02	0.40	0.03	0.78	−1.53	n.d.	n.d.
46	Chiassale	w	17.5	339	7.04	0.69	780	170	7	13	3.8	482	25	39	16.5	0.05	20.5	0.02	0.20	0.11	0.69	−1.51	−45.8	−7.35
47	Godiolo	w	17	327	7.1	1.49	1167	174	77	66	1.4	519	54	236	17.0	0.20	18.0	0.04	0.60	0.01	0.64	−1.55	n.d.	−6.52

Table 1 (*continued*)

No.	Name	Type[a]	T°C	Elev.[b]	pH	Cond.[c]	TDS	Ca	Mg	Na	K	HCO$_3$	SO$_4$	Cl	SiO$_2$	Br	NO$_3$	Li	F	NH$_4$	B	pCO$_2$	δD	δ ^{18}O
48	Ficaiole	w	14.5	312	7.04	0.71	621	107	11	24	6.3	329	55	21	12.0	0.15	50.0	0.05	0.65	0.01	0.84	−1.69	n.d.	−6.72
49	Bagnaccio	w	16	212	7.27	1.3	831	139	17	33	12.9	451	76	32	17.5	0.10	48.0	0.01	0.20	0.06	0.64	−1.75	n.d.	n.d.
50	Sorg. Cappella	s	18	209	7.54	0.83	759	134	10	24	9.8	409	47	27	20.3	0.15	74.0	0.01	0.15	0.01	0.77	−2.03	n.d.	−6.38
52	Montagna	w	19	438	7.34	0.76	786	89	31	49	2.7	525	36	29	20.5	0.10	0.9	0.02	0.25	0.02	0.72	−1.72	−43.2	−6.94
53	Nistiola	s	20	346	7.41	0.59	608	81	22	28	1.8	409	21	21	17.5	0.10	2.0	0.01	0.20	0.02	0.64	−1.89	−44.4	−7.05
54	Sasseto	s	17	278	6.98	1.9	1858	206	97	139	17.8	561	675	118	22.0	0.50	2.5	0.34	1.00	0.10	3.03	−1.42	−40.1	−5.9
55	Acquaviva	w	17	285	7.3	1.18	1127	174	34	57	9.2	494	242	70	16.5	0.40	22.0	0.09	1.00	0.03	1.07	−1.74	n.d.	n.d.
56	Ambra 12	wg	15	310	6.49	2.55	3131	623	29	21	2.0	2379	35	24	14.8	0.05	0.2	0.04	0.60	0.03	0.40	−0.47	−40.0	−7.52
58	Ambra fiume	r	19.7	275	7.52	0.71	702	132	15	16	1.1	476	34	16	8.3	0.05	3.0	0.01	0.20	0.09	0.31	n.c.	n.d.	n.d.
59	Ombrone (after) 8/9/99	r	21.5	174	7.65	2.2	2208	190	117	264	26.8	616	730	204	17.5	0.30	8.0	0.56	0.80	0.21	5.68	n.c.	n.d.	n.d.
59A	Ombrone (before) 2/11/99	r	14	230	7.33	0.81	763	131	23	38	2.0	378	126	47	14.0	0.02	3.8	<0.01	0.25	0.39	0.03	n.c.	n.d.	n.d.
59B	Ombrone (after) 2/11/99	r	14.5	174	7.85	1.9	1944	216	96	194	18.3	580	614	199	14.8	0.37	11.3	0.39	0.87	0.48	0.56	n.c.	n.d.	n.d.
60	Fontanelle	s	15.7	331	7.84	2.4	2392	308	163	102	27.4	372	1240	130	14.3	0.10	29.0	0.05	0.60	0.08	0.80	−2.36	n.d.	n.d.
61	Torre a Castello 2	s	18	319	7.7	0.79	695	92	23	29	30.6	397	51	29	21.9	0.06		0.01	0.44	0.03	0.51	−2.19	−42.7	−6.9
62	Torre a Castello	w	15.5	329	7.12	1.06	913	127	32	38	49.9	421	112	25	20.5	0.08	84.0	0.02	0.25	0.21	0.56	−1.66	n.d.	n.d.
63	Casino	s	17	230	7.75	0.84	710	112	14	49	20.3	262	121	69	14.3	0.05	42.0	0.03	0.70	0.44	0.60	−2.43	n.d.	−5.49
64	Grottoli	s	14.9	230	7.21	0.93	908	178	13	33	7.7	390	131	51	12.8	0.20	87.5	0.02	0.55	0.26	0.28	−1.77	−46.3	−6.38
65	Podere Grillo	w	17.5	218	7.2	1.8	1718	205	103	77	24.8	573	575	66	14.5	0.20	75.0	0.02	0.22	0.46	0.52	−1.60	n.d.	−6.5
66	Colonna del Grillo	w	17.5	232	7.3	1.62	1507	181	81	88	3.2	555	445	82	18.0	0.30	50.0	0.01	0.26	0.58	0.36	−1.70	n.d.	n.d.
67	S. Cristoforo	s	15	270	7.15	1.95	2025	354	55	85	1.8	811	610	88	15.3	0.20	0.2	0.01	0.18	0.54	0.40	−1.43	n.d.	−5.91
68	Monteluco	w	14	n.d.	7.2	1.1	696	96	32	32	11.7	390	67	36	6.5	n.d.	25.0	0.01	n.d.	<0.01	<0.03	n.c.	n.d.	n.d.
69	Le Fontacce	s	11	n.d.	7.2	0.4	359	60	11	9	3.9	226	14	11	7.5	n.d.	11.5	<0.01	n.d.	<0.01	0.91	n.c.	n.d.	n.d.
70	Spiritellino	w	17	n.d.	7.3	1.2	736	68	40	67	3.9	439	38	71	8.5	n.d.	0.7	0.01	n.d.	<0.01	<0.03	n.c.	n.d.	n.d.
71	Modanella	w	16	n.d.	6.7	0.3	183	28	7	7	3.9	110	5	11	6.0	n.d.	5.5	<0.01	n.d.	<0.01	<0.03	n.c.	n.d.	n.d.
72	Ferrovia	w	17	n.d.	7.4	1.0	595	106	11	35	3.9	317	62	43	8.5	n.d.	8.4	0.01	n.d.	<0.01	0.98	n.c.	n.d.	n.d.

[a] s = cold spring; sg = cold spring with gas; tsg = thermal spring with gas; w = cold well; wg = cold well with gas; twg = thermal well with gas; r = river.

[b] elev = elevation of spring (in m)

[c] cond = electrical conductivity (in mS/cm); all elements in mg/kg; δD and δ^{18}O in ‰ vs. SMOW.

Table 2
Chemical and isotopic composition of gas samples from the Rapolano area[a]

No.	Name	He	Ar	Ne	N₂	O₂	CO₂	H₂S	H₂	CH₄	δ¹³C	³He/⁴He	Etane	Propane	Propene	i-Butane	n-Butane	1-Butene	i-Pentane	n-Pentane	Benzene
7	Bagni Freddi 1	0.000096	0.0119	0.000008	0.55	0.0018	99.44	<0.005	0.000008	0.00311	−7.59	0.09*	0.044	0.004	<0.005	<0.001	<0.001	<0.001	<0.004	<0.002	<0.001
8	Bagni Freddi 2	0.000370	0.0330	0.000025	1.78	0.0160	98.17	<0.005	0.000034	0.00212	−6.58	n.d.	0.066	0.003	<0.005	0.006	0.007	0.006	0.040	0.003	0.002
1B	Borra 2	0.000339	0.0015	<0.000001	0.43	0.0008	99.56	<0.005	0.000005	0.10700	−5.78	n.d.	0.406	0.063	<0.005	0.013	0.021	0.021	0.005	0.005	0.001
1A	Borra 1	0.000306	0.0016	<0.000001	0.35	0.0005	99.65	<0.005	0.000004	0.06500	−6.06	0.15*	0.401	0.050	<0.005	0.008	0.016	0.017	0.007	<0.002	0.001
5	Borra Ferruginosa	0.000155	0.1530	0.000091	8.15	0.2180	90.95	<0.005	<0.000001	0.53800	−5.21	n.d.	42.874	3.720	<0.005	<0.001	0.936	1.352	1.872	0.256	<0.001
14A	Serre 1	0.001624	0.2192	0.000168	10.09	0.2172	89.48	<0.005	0.000129	0.02610	−6.84	n.d.	1.702	0.060	<0.005	<0.001	<0.001	0.030	<0.004	<0.002	<0.001
14B	Serre 2	0.003516	0.3940	0.000312	20.09	5.2023	74.32	<0.005	0.000102	0.04700	−6.69	n.d.	2.375	0.152	<0.005	<0.001	<0.001	<0.001	<0.004	<0.002	<0.001
19	Terme. S. Giovanni	0.000002	0.0003	<0.000001	0.02	0.0002	99.86	<0.005	0.000013	0.00001	n.d.	n.d.	0.005	0.001	<0.005	<0.001	<0.001	0.020	<0.004	<0.002	0.001
13	Terme Querciolaia	0.000204	0.0076	0.000005	0.42	0.0011	99.57	0.122	0.073630	0.00237	−7.95	n.d.	0.163	0.027	0.008	0.006	0.006	0.018	0.004	0.003	0.001
11	Pozzo Cimitero	0.000004	0.0007	<0.000001	0.03	0.0003	99.89	0.075	0.000002	<0.000001	−9.21	0.99	<0.005	0.005	<0.005	<0.005	<0.001	<0.001	<0.004	<0.002	<0.001
21	Puzzola	0.000063	0.0200	0.000016	1.45	0.0327	98.49	<0.005	0.000012	0.00440	n.d.	0.35	0.234	0.010	0.005	0.004	0.004	<0.001	0.005	0.002	0.002
31	Bogliole 1	0.004201	0.2336	0.000187	10.81	0.4335	88.52	<0.005	0.000559	0.06997	n.d.	n.d.	2.737	0.073	<0.005	0.033	0.025	0.036	0.047	0.022	0.012
33	Bogliole 2	0.000634	0.0321	0.000026	1.87	0.1873	97.91	0.005	0.000020	0.01123	−6.75	n.d.	0.392	0.012	<0.005	<0.001	<0.001	0.003	0.004	<0.002	0.001
29	Poggio S. Cecilia	0.001218	0.0683	0.000055	3.40	0.0010	96.53	0.005	0.000452	0.10037	−6.07	n.d.	<0.005	<0.001	<0.005	<0.001	<0.001	<0.001	<0.004	<0.002	<0.001
41	Borro Temperone	0.000017	0.0143	<0.000001	0.87	0.4038	98.71	<0.005	0.000075	0.00182	n.d.	0.65	0.040	0.008	<0.005	0.002	<0.001	<0.001	0.005	<0.002	<0.001
56	Ambra	0.004812	0.0121	<0.000001	9.92	0.0089	89.98	0.010	0.000155	2.46676	−6.08	0.08	<0.005	<0.001	<0.005	<0.001	<0.001	<0.001	<0.004	<0.002	<0.001

[a] He, Ar, Ne, N₂, O₂, CO₂, H₂S, H₂ and CH₄ are in % by vol.; δ¹³C in CO₂ in °/₀₀ PDB; light hydrocarbons in ppmv.
*Data from Minissale et al. (1997a).

kg). Apart from thermal springs No. 1 and No. 5 emerging in the centre of the Siena basin being characterised by Na-Cl and with high salinity, all the remaining thermal and cold samples align along two different trends, suggesting the presence of two relatively saline end-members at depth. One is cold (trend I) and relatively HCO₃-depleted (Na-Cl-rich), while the other (trend II) is hot, Ca-HCO₃(SO₄) in composition, with increasing salinity and slightly decreasing HCO₃ percentage with respect to total anions due to a relative increase in SO₄. Both the two groups converge towards the composition of typical groundwaters in temperate regions, where total HCO₃ ion concentration is about 70–80% of total anions, and salinity is generally lower than 500 mg/kg. Water samples lying on the two trends clearly represent mixing processes between deep and shallow groundwaters. Besides, S. Giovanni (No. 19) and Cemetery Well (No. 11) can be considered the deeper, less shallow groundwater-contaminated emergences among all the thermal waters of Rapolano. If thermal waters circulate inside the Mesozoic limestones, cold Na-Cl waters are generally related to semi-confined aquifers inside the clay-rich Neogene sediments, while Ca-HCO₃ waters derive from very shallow aquifers in both the Neogene sediments not affected by the confined Na-Cl aquifers and the flysch formations lying above the limestones. On the basis of such established hydrogeochemical features in central Italy, Fig. 2 also suggests that mixing between waters from the thermal aquifer and the confined Na-Cl aquifer(s) is very reduced at Rapolano.

Despite the fact that at least 3 different aquifers have been identified, δD and δ¹⁸O values of both cold and thermal samples suggest a common meteoric origin (Fig. 3a and b), with a relatively restricted range of variation: from −40.0 to −46.0 (°/₀₀ SMOW) and from −6.0 to −8.0 (°/₀₀ SMOW), respectively. Most samples in Fig. 3b are aligned between the Global Meteoric Water Line (GMWL; Craig, 1963) and the Mediterranean Meteoric Water line (MMWL; Gatt and Carmi, 1970). Only a few samples, associated with CO₂ emissions (No. 7, 23, 29, 56), have lower δ¹⁸O values since they are likely affected by an isotopic exchange between water and CO₂, according to the reaction (Negrel et al., 1999):

$$0.5\ C^{16}O_2 + H_2O = 0.5\ C^{18}O_2 + H_2O$$
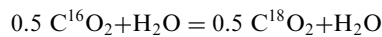
By contrast, the two samples from the middle Siena basin (Acqua Borra Nos. 1 and 5) plot to the right side of the GMWL and the MMWL lines indicating a slight positive ¹⁸O-shift. Although this shift has been interpreted as due to evaporation of deep fluids in a system at 150 °C temperature (Panichi, 1982), the authors suggest that it can simply derive from the interaction of ions in solution and water molecules in a fluid system at high salinity, even at low temperature (Gonfiantini, 1986). Moreover, since the salinity of these samples may

be as high as 15 g/l (Table 1), a certain contribution of isotopically heavy connate waters of confined shallow aquifers contacting the thermal path cannot be ruled out. As a consequence, any ^{18}O-shift due to the presence of medium-to-high-enthalpy systems may be excluded for the two samples emerging in the middle of the Siena basin.

All the samples, although belonging to at least 3 different aquifers, including one with deep circulation, show a negative correlation between emergence elevation of springs and their relative δ^{18}O (Fig. 3c). This suggests for both thermal and cold water samples a "local" origin and/or recharge areas in the range 200–800 m. Although deep thermal waters cannot have a local origin, elevations of hills in a large sector of the pre-Apennine belt of central Italy are similar (< 1000 m) and this can justify the apparent local isotopic signature of thermal waters.

3.2. Gas chemistry

Sixteen gas emissions have been sampled at 11 sites, generally in association with the thermal springs. All samples are CO_2 dominated, sometimes with CO_2 relative concentration greater than 99% by volume (Nos. 1, 7, 11, 13, 19). Most of the gas manifestations are located in the structural top of limestones at Rapolano, whereas 3 gas emissions (Acqua Borra and Ambra) are located along the NW–SE trending transpressive Follonica-Rimini tectonic lineament (Fig. 1). These two different geological situations are reflected in the N_2–Ar–He diagram (Giggenbach et al., 1983) shown in Fig. 4. In this diagram some end-members are reported based on the

N_2/Ar ratio and the crustal enrichment in He after long residence in the crust, and magmatic or metamorphic enrichment in N_2 (N_2/Ar = 800 in andesitic magmas). All the Rapolano gas samples fall inside the triangle defined by the He corner and the N_2/Ar ratios equal to 83 (i.e. that in the air at 25 °C) and 38 (i.e. that in air-saturated water (ASW) at 25 °C). By contrast, samples from Ambra (No. 56) and Acqua Borra (No. 1a and 1b) show a N_2/Ar ratio higher than that of air or ASW: 827, 287 and 219, respectively. This would suggest an excess N_2 due to denitrification processes with respect to the

Fig. 3. δD-δ^{18}O diagram (a and b) and δ^{18}O versus elevation of spring discharge (c).
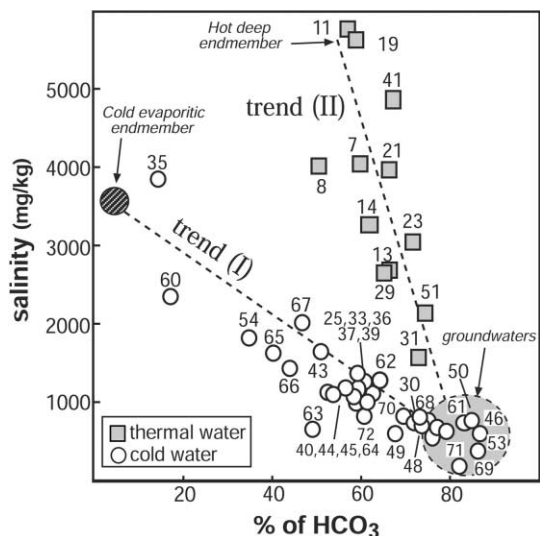
Fig. 2. HCO_3 concentration (in terms of meq.% with respect to total anions) plotted versus salinity. Two different mixing lines: one for cold saline waters and one for thermal waters are evident.
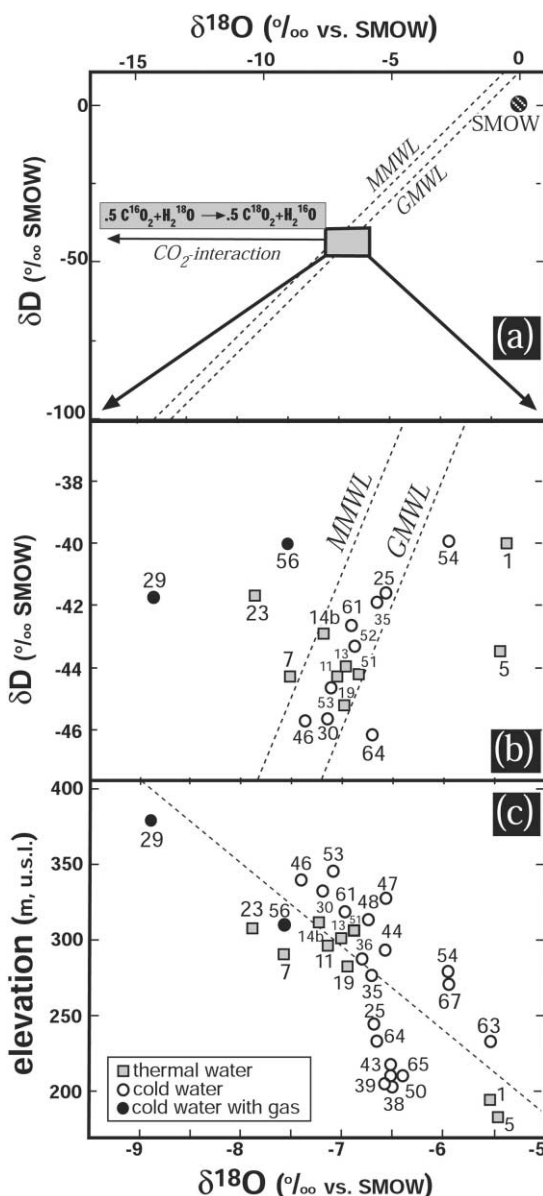
likely meteoric source of N_2 at Rapolano. They also have higher CH_4 concentration (No. 56: 2.4%, No. 1b: 0.11% by vol.) with respect to the Rapolano samples, the latter having CH_4 generally $<0.1\%$ by vol.

The relatively high concentration of N_2 from Ambra (No. 56: $N_2 = 9.9\%$ by vol.) is comparable with some of those found in Rapolano (e.g. No. 31: $N_2 = 10.8\%$ by vol.). The same is true when the low concentrations of N_2 from Acqua Borra (No. 1a and 1b: $N_2 < 0.5\%$ by vol.) are taken into account, these low values again being similar to some of those from Rapolano gas samples (e.g. No. 19 and 12) where $N_2 = 0.02$ and 0.42% by vol., respectively. To explain these differences a mechanism of N_2 enrichment deriving from the exsolution of N_2 from air-saturated waters in the top part of the circulating system that the gas flows through, where O_2 has already been consumed during alteration processes of both organic and inorganic material is suspected. In fact, the Borra Ferrugginosa gas No. 5, very close to the Borra No. 1, possibly gains part of its higher N_2 value from the river (1.5 m deep) which this gas flows through. Similar mechanisms, although more complex, together with different dilution rates with rising CO_2, can explain why these 3 sites have different N_2 concentrations, even among the gas emergences of Rapolano.

The somehow restricted range of $\delta^{13}C$–CO_2 in all samples (from –5.2 to –8.0 $^o/_{oo}$ PDB) suggests, by contrast, that CO_2 is likely to have a deep common source everywhere. Moreover, $\delta^{13}C$–CO_2 values in the study area are quite different from many other CO_2 emissions
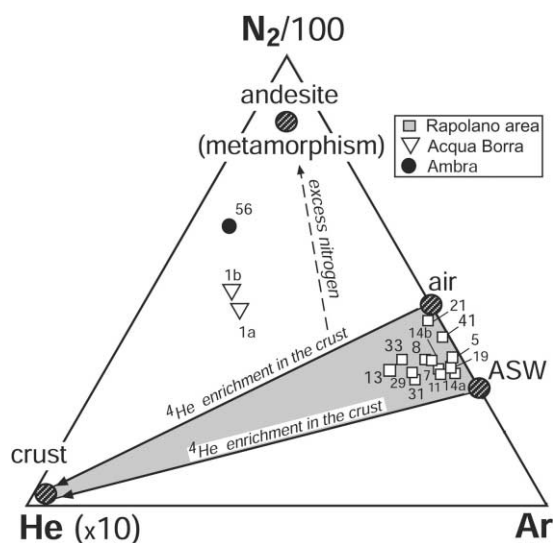
in central Italy where they range on the average, from –2 to $+2$ $^o/_{oo}$ (Minissale et al., 1997b). The latter represents typical $^{13}C/^{12}C$ ratios of CO_2 deriving from metamorphic reactions involving carbonate rocks (Rollinson, 1993).

The $^3He/^4He$ ratio, reported in Table 2 as R/Ra (R: $^3He/^4He_{(measured)}$ and Ra: $^3He/^4He_{(air)} = 1.36 \times 10^{-6}$, Mamyrin and Tolstikhin, 1984), ranges from typical crustal values (i.e. R/Ra = 0.08 in No. 56) to values as high as 0.99 R/Ra (No. 11, Cemetery well). As the concentration of Ne in No. 11 is $<0.000001\%$ by vol., i.e. two order of magnitude less than that in the air (0.0018% by vol.), any influence of both air (where R/Ra = 1) in the gas path and bad sampling can be excluded. Thus, the presence of a primary ^3He mantle component in this sample can be assumed.

3.3. Origin of components in the springs and gas vents

As shown by their isotopic signature (Fig. 3b), both cold and thermal waters have a common meteoric origin from rainfall ranging 200–800 m in elevation and this is compatible with many other thermal springs of central Italy (Minissale, 1991). Chemical characteristics of springs mostly derive from the different geological formations they flow through, with a marked SO_4 signature in thermal springs deriving from the leaching of Triassic anhydrite layers. Compared with cold springs, thermal springs have greater B and NH_4 concentration (Table 1). Mean values for the thermal waters (11 samples) from Rapolano are: 98 mg/L for H_3BO_3 and 5 mg/L for NH_4. On the other hand, mean values for cold springs and wells (34 samples) are: 6.5 and 0.2 mg/L, respectively (Table 1). Such remarkably different concentrations are clearly due to different and longer circulation paths for thermal springs, as well as enrichment when they get in contact with the evaporitic Triassic material. On the other hand, since the Siena basin is not far from the steam-dominated geothermal area of Larderello, where the heat flow is up to 120 mW/m² (Mongelli et al., 1982), contributions of B and NH_4-rich steam condensates added to the regional aquifer hosted in the Mesozoic limestones cannot be excluded.

As far as CO_2 is concerned, several sources have been proposed in the literature: (i) hydrolysis at temperature as low as 150 °C, of buried Mesozoic limestones (Kissin and Pakhomov, 1967 cited by Panichi and Tongiorgi, 1976); (ii) deep carbonatite magma intrusions (Panichi and Tongiorgi, 1976); (iii) upper-mantle degassing (Minissale, 1991; Marini and Chiodini, 1994); (iv) decarbonation of marine limestones (Giggenbach et al., 1988); (v) metamorphism of impure limestones from the Paleozoic basement at temperature >150 °C (Gianelli, 1985). Some of the springs and wells in the study area discharge large amounts of CO_2 to the atmosphere. Santa Cecilia and Ambra wells produce about 150 t/day

Fig. 4. Relative Ar–He($\times 10$)–N_2(/100) diagram (Giggenbach et al., 1983) showing a similar atmospheric origin for N_2 in the Rapolano area (see text), with respect to the gas samples in the Siena basin that have excess N_2 deriving from other sources.

of free ("dry") CO_2 for industrial purposes (Rogie et al., 2000). To this quantity, which does not include the free CO_2 discharged from springs after the final depressurization of rising water, CO_2 discharge due to the precipitation of travertine must be added. This has been estimated on a mass balance of the carbonate species concentrations of the Ombrone river, sampled before and after Rapolano, to be about 2–4 t/day (Grechi, 2000).

Whatever the origin of CO_2, during its rise to the surface it can be temporarily stored inside the Mesozoic limestones in buried CO_2-pressured structural traps (Barelli et al., 1977) and then discharged to the surface where the deep P_{CO_2} exceeds the hydrostatic pressure. Depending on the equilibration temperature of such deep traps, gas–water, gas–gas and mineral–water reactions, the formation of other gas components such as H_2, CH_4, CO... etc. may be possible (Giggenbach, 1980). A combination of the resulting composition of the gas phase, the speed of ascent to the surface and interaction (dissolution and/or re-equilibration) with shallow descending groundwaters will affect the final composition of gases at the surface. The gas–water interaction in the Rapolano and the Siena basin is described in detail below, to show mixing processes at very shallow levels in the crust.

3.4. Mixing processes between gases at Rapolano

From a hydrodynamic point of view the Mesozoic limestones, characterised by a very high secondary permeability, are potentially good collectors for both hot fluids rising from depth and cold meteoric-derived descending fluids. In particular, shallow fluids are channeled into the limestones from the overlying formations, especially where Pliocene unconsolidated sediments undergo compaction and diagenetic processes. If, as at Rapolano, the Mesozoic limestones crop out, it is very likely that all types of shallow and deep fluids will converge and emerge, possibly after undergoing mixing processes.

In order to describe mixing processes among gas components a multiple N_2–Ne, N_2–He, N_2–R/Ra and N_2–$\Sigma_{\text{light hydrocarbons}}$ diagram is shown in Fig. 5. In
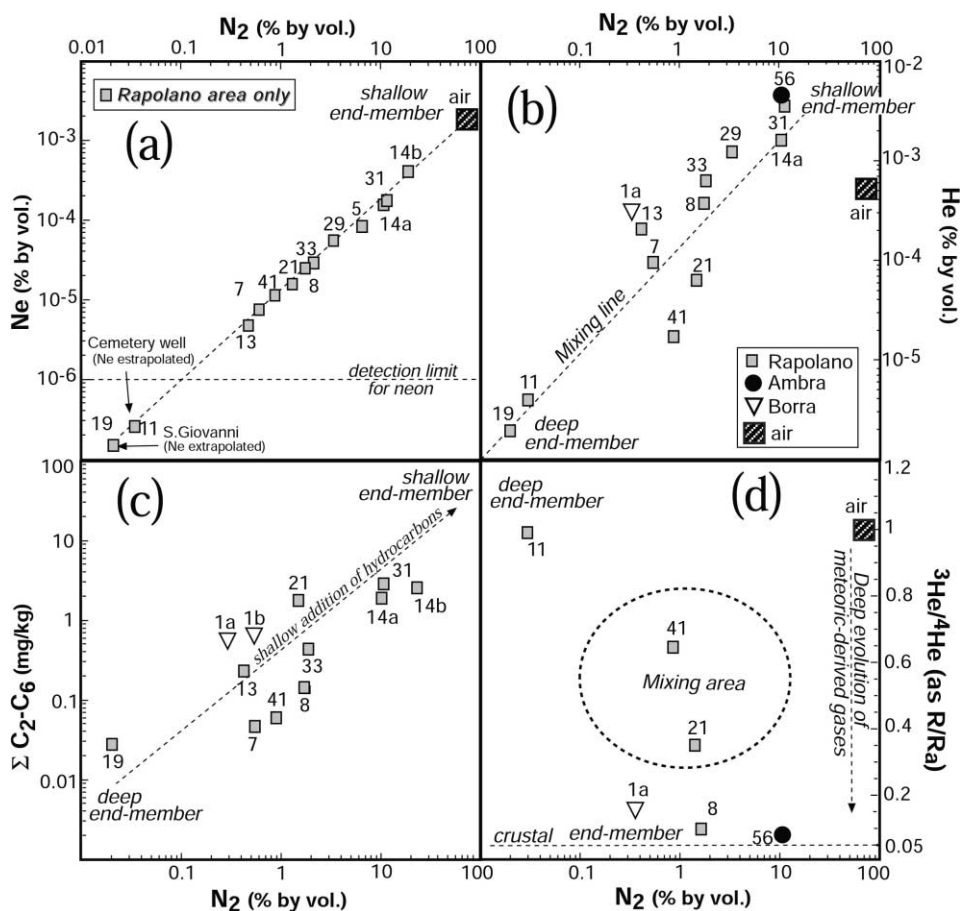

Fig. 5. Multiple diagram of N_2 plotted versus Ne (a), He (b), light hydrocarbons (c) and ^{3}He/^{4}He ratio (d). All plots suggest the presence of a mixing between a deep Ne, He and light hydrocarbons depleted end member and a shallow N_2-enriched end member.

Fig. 5a the N_2 concentration has been plotted against Ne for the gas emissions of Rapolano only. Since air is the only reasonable source of Ne, all samples are well aligned along a mixing line from the air (Ne is 18 ppmv), and a deep Ne-depleted component that at Rapolano is represented by samples 11 and 19. Although Ne concentrations in these samples were not detected, being below the instrumental detection limit of 1ppbv, it is likely that these two gas discharges represent the deepest fluids of Rapolano. In fact, sample 19 (San Giovanni) has: (i) the highest emergence temperature (40 °C), (ii) the largest emission of free CO_2 and (iii) in comparison with the other springs it still precipitates abundant travertine. Sample 11 (Cemetery well) discharges thermal water and gas from a well several hundreds of meters deep. Thus, taking into account that the extrapolated position of these samples in Fig. 5a is reasonable, it is evident that all samples lie on a mixing line where the more atmospheric contaminated sample of Rapolano (No. 14b) has about 20% O_2-depleted air.

A similar mixing line can be observed by plotting N_2 vs. He (Fig. 5b), not only for the samples from Rapolano but also for all the gases from the Siena basin (Acqua Borra and Ambra). Although air has less He than some samples (No. 14, 29, 31 and 56), likely affected by the addition of radiogenic ^4He produced by the decay of U and Th in the shallow crust, the position of samples No. 19 and No. 11 should be noted. They are still the least air-contaminated samples and this justifies their extrapolated position in Fig. 5a. Moreover, although the deeper and longer circulating samples of gas should have the highest concentration of He, He being a gas of clear crustal origin (O'Nions and Oxburgh, 1988), He at Rapolano, with respect to CO_2, seems to be an "atmospheric contaminated" component.

Additional insights can be derived by examination of the relative concentrations of N_2 and light hydrocarbons (Σc_2-c_6; Fig. 5c). As already observed for the N_2–He and the N_2–Ne diagrams (Figs. 5a and b), the deeper sample from Rapolano (No. 19) has the lowest concentration of light hydrocarbons (and CH_4), whereas the other samples tend to have higher abundances of light hydrocarbons (and CH_4) with increasing N_2. Because light hydrocarbons cannot enter deep hydrologic circuits together with N_2 as dissolved components in rainfall (CH_4 is generally <2 ppmv in the atmosphere), they have to be derived from the alteration of organic material at very shallow level in the crust, not far from the emergence areas of gases. In particular, the Siena basin being filled with unconsolidated Pliocene marine sediments, they likely represent the shallow source for light hydrocarbons that mix with a rising gas phase, practically constituted of pure CO_2. As N_2 and Ne concentrations lie in a straight line (Fig. 5a), any relation between N_2 and light hydrocarbon can be excluded in terms of a common organic source.

Further considerations on shallow and deep components can be derived from the N_2 vs. $^3He/^4He$ (R/Ra) diagram (Fig. 5d), where the position of air is reported for reference. One of the deeper samples from Rapolano (No. 11) has a R/Ra similar to air. Since the N_2 concentration is only 0.02% (by vol.) and the total He several orders of magnitude lower than air (Fig. 5b), the R/Ra value in sample 11 (0.99) must be considered the highest and deepest of the entire studied area. According to Marty et al. (1992), a R/Ra ratio greater than 0.2 suggests that a mantle ^3He component is present in a gas mixture. On the other hand, the two samples from the Siena basin (Acqua Borra and Ambra), as well as one sample from near Rapolano (No. 8) exhibit typical crustal R/Ra ratios (0.08–0.15). Two other samples from the Rapolano area (No. 21 and 41) are located on a mixing area between a hypothetical meteoric derived gas component having crustal $^3He/^4He$ ratio and the deep gas sample No. 11. By considering a value of 6.0 for the R/Ra in the European mantle (Dunai and Baur, 1995), No. 11 should have a 15% mantle-derived gas component and be considered the deeper gas emerging in the study area.

3.5. Mixing processes in liquid phase

As already shown in Fig. 2 thermal spring and thermal well-waters emerging north and south of the Mesozoic carbonate ridge of Rapolano are aligned along a mixing line indicating that water samples Nos. 11 and 19 have the deepest origins in the area. This agrees well with the conclusions already drawn with regard to the gas component. Besides, HCO_3 ions in the thermal springs, although largely depending on the CO_2 partial pressure of solution, can be considered a deep component and in fact, samples 11 and 19 have the highest HCO_3 ion concentrations (47 meq/L, Table 1) among the Rapolano thermal springs.

By plotting elements in the gas phase against elements in the liquid phase for thermal samples, apart from HCO_3, further corroboration of the mixing process between the deep and the shallow fluid phases can be shown. In Fig. 6, for example, B in the liquid phase in thermal springs is plotted versus N_2 in the gas phase and, once more, samples No. 11 and No. 19 show both the highest concentrations of B and a mixing trend with shallow B-depleted, N_2-rich waters. Boron can be considered a deep component since it can be related to: (i) evaporitic anhydrite-rich Triassic layers lying at the base of the Mesozoic limestone series; (ii) deep steam condensates leaking at the boundaries of the steam-dominated Larderello field that is very rich in boric acid (D'Amore and Truesdell, 1979). Although the anhydrite "Burano" formation does not crop out near Rapolano, anhydrite layers are likely to be present below the sediments filling the Siena basin, whereas the Larderello
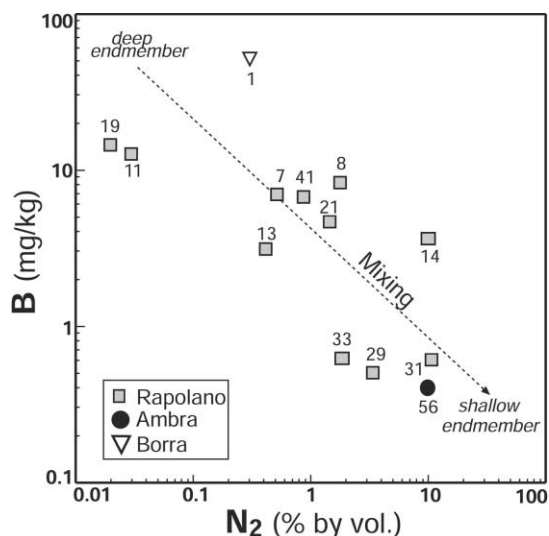
Fig. 6. B concentration in liquid phase plotted against N_2 in the gas phase.

geothermal field is located west of the Siena basin. Both sources are potential suppliers of B to long-term deep convective circulating liquid phases inside the carbonate reservoir, and thermal springs in central Italy quite often show anomalous concentration in this element (Bencini and Duchi, 1986).

4. Discussion

The Rapolano area represents one of the many emergence areas of the deep regional circulation of thermal waters in central Italy, well studied from a hydrogeochemical point of view since the beginning of this century (Lotti, 1910; Trevisan, 1951; Baldi et al., 1973; Bencini et al., 1977; Minissale, 1991). Some of these areas host focused emissions with only one spring, generally with high flow rate, associated with either a N_2-rich or CO_2-rich gas phase, whereas other areas are similar to Rapolano, with multiple spring discharges. Areas with multiple fluid emissions (including steam as at Larderello) are generally concentrated near the active geothermal areas of central Italy, one of which at the Mt. Amiata volcano (and surrounding areas) has previously been studied with a similar chemical and isotopic approach to that carried out in the present study (Minissale et al., 1997a). The presence in these areas of shallow active hydrothermal systems generating different types of fluids, phase separations (steam condensation) and re-equilibration reactions at shallow depth, provides mixing processes of fluids of different source inside the Mesozoic limestones. As a consequence, geochemical signatures of fluids are difficult to interpret and

deep end-members cannot easily be recognised. The Rapolano thermal discharges, being far from active hydrothermal areas and being less affected by the above mentioned processes, allow better understanding of the fluid circulation and mixing processes that fluids of deep origin undergo during their ascent to the surface.

Several hypotheses have been proposed for the origin of heat of thermal springs in central Italy, such as: (i) exothermic heat release after the hydration of anhydrite to form gypsum inside the deep Triassic anhydrite layers (Trevisan, 1951); (ii) deep convective circulation inside the limestones (Baldi et al., 1973) and (iii) mixing with geothermal brines or steam condensates leaking from the active geothermal systems into the carbonate reservoir (Gianelli and Scandiffio, 1989). Several sources for CO_2 have also been proposed for the huge widespread flow of this gas in central Italy: (i) mantle degassing (Minissale 1991; Marini and Chiodini, 1994); (ii) hydrolysis of limestones (Panichi and Tongiorgi, 1976); (iii) hydrothermal metamorphism of impure limestones inside the metamorphic Paleozoic basement (Gianelli, 1985).

Although limestones typically undergo convective circulation, it seems reasonable to suppose that in central Italy the huge production of CO_2 from the deep hydrothermal systems and its expulsion towards the surface enhances this convection. Such CO_2 transfer from depth is maintained by the fact that the Mesozoic limestones are an open system that favours the expulsion of CO_2 towards the atmosphere. This continuous discharge allows more dissolution of limestones at depth and their transfer to the surface (travertine precipitation) as an ongoing process. For this reason it is appropriate to discuss the origin of deep CO_2 at a site such as Rapolano where, although shallow mixing processes with atmospheric and meteoric fluids have proved to occur, hundreds of tons per day of CO_2 are discharged into the atmosphere.

One powerful tool to investigate the origin of CO_2 in a gas mixture is its $^{13}C/^{12}C$ isotopic ratio. At least 4 potential sources can be proposed in the investigated area, and more generally in central Italy, with different isotopic ratios: (i) CO_2 from mantle degassing, where $\delta^{13}C$ ranges from -4.0 to -7.0 $^o/_{oo}$ (Javoy et al., 1982); (ii) solubilized CO_2 in rainwater in equilibrium with atmospheric CO_2, with $\delta^{13}C = -7.0^o/_{oo}$ (Faure, 1977) that easily infiltrates the carbonate outcrop areas; (iii) soil-biogenically produced CO_2 with $\delta^{13}C < -20$ $^o/_{oo}$ (Cerling et al., 1991) enhanced in infiltrating rainfall before entering the karstic circuits; iv) hydrothermal CO_2 deriving from limestone dissolution where $\delta^{13}C$ is in the range -1.0 to $+2.0^o/_{oo}$ (Rollinson, 1993). In fact, a multiple source for CO_2 has already been proposed in central Italy (Minissale et al., 1997b) and quantified in terms of deep versus shallow CO_2 in some aquifers of central-southern Italy (Chiodini et al., 2000).

If the mixing model between deep-convective and shallow-meteoric components in both gas and liquid phases, previously described, can be considered reasonable, the deeper sample in the gas phase recognised at Rapolano (sample 11) should have more positive $\delta^{13}C$ values than $-7.0^o/_{oo}$ (the atmospheric value). Potential deep sources of CO_2 should indeed produce C with more positive $\delta^{13}C$ than this value, possibly even positive values if "hydrothermal" CO_2 deriving from the dissolution of deep Mesozoic limestones is added to the likely minor deep rising mantle CO_2. This is reasonable if we also consider that the uprising CO_2 from mantle degassing at Rapolano is low (max 15%), as suggested by the low R/Ra ratios measured, and by the fact that $\delta^{13}C$ values of several carbonate formations in central Italy have $\delta^{13}C$ values ranging from $+1.8$ to $+3.5^o/_{oo}$ (Cortecci and Lupi, 1994). Also, since CO_2 in central Italy mostly derives from the decarbonation of limestones, a large portion of central Italy along the peri-Tyrrhenian sector has, indeed, CO_2 vents with $\delta^{13}C$ values near $0^o/_{oo}$ PDB (Minissale et al., 1997b).

The $\delta^{13}C$ of CO_2 for the deeper gas discharges at Rapolano (No. 11 and No. 19) have been found to have the lowest $\delta^{13}C$ measured values ($\delta^{13}C = -9.21$ and $-7.96^o/_{oo}$ PDB, respectively). This unusually low $\delta^{13}C$ value for CO_2 rising from a deep storage/source zone could possibly be explained by the presence of either a reservoir of deep organic material under alteration, or a huge transfer in the deep storage zone of isotopically depleted soil-derived CO_2 from infiltration of rainfall, but both these mechanisms are extremely unlikely, especially when the large CO_2 flow at Rapolano is taken into account without consistent quantities of associated "shallow-produced" CH_4. Another possible mechanism

for such low deep $\delta^{13}C$–CO_2 is a multiple (single) step precipitation of calcite along the pathway from the deep hydrothermal source zone to the surface. This would produce an isotopic fractionation, after precipitating isotopically heavy C-rich calcite at depth, with a fractionation factor that increases as temperature decreases (Ohmoto and Rye, 1979). Marini and Chiodini (1994) have discussed in theoretical terms the possibility of calcite precipitation at depth in other areas of central Italy, where calcite (and/or anhydrite) precipitation inside the limestones can be induced by changes in CO_2 partial pressure (for example after a seismic event).

Whatever the process that gives the deeper $\delta^{13}C$ values of rising CO_2 at Rapolano as low as $-9.21^o/_{oo}$ PDB, it is a fact that the more atmospheric and/or shallow contaminated gas samples measured (Nos. 7, 8, 14... etc), have more positive values (Table 2). Most of them have a CO_2 even more positive than the atmosphere, that should be the main contaminant agent in terms of shallow CO_2, and this without considering that much more negative values are also expected if soil-derived CO_2 is involved in the overall mixing process. To justify such more positive $\delta^{13}C$ values in CO_2 for the more air-contaminated gas samples at Rapolano, it can be hypothesized that low-temperature "shallow" dissolution of both Mesozoic limestones and/or travertines by the shallow circulating (descending) waters produces "shallow" isotopically heavy CO_2. This shallow isotopically heavy CO_2, likely produced inside the outcrop areas of limestones or travertine, after mixing with the deep rising isotopically low deep CO_2, brings about the values measured. The described mechanism should also be applied to the gas samples emerging along the Follonica-Rimini fault line (Acqua Borra and Ambra samples), where $\delta^{13}C$-CO_2
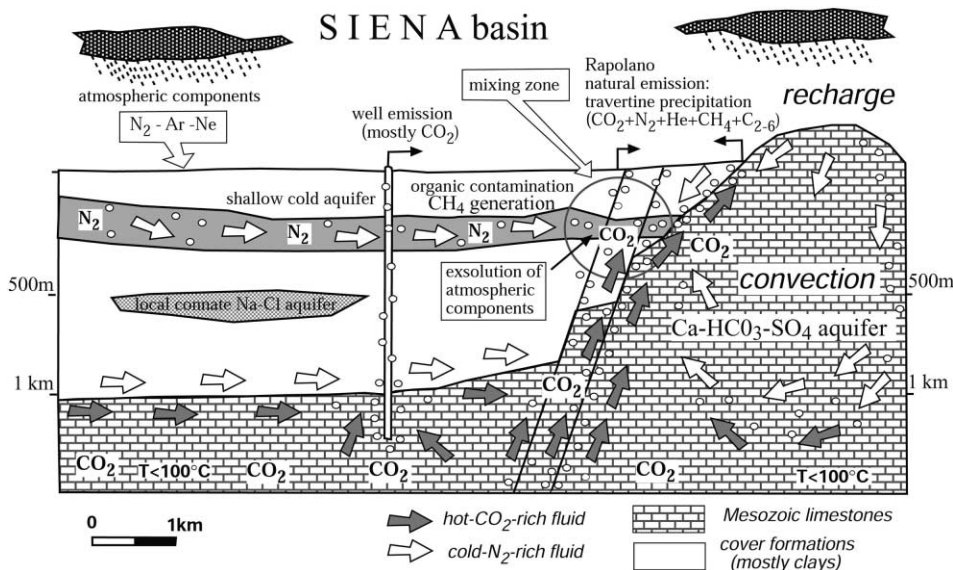

Fig. 7. Schematic and idealized hydrogeological E-W section across the Siena basin (see text).

are: −5.21 and –6.08°/₀₀ PDB, respectively. These values are very similar to the more shallow-contaminated samples of Rapolano.

5. Conclusions

Thermal springs emerging at Rapolano have proved the complexity of the hydrogeology of Mesozoic limestones in central Italy, even in areas relatively far from active geothermal areas, where phase-separation is not a major process. Three chemically different end-members have been identified among the spring and well waters sampled at Rapolano and surrounding areas. One is represented by cold saline Na-Cl type waters hosted in confined aquifer(s) inside the Neogene sedimentary formations of the Siena basin. These saline waters are relatively isolated and do not mix with the thermal waters circulating in the Mesozoic limestone formations. The other two, circulating (or gathering) inside the Mesozoic limestones and associated travertines, are well mixed with end-members being represented by shallow cold Ca-HCO$_3$ groundwaters and deep thermal saline CO$_2$-rich Ca-SO$_4$(HCO$_3$) waters. The schematic cross-section shown in Fig. 7 summarises the distribution and the overall circulation of all the described fluids. Travertine deposition, abundant CO$_2$ emission to the atmosphere, relative low total Ne, He and light hydrocarbons and relative high ^{3}He/^{4}He values characterise the emission of the deeper and hotter fluids. In contrast, relatively high N$_2$ and He concentrations and low ^{3}He/^{4}He ratios are distinctive for the more shallow-water-and-air-contaminated colder emissions.

With respect to the most part of CO$_2$ emissions of central-southern Italy, CO$_2$ discharging at Rapolano displays anomalously low isotopic δ^{13}C values. These low values, as well as others located in this northern sector of central Italy (Minissale et al., 1997a), are difficult to be interpreted because all deep reasonable sources of CO$_2$ should have more positive values than the less air-contaminated gas samples at Rapolano (No. 11 and No. 19). Although either a mantle origin for CO$_2$ has been proposed for this sector of Italy (Marini and Chiodini, 1994), or an origin from alteration of organic matter within the Neogene sediments (Panichi and Tongiorgi, 1976; Minissale et al., 1997a), the authors propose here a multiple (single) step calcite precipitation process at depth inside the carbonate reservoir for the rising (or laterally flowing) metamorphic-derived CO$_2$. This interpretation seems reasonable since, with respect to other CO$_2$ emissions from central-southern Italy, known geothermal or volcanic systems are quite far from Rapolano. The lateral and long-distance movement of CO$_2$ from potential hydrothermal sources inside the Mesozoic limestones (such as Larderello) or the vertical and lateral motion from the metamorphic base-ment to areas such as Rapolano, is likely to be controlled by convection. A very well developed convective system at depth inside a quasi-continuous reservoir, such as the one represented by the Mesozoic limestones in central Italy, could support the proposed mechanism of C isotopic fractionation in CO$_2$.

Acknowledgements

References

Baldi, P., Ferrara, G.C., Masselli, L., Pieretti, G., 1973. Hydrogeochemistry of the region between Mt Amiata and Rome. Geothermics 2, 124–141.

Barazzuoli, P., Izzo, S., Menicori, P., Micheluccini, M., Salleolini, M., 1991. Un esempio di acquifero alimentato da acqua termale (Rapolano Terme, Siena). Boll. Soc. Geol. Ital. 110, 3–14.

Barelli, A., Celati, R., Manetti, G., 1977. Gas-water interface rise during early exploitation tests in Alfina geothermal field, northern Latium, Italy. Geothermics 6, 199–209.

Bencini, A., Duchi, V., 1986. Boron content of thermal waters of Tuscany and Latium, central Italy. Proc. 5th W.R.I., Reykjavik, Iceland, 8–17 Aug., 45–47.

Bencini, A., Duchi, V., Martini, M., 1977. Geochemistry of thermal springs of Tuscany Italy. Chem. Geol. 19, 229–252.

Cerling, T.E., Solomon, D.K., Quade, J., Bowman, J.R., 1991. On the isotopic composition of carbon in soil carbon dioxide. Geochim. Cosmochim. Acta 55, 3403–3405.

Chiodini, G., Frondini, G., Cardellini, C., Parello, F., Peruzzi, L., 2000. Rate of diffuse carbon dioxide Earth degassing estimated from carbon balance of regional aquifers: the case of central Apennine Italy. J. Geophys. Res. 105, 8423–8434.

Cipriani, N., Ercoli, A., Malesani, P., Vannucci, S., 1972. I travertini di Rapolano Terme (Siena). Mem. Soc. Geol. Ital. 11, 31–46.

Cortecci, G., Lupi, L., 1994. Carbon, oxygen and strontium isotope geochemistry of carbonate rocks from the Tuscan nappe. Mineral. Petrol. Acta 27, 63–80.

Craig, H., 1963. Isotopic variations in meteoric waters. Science 123, 1702–1703.

D'Amore, F., Truesdell, H.A., 1979. Models for steam chemistry at Larderello and The Geysers. Proc. 5th Work. on Geothermal Reservoir Engineer., Stanford, California, pp. 283–297.

Duchi, V., Minissale, A., Rossi, R., 1986. Chemistry of thermal springs in the Larderello-Travale geothermal region, southern Tuscany Italy. Appl. Geochem. 1, 659–667.

Duchi, V., Minissale, A., Prati, F., 1987. Chemical composition of thermal springs, cold springs, streams, and gas vents in the Mt. Amiata geothermal region (Tuscany, Italy). J. Volcanol. Geotherm. Res. 31, 321–332.

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 Mt. Amiata, Torre Alfina, and Latera (central Italy). Geothermics 21, 401–413.

Dunai, T.J., Baur, H., 1995. Helium, neon and argon systematics of the European subcontinental mantle: implications for its geochemical evolution. Geochim. Cosmochim. Acta 59, 2767–2783.

Faure, G., 1977. Principles of Isotope Geology. J. Wiley, New York.

Gatt, J.R., Carmi, I., 1970. Evolution of the isotopic composition of atmospheric waters in the Mediterranean Sea area. J. Geophys. Res. 75, 3032–3048.

Gianelli, G., 1985. On the origin of geothermal CO_2 by metamorphic processes. Boll. Soc. Geol. Ital. 104, 575–584.

Gianelli, G., Scandiffio, G., 1989. The Latera geothermal system (Italy): chemical composition of the geothermal fluid and hypotheses on its origin. Geothermics 18, 447–463.

Giggenbach, W.F., 1980. Geothermal gas equilibria. Geochim. Cosmochim. Acta 44, 2021–2032.

Giggenbach, W.F., Gonfiantini, R., Jangi, B.L., Truesdell, A.H., 1983. Isotopic and chemical composition of Parbaty Valley geothermal discharges, NW-Himalaya. Geothermics 12, 199–222.

Giggenbach, W.F., Minissale, A., Scandiffio, G., 1988. Isotopic and chemical assessment of geothermal potential of the Colli Albani area, Latium region Italy. Appl. Geochem. 3, 475–486.

Gonfiantini, R., 1986. Environmental isotopes in lake studies. In: Fritz, P., Fontes, J.Ch. (Eds.), Handbook of Environmental Isotope Geochemistry, Elsevier. pp. 113–168.

Grechi, G., 2000. Indagine geochemica-isotopica delle acque e dei gas nell'area di Rapolano Terme (Siena). Unpubl. Thesis, Univ. Florence, Italy.

Guo, L., Riding, R., 1998. Hot-spring travertine facies and sequences, Late Pleistocene, Rapolano Terme Italy. Sedimentol. 45, 163–180.

Javoy, M., Pineau, F., Allegre, C.J., 1982. Carbon geodynamic cycle. Nature 300, 171–173.

Kissin, I.G., Pakhomov, S.I., 1967. The possibility of carbon dioxide generation at depth at moderately low temperature. Dokl. Akad. Nauk SSSR 174, 451–454.

Lotti, B., 1910. Geologia della Toscana. Mem. Descrittive della Carta Geolgica d' Italia Tipografia Nazionale Roma, Italy.

Mamyrin, B.A., Tolstikhin, I.N, 1984. Helium isotopes in nature. Elsevier, Amsterdam.

Marini, L., Chiodini, G., 1994. The role of CO_2 in the carbonate-evaporite geothermal systems of Tuscany and Latium, Italy. Acta Vulcanol. 5, 95–104.

Marty, B., O'Nions, R.K., Oxburgh, E.R., Martel, D., Lombardi, S., 1992. Helium isotopes in Alpine regions. Tectonophys. 206, 71–78.

Minissale, A., 1991. Thermal springs in Italy: their relation to recent tectonics. Appl. Geochem. 6, 201–212.

Minissale, A., Evans, W., Magro, G., Vaselli, O., 1997a. Multiple source components in gas manifestations from north-central Italy. Chem. Geol. 142, 175–192.

Minissale, A., Magro, G., Vaselli, O., Verrucchi, C., Perticone, I., 1997b. Geochemistry of water and gas discharges from the Mt. Amiata silicic complex and surrounding areas (central Italy). J. Volcanol. Geotherm. Res. 79, 223–251.

Mongelli, F., Tramacere, A., Grassi, S., Perusini, P., Squarci, P., Taffi, L., 1982. Misure di flusso di calore nel Graben di Siena. In: CNR (Italian Council for Research Ed.), Il Graben di Siena, PFE-RF9, Rome, Italy, 150–162.

Negrel, P., Casanova, J., Azaroual, M., Guerrot, C., Cocherie, A., Fouillac, C., 1999. Isotope geochemistry of mineral spring waters in the Massif Central France. In: Armannsson H. (Ed.), Geochem. of Earth's Surface, Rotterdam, The Netherlands.

Ohmoto, H., Rye, R.O., 1979. Isotopes of sulfur and carbon. In: Barnes H.U. (Ed), Geochemistry of hydrothermal ore deposits, pp. 509–567. J. Wiley, New York.

O'Nions, R.K., Oxburgh, E.R., 1988. Helium, volatile fluxes and the development of continental crust. Earth Planet. Sci. Lett. 90, 331–347.

Panichi, C., 1982. Aspetti geochimici delle acque termali. In: C.N.R. (Italian Council for Research Ed.). Il graben di Siena, PFE-SPEG-RF-9, Rome, Italy, 61–72.

Panichi, C., Tongiorgi, E., 1976. Carbon isotopic composition of CO_2 from springs, fumaroles, mofettes and travertines of central and southern Italy: a preliminary prospection method of geothermal areas. Proc. 2nd U.N. Symp. on the Develop. and Use of Geotherm. Energy, San Francisco, USA., 20–29 May 1975, pp. 815–825.

Rogie, J.D., Kerrick, D.M., Chiodini, G., Frondini, F., 2000. Flux measurements of nonvolcanic CO_2 emission from some vents in central Italy. J. Geophys. Res. 105, 8435–8445.

Rollinson, H., 1993. Using Geochemical Data. Longman Group, London

Trevisan, L., 1951. Una nuova ipotesi sulla origine di alcune sorgenti termali della Toscana. L'Industria Mineraria 2, 41–42.