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Hydrogeochemistry of the Campania region in southern Italy

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Abstract

A geochemical study of thermal springs, cold springs, stream waters and natural gas emissions has been carried out in the Campania region of southern Italy. This region hosts four Quaternary volcanic areas, and thermal springs and gas emissions occur in three of them. Most thermal springs discharge Na-Cl composition waters of connate origin derived from post-orogenic volcanic and sedimentary formations. Although high-enthalpy systems are present in two of the four volcanic areas, there appear to be no magmatic contributions to the thermal springs. Solute geothermometers are unreliable as spring waters are strongly affected by mixing with "shallow" brines before discharging.

Thermal springs and gas emissions also occur in non-volcanic areas, where an extensive carbonate unit acts as a regional aquifer for cold, low-salinity, bicarbonate waters. Thermal features in these areas occur in fractured zones associated with active faults. Their compositions are determined only by the type of rock encountered by solutions before surface discharge.

As in other areas of north-central Italy, the widespread occurrence of hot and cold CO_2-rich springs, and gas emissions in both volcanic and non-volcanic zones, suggests a deep origin for the CO_2.

1. Introduction

There are four main Quaternary volcanic areas in the belt of central-southern Italy lying between the Tyrrhenian Sea and the Apennines: Roccamonfina, Vesuvio, Campi Flegrei and Ischia (Fig. 1). At Campi Flegrei and the Isle of Ischia there are fumaroles, boiling pools, thermal springs and wells, whereas Roccamonfina features only thermal springs and gas emissions at the foot of the volcano. Vesuvio has no surficial hydrothermal features.

Thermal springs (27–40°C) and CO_2-rich cold springs (soda springs) also occur in areas not associated with these recently active volcanic areas. This suggests that anomalous regional heat flow is partly related to tectonic activity.

Several geochemical studies were carried out on the natural thermal manifestations occurring in the surroundings of Campi Flegrei (Baldi et al., 1975; Cortecci et al., 1978), on the fumaroles of the "Solfatara" volcano in Pozzuoli (Cioni et al., 1984; Bolognesi et al., 1986; Tedesco and Sabroux, 1987) and on thermal features of Ischia (De Gennaro et al., 1984) and Roccamonfina (Fanelli et al., 1985, cited by Watts, 1987), in order to assess the geothermal potential of these volcanic areas and also to assess the risk of eruptions in the Pozzuoli area.

The first geothermal research work at Campi Flegrei, with drilling of deep wells, was done in the 1940's and 1950's (Penta, 1949, 1955), when temperatures above 300°C were found at 1840 m (Minucci, 1964). Subsequent exploration drilling was carried out more recently by AGIP (Italian National Oil Company) in a

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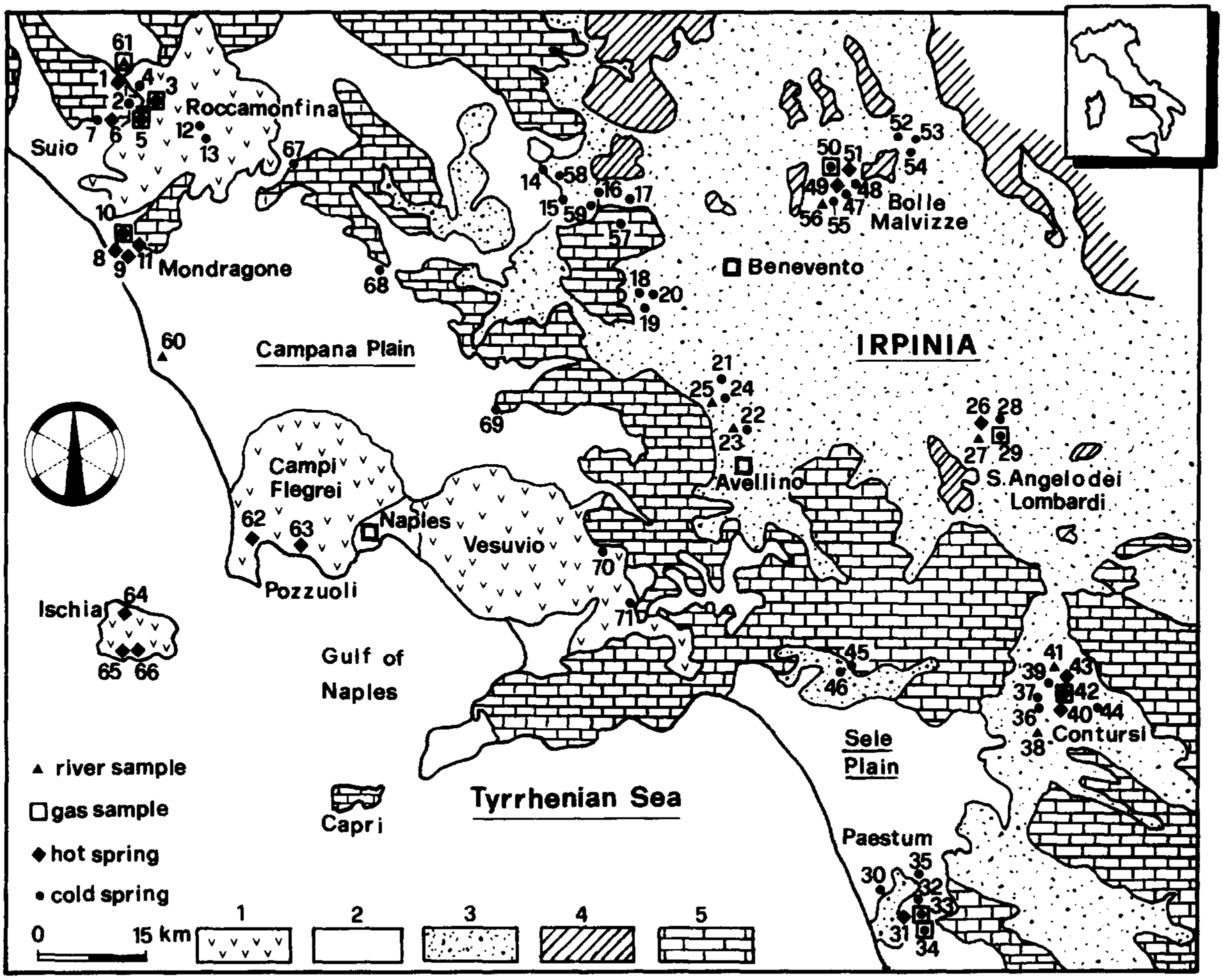

Fig. 1. Geological sketch map of the Campania region showing sampling points. 1 = Quaternary volcanics; 2 = Neogene sediments; 3 = allochthonous Cretaceous–Oligocene flysch formations and Tertiary synorogenic clastic formations; 4 = Mesozoic carbonate "Irpinian" series; 5 = Mesozoic carbonate "Campanian" series. Numbers correspond to sample numbers in Tables 1, 2 and 3.

joint venture with ENEL (Italian National Electricity Board) as part of new regional geological and geophysical studies (Barbier et al., 1970; Cameli et al., 1975; Baldi et al., 1976). A strong thermal anomaly was found at Campi Flegrei, with temperatures over 420°C measured at 3040 m depth (De Vivo et al., 1989; Piovesana and Guidi, 1991). However, owing to the low permeability of the system, fluid production was not possible.

Geothermal research was carried out on the Isle of Ischia in the 1940's (Penta and Conforto, 1951). Several wells were drilled there and the hottest temperature of 232°C was measured in the deepest well at 1150 m (Penta, 1963). An 880-m-deep well was recently drilled in the summit caldera of Roccamonfina by UNOCAL Corporation (Watts, 1987), where a cool bottom-hole temperature (36°C) was found. This temperature is cooler than the thermal springs surrounding the volcano. No thermal manifestations are present in the vicinity of Vesuvio, though it erupted as recently as 1944.

The studied area is also seismically unstable. Two periods of bradyseism occurred at Pozzuoli in 1970–1971 (Dall'Aglio et al., 1972) and 1983–1984 (Barberi et al., 1984), and there was a large earthquake ($M_s = 6.9$) in the Irpinia region in November 1980

(Bernardi and Zollo, 1989), whose epicenter was near S. Angelo dei Lombardi (Fig. 1).

Owing to the intense volcano-tectonic activity of this area, many thermal springs and gas emissions and, for comparison, cold springs and running waters were sampled and chemically analyzed. For the Isle of Ischia and Campi Flegrei, data were compiled from the literature. The aims of this survey are to assess the regional hydrology associated with hydrothermal activity in the context of the geological setting, and to evaluate solute geothermometers on hot spring waters in volcanic areas where vertical temperature gradients from wells are known.

2. Hydrogeological background

The geology within the study area is dominated by two Mesozoic carbonate platform sequences (''Piattaforma Campana'' and ''Piattaforma Irpina'') separated by basins that formed at the boundary between the African and the Eurasian plates. Since the Miocene, these units have been thrusted eastwards and today form the backbone of the central-southern Apennines. Overlying the carbonate units is a complex thrust sequence of allochthonous Cretaceous–Oligocene flysch and interfingered synorogenic clastic sediments of Tertiary age (Pescatore and Ortolani, 1973). This heterogeneous sequence of clastic units (symbol 3, Fig. 1) includes Miocene evaporites and, as a whole, is of relatively low permeability. The two plains (''Campana Plain'' and ''Sele Plain'') in Fig. 1 are made up of Plio-Pleistocene marine and continental sediments and modern alluvium. Thick piles of young erupted volcanics locally overlie the sedimentary sequence at Roccamonfina, Vesuvio, Ischia and Campi Flegrei. Volcanic deposits consist mainly of K-rich, leucite-bearing pyroclastic products, with tephritic and phonolitic compositions (Peccerillo and Manetti, 1985).

Mesozoic carbonate units, exceeding 4000 m thickness, are highly fractured and act as a regional aquifer. Where the aquifer is intersected in topographic lows, cold springs supply numerous, low-salinity waters, particularly in the western part of the study area (Celico, 1978; Celico et al., 1980; Corniello, 1988). Where poorly permeable rocks underlie the coastal plains and the northwestern study area, natural springs are confined to fracture zones and discharge saline, thermal waters (Celico et al., 1979; Ortolani et al., 1981).

Permeability within the volcanic formations is highly variable and is related to rock type (high in lavas and low in pyroclastics). Within the volcanic areas of Campi Flegrei, Ischia and Roccamonfina, there are many cold springs that discharge from the highly fractured lavas, whereas thermal springs and wells are located on major active faults.

The thermal springs in these volcanic areas are the main subject of this study, together with those of Bolle Malvizze and S. Angelo dei Lombardi in Irpinia, and Contursi and Paestum in the valley and plain of the river Sele (Fig. 1).

3. Sampling and analysis procedures

The sampling locations for waters and gases are shown in Fig. 1, and Tables 1 and 2 report the analytical results. Some literature data were used for Pozzuoli thermal springs (62–63: Martini et al., 1991), Isle of Ischia thermal waters (64–66: De Gennaro et al., 1984) and cold water samples from the Campana plain (67–71: Celico et al., 1980).

For samples collected by the authors, temperature, pH, electrical conductivity, SiO_2, Ca^{2+}, HCO_3^- and NH_4^+ were measured in the field. HCO_3^- was titrated with HCl and methyl orange as indicator; Ca^{2+} was titrated with EDTA using calceine as indicator; SiO_2 and NH_4^+ were determined using a portable spectrophotometer with the molybdate and Nessler methods, respectively. The remaining elements were analyzed later in the laboratory with techniques described by Duchi et al. (1986). The gas samples, apart from those of the Pozzuoli area, were collected with two 100-ml Rotoflow flasks, one containing 50 ml of 4 *N* NaOH solution to concentrate the non-reactive components (Giggenbach, 1975), and later analyzed by gaschromatography.

4. Chemistry of the water samples

All samples listed in Table 1 are plotted in the Cl–SO_4–HCO_3 ternary diagram (Fig. 2), with symbols distinguishing cold (<25°C) and hot samples. Apart from sample 27, whose relatively high sulfate composition is likely due to contact with gypsum-rich Tertiary

Table 1
Chemical and isotopic composition of water samples from Campania

Sample No.	Name	Type	T (°C)	pH	TDS	Ca	Mg	Na	K	HCO$_3$	Cl	SO$_4$	SiO$_2$	NH$_4$	H$_3$BO$_3$	Li	NO$_3$	δD	δ^{18}O
1	Terme Suio	ts	51	6.5	3289	370	115	265	70	1616	156	547	72	8.1	74.2	0.97	1.2	nd	nd
2	Suio	s	16	6.3	247	14	4	16	23	110	11	14	47	0.1	<0.1	<0.01	3.1	nd	nd
3	Acqua Inferno[a]	tsg	26	2.1	4213	92	35	53	133		18	3264	135	38.5	4.3	0.17	14.3	nd	nd
4	Fontanafredda	s	18	6.2	235	10	4	18	20	92	11	19	56	0.1	0.6	<0.01	0.4	−43	−7.08
5	Cadecchia	twg	52	6.4	2568	290	113	140	62	1586	163	106	67	7	34	0.42	1.2	nd	nd
6	Terme Suio 2	ts	58	6.7	3028	336	120	237	74	1525	209	384	62	11.5	73.5	0.83	1.2	nd	nd
7	Santa Maria	s	18	6.7	838	136	39	7	4	549	11	50	23	1.8	1.3	<0.01	1.2	nd	nd
8	Mondragone	ts	31	6.7	3722	348	91	614	70	1129	880	490	31	10.3	66.7	0.21	1.7	nd	nd
9	Mondragone 2	ts	38	5.8	4282	492	100	644	70	885	959	1027	35	7.4	69.2	0.21	1.2	nd	nd
10	Mondragone 3	tsg	52	6.6	4616	486	119	651	70	1617	923	624	40	21.1	68	0.21	2.5	nd	nd
11	Mondragone 4	ts	50	6.8	4371	464	106	656	66	1537	958	480	40	7.4	63	0.21	1.2	nd	nd
12	Valogno	sg	15	6	1036	88	19	67	98	659	14	14	65	0.5	1.7	0.14	1.2	nd	nd
13	San Felice	s	15	6	997	70	24	64	105	634	14	10	70	0.5	1.5	0.14	3.1	nd	nd
14	Telesino	s	17	6.9	823	150	21	14	4	622	7	5	3	0.1	0.7	0.04	3.1	nd	nd
15	Terme Telese	s	18	6.3	2784	478	69	124	19	1879	149	34	8	8.8	18.7	0.76	1.2	nd	nd
16	Santa Cristina	s	16	6.5	1131	254	7	7	4	836	11	5	7	0.1	<0.1	<0.01	3.1	nd	nd
17	San Pietro	s	15	7.1	627	132	6	9	4	329	25	82	22	0.4	<0.1	<0.01	13	nd	nd
18	Castelpoto	s	14	6.9	849	164	16	23	4	488	18	77	28	0.2	<0.1	0.03	24.2	nd	nd
19	Il lago[b]	s	15	8.6	1081	2	1	299	4	653	78	5	6	1.4	11.6	0.01	1.2	nd	nd
20	Masserizia	ts	20	7.6	602	16	12	120	4	384	39	5	16	0.5	2.3	0.03	1.2	nd	nd
21	A. Irpina	s	14	7.4	503	88	2	18	12	323	18	5	30	0.1	2.3	<0.01	6.2	nd	nd
22	Picarelli	s	16	7.8	73461	880	334	27485	51	439	42245	2054	20	35.5	18.5	0.14	8.1	nd	nd
23	Cardogneto	r	16	7.1	669	116	10	35	16	305	25	120	19	0.3	0.2	<0.01	18.6	nd	nd
24	Grottolella	s	16	6.8	1038	178	33	30	16	396	39	317	27	0.1	0.1	0.03	2.5	nd	nd
25	Campo	r	14	7.3	761	134	19	30	20	329	35	192	2	0.2	0.5	<0.01	0.4	nd	nd
26	San Teodoro 2	ts	27	6.4	1314	190	60	51	8	915	36	38	17	1.8	0.7	0.03	0.4	−48	−7.2
27	San Teodoro	r	15	7.3	1028	178	23	62	16	317	39	384	8	0.1	0.6	0.03	1.2	−48	−7.13
28	Rocca S. Felice	s	15	3.2	2480	610	34	41	23		50	1699	15	2.2	0.8	<0.01	7.4	nd	nd
29	Mefite	sg	15	5.8	2028	226	103	196	23	683	71	710	13	3.8	1.5	0.04	0.4	−15.9	−5
30	Paestum	s	17	6.6	5079	242	163	1300	43	610	2272	422	9	0.5	4.8	0.03	22.9	nd	nd
31	Paestum 2	w	20	7.2	1821	170	61	311	23	531	533	192	8	0.9	1.5	0.1	0.4	nd	nd
32	Capaccio V.	s	16	6.4	6682	328	199	1700	55	817	3195	394	4	0.1	3.8	0.05	1.2	nd	nd
33	Capaccio V. 2	sg	16	6.4	6591	304	216	1700	51	884	3018	374	4	<0.1	3	0.1	1.2	nd	nd
34	Capaccio V. 3	sg	15	6.4	2910	250	97	570	16	854	976	144	4	0.1	0.7	0.06	0.9	nd	nd
35	Feudo	s	15	6.4	8730	360	264	2440	82	860	4083	653	4	<0.1	2.6	0.04	1.2	nd	nd
36	Cantini	s	18	5.9	1790	332	35	62	12	1244	67	34	4	20.1	9.9	0.37	0.9	nd	nd
37	Cantini 2	s	15	6.1	1390	264	39	37	8	982	46	10	2	<0.1	5.4	0.21	1.3	nd	nd
38	Sele	r	16	7.1	370	68	10	12	4	250	4	19	2	0.1	0.6	<0.01	3.1	nd	nd
39	Volpacchio	s	17	6.3	1811	324	51	62	12	1275	7	5	4	0.2	10	0.4	0.4	nd	nd
40	Contursi	ts	30	6.1	3335	330	95	430	59	2166	511	307	16	14.4	22.1	2.98	0.4	nd	nd
41	Sele	r	16	7.4	389	68	12	9	4	238	4	24	2	<0.1	0.5	<0.01	3.1	nd	nd
42	Contursi 2	tsg	40	6.1	4021	370	115	550	82	1891	710	192	21	20.9	74.2	8.74	1.9	−47.8	−7.41
43	Contursi 3	ts	39	6.1	3878	342	123	524	82	1830	660	202	22	9.4	91.5	8.74	1.2	nd	nd
44	Contursi 4	s	14	6.8	594	130	4	16	4	397	14	29	5	0.1	<0.1	<0.01	2.2	nd	nd
45	Ornito	s	13	6.6	10150	230	79	3599	4	458	5396	384	13	0.6	1.1	<0.01	1.9	nd	nd
46	Ornito 2	s	14	7.2	522	72	24	18	4	366	21	9	4	0.1	<0.1	<0.01	4.3	nd	nd
47	Bolle Malvizza	s	22	7.6	13218	56	22	4499	8	2745	5432	19	8	0.9	433	0.04	16.7	nd	nd
48	Bolle Malvizza 2	s	20	7.6	13000	36	34	4600	8	2550	5325	5	7	1.7	392	0.22	21.7	nd	nd
49	Bolle Malvizza 3	ts	25	8.1	15146	26	17	5350	8	3062	6035	29	7	0.8	510	0.35	24.8	nd	nd
50	Bolle Malvizza 4	sg	23	7.8	13255	20	16	4600	12	2910	5183	134	7	0.3	377	0.49	18.6	nd	nd

Sample No.	Name	Type	T (°C)	pH	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4	SiO_2	NH_4	H_3BO_3	Li	NO_3	δD	$\delta^{18}O$
51	Bolle Malvizza 5	ts	29	8.2	15839	30	27	5589	8	3062	6390	182	8	1	541	0.21	20.5	nd	nd
52	Roseto	s	12	6.7	521	90	12	21	4	336	21	24	8	0.1	<0.1	<0.01	0.4	nd	nd
53	Castelfranco	s	12	6.8	832	112	39	23	39	525	28	53	14	0.5	<0.1	0.01	0.9	nd	nd
54	Castelfranco 2	s	11	6.9	770	114	36	21	4	506	32	43	15	0.3	<0.1	0.01	1.7	nd	nd
55	Buonalbergo[b]	s	12	8.5	2761	4	1	849	4	1061	401	408	6	8.1	3.7	0.04	1.3	nd	nd
56	Buonalbergo 2	r	14	7	796	120	15	60	8	397	7	182	7	<0.1	0.3	<0.01	1.3	nd	nd
57	Solopaca	s	18	6.8	165	26	1	7	8	92	4	14	18	<0.1	<0.1	<0.01	1.3	nd	nd
58	Hotel Relax	s	19	6.3	2014	360	52	74	12	1403	82	14	2	1.7	11.1	0.49	2.5	nd	nd
59	Calore	r	17	7.4	475	72	11	30	12	268	28	5	5	<0.1	0.6	<0.01	0.4	nd	nd
60	Volturno	r	17	7.2	684	120	15	28	8	427	21	62	1	<0.1	0.7	0.01	1.7	nd	nd
61	Garigliano	rg	16	6	559	110	6	18	4	409	3	10	<1	<0.1	0.1	<0.01	1.3	nd	nd
62	Ter. Nerone (1)	ts	71	6.6	19940	262	39	7245	51	214	11254	706	171	9.3	142	10.1	nd	12	1.2
63	Ter. Puteolane (1)	ts	51	7.1	7215	20	49	2346	137	2379	1633	653	140	1.7	149	1.02	nd	−12	−3.3
64	Ischia (2)	tw	57	7	3510	42	30	994	105	976	934	379	50	3	54.4	0.3	nd	−33.5	−5.91
65	Ischia 2 (2)	tw	65	7	12287	146	107	4163	121	354	6213	1094	90	3	274	1.38	nd	−18.4	−2.45
66	Ischia 3 (2)	tw	99	7.5	12290	72	28	4393	160	323	6710	446	158	nd	344	3	nd	−20.6	−3.33
67	Ferrarelle (3)	s	15	6.1	2879	600	23	58	47	2123	25	5	98	nd	nd	nd	nd	−35.1	−6.41
68	spring D (4)	s	13	6.5	888	226	56	32	8	952	67	5	16	nd	nd	nd	nd	−37	−6.7
69	spring O (4)	s	14	6.6	847	192	30	81	12	665	146	29	26	nd	nd	nd	nd	−39	−6.45
70	spring P (4)	s	11	7	459	102	27	32	11	384	60	38	21	nd	nd	nd	nd	−42.9	−7.36
71	spring T (4)	s	14	6.8	605	144	38	25	16	580	50	29	33	nd	nd	nd	nd	−35.6	−6.31

TDS = total dissolved solids, Ca, Mg, Na, K, HCO_3, Cl, SO_4, SiO_2, NH_4, H_3BO_3, Li and NO_3 in mg/kg; δD and $\delta^{18}O$ in ‰ vs. SMOW.

s = cold spring; sg = cold spring with gas; ts = thermal spring; tsg = thermal spring with gas; w = cold well; tw = thermal well; twg = thermal well with gas; r = stream sample; rg = stream sample with gas.

(1) = Martini et al. (1991); (2) = De Gennaro et al. (1984); (3) = Corniello (1988); (4) = Celico et al. (1980).

[a] Sample 3: Al = 1026 mg/kg and Fe = 146 mg/kg.

[b] Samples 19 and 55: CO_3 is 26 and 40 mg/kg, respectively.

evaporites, all stream waters (23, 25, 38, 41, 56, 59, 60 and 61) lie near the HCO_3 corner. Most cold springs also plot near the HCO_3 corner, being derived from carbonate-hosted aquifers. Exceptions are represented by the samples from near Paestum (30–35) and samples 22 and 45, which lie in the Cl sector (Fig. 2). Samples 22 and 45 are extremely saline [TDS (total dissolved solids) > 10,000 mg/kg), probably a consequence of pore-water leakage from evaporitic strata (as suggested by the Na/Cl ratio = 1 in Fig. 3) embedded in the synorogenic formations covering the carbonate rocks. Samples from near Paestum appear to be the result of mixing between a relatively deep, hot, low-salinity, conductively heated endmember fluid of meteoric origin (represented by sample 31: TDS = 1821 mg/kg and $T = 20°C$) and a Cl-rich, cold marine component (represented by sample 35: TDS = 8730 mg/kg and $T = 15°C$). This mixing is evident in the Na–Cl diagram in Fig. 3, where samples 31–35 align along a seawater–meteoric water mixing trend.

Among cold springs, sample 3 from the Suio area near Roccamonfina volcano and sample 28 from near S. Angelo dei Lombardi in Irpinia are acid-sulfate waters (Table 1; Fig. 2), in which H_2SO_4 is derived from the oxidation of continuously flowing H_2S in the associated gas phase under subaerial, oxidizing conditions.

Waters with temperatures > 25°C show a variety of compositions: (1) Ca(Mg)–HCO_3 near Suio (samples 1, 4, 5 and 6); (2) Na(Ca)–Cl(HCO_3) near Contursi (40, 42 and 43) and Mondragone (8–11); (3) markedly Na–Cl at Bolle Malvizze (47–51), Campi Flegrei (62–63) and the Isle of Ischia (64–66).

5. Isotopic composition of water samples

Detailed oxygen and hydrogen isotopic investigations on thermal and cold springs in the study area have been published by Cortecci et al. (1978) for the Campi

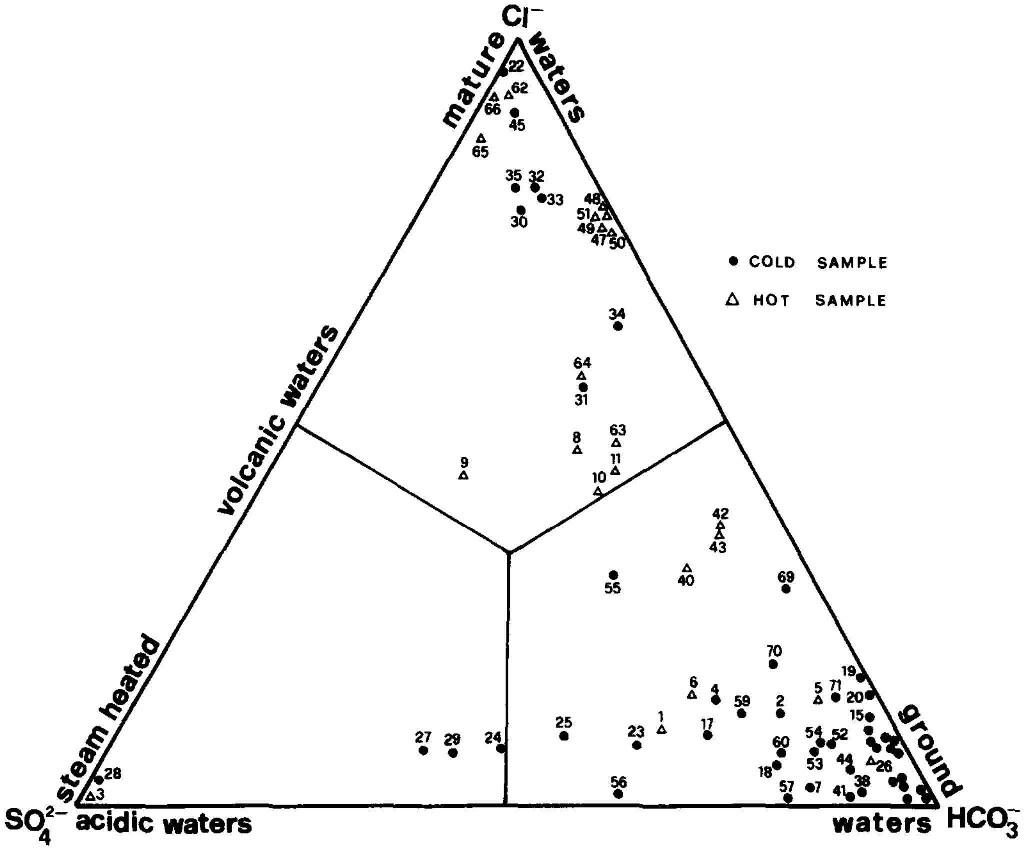

Fig. 2. Cl–SO_4–HCO_3 ternary diagram (in meq/l) for the samples investigated.

Flegrei area, by De Gennaro et al. (1984) for the Isle of Ischia, by Celico et al. (1980) for the eastern boundary of the Campania plain, by Celico et al. (1979) for the Contursi area (sample 42, Table 1), and by De Gennaro et al. (1982) for the San Teodoro area (sample 26 and 28, Table 1). Some isotopic values for cold springs in the Roccamonfina volcanic area were reported by Watts (1987) (sample 4 in Table 1).

All the data are plotted on the δD–$\delta^{18}O$ diagram of Fig. 4 (numbers are reported only for locations also sampled in this study). Most cold springs (all samples from Roccamonfina and Campana plain), sample 42 from Contursi, sample 26 from near S. Angelo dei Lombardi and some cold waters from Pozzuoli and Ischia, lie along the Mediterranean meteoric water line (M.M.W.L.; Gat and Carmi, 1970). In contrast, thermal samples from Pozzuoli (62–63) and Ischia (65–66) lie on evaporation lines typical of all Italian volcanic areas (Minissale, 1991).

Baldi et al. (1975) and Cortecci et al. (1978) suggested that the isotopic compositions of sample 62 and 63 in the Campi Flegrei area can be explained by mixing between local, meteoric water and a "deep" marine component. By contrast, De Gennaro et al. (1984) argued that the high $\delta^{18}O$ values measured at Ischia (65 and 66) are due to partial ^{18}O shifts caused by water–rock interaction at high temperature involving solutions derived by mixing of a hot, deep, marine component and a shallow, cold, meteoric component. Although these suggested mechanisms cannot completely be ruled out, we believe that evaporation at shallow levels of fluids formed by mixing between meteoric and Cl-rich endmembers without any ^{18}O shift is a more likely process. Support for this mechanism is given by the Cl–$\delta^{18}O$ and Cl–δD diagrams (Fig. 5), where the Pozzuoli and Ischia samples are clearly aligned along evaporation lines.

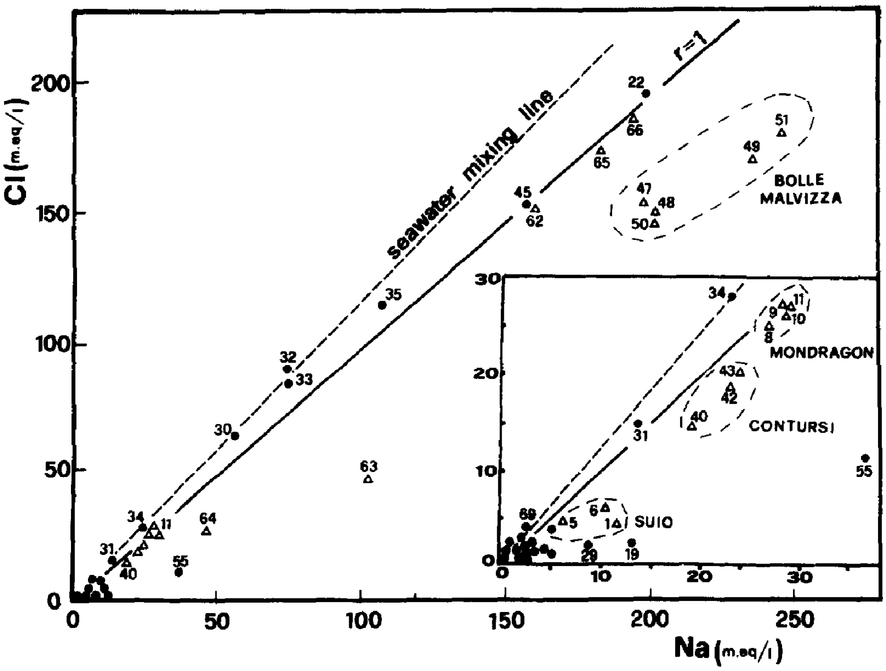

Fig. 3. Na–Cl diagram (in meq/l) for the samples investigated. Symbols as in Fig. 2.

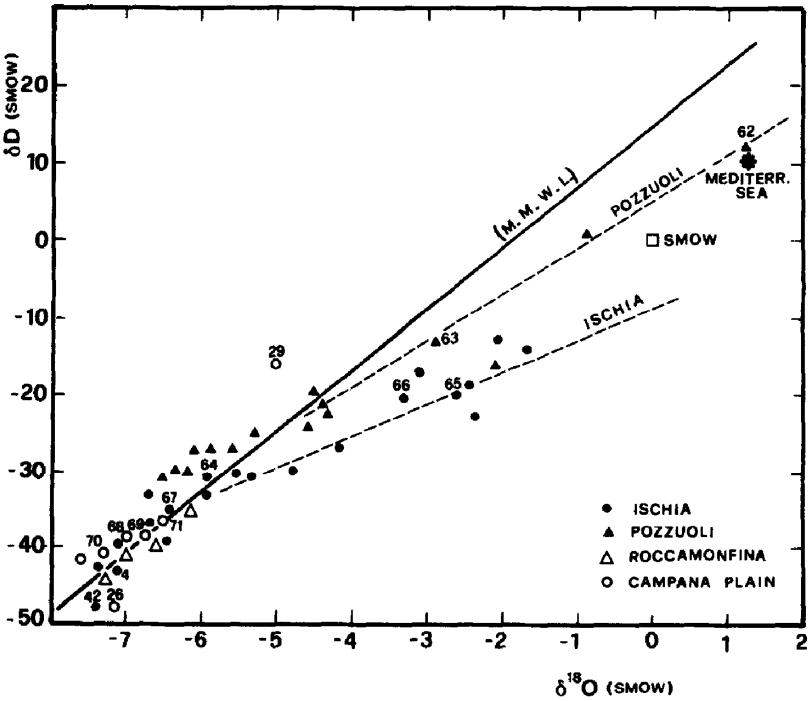

Fig. 4. δD plotted vs. $\delta^{18}O$ (‰ vs. SMOW) for water samples from Campania. Mediterranean water line (MMWL) shown for reference (Gat and Carmi, 1970). Dashed lines were regressed for the data of Pozzuoli and Ischia.

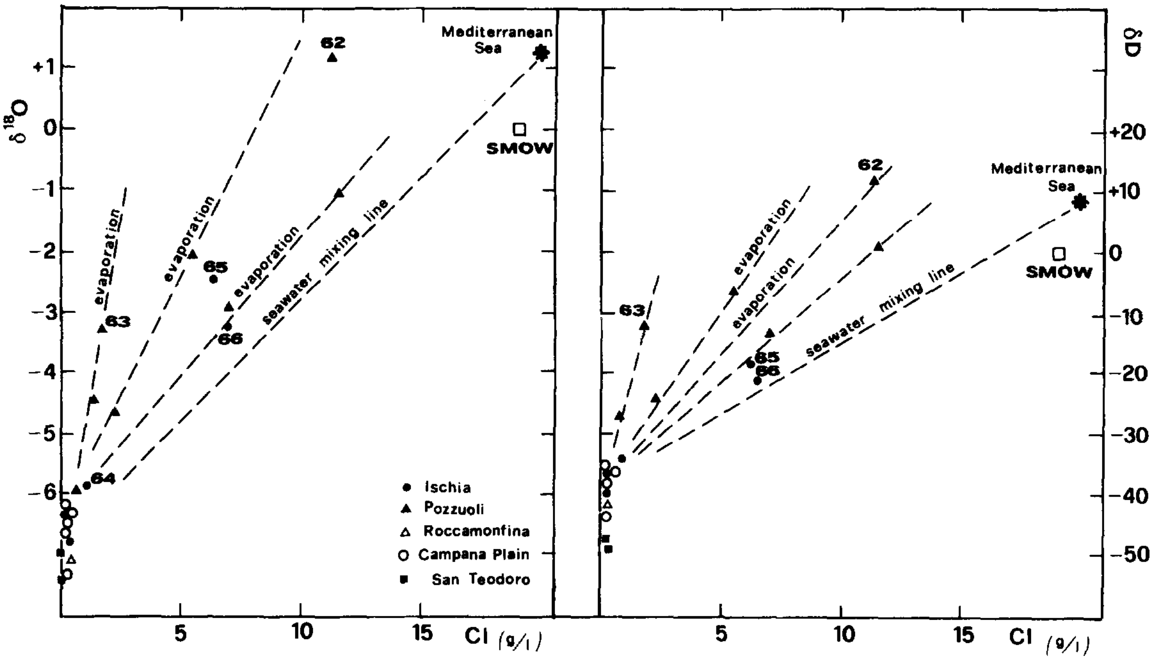

Fig. 5. Cl–$\delta^{18}O$ and Cl–δD diagrams for some of the samples investigated. The Pozzuoli (62–63) and Ischia (64–66) samples are aligned along evaporation lines. Mediterranean Sea values are from Shinohara and Matsuo (1986).

6. Gas compositions

Of the three Pozzuoli area gas samples from the literature, one comes from a 160°C fumarole ("Bocca Grande") at "Solfatara" volcano (Bolognesi et al., 1986), one is from a boiling pool ("Pisciarelli") outside the Solfatara (Martini et al., 1984) and the third is from the bay off Pozzuoli (Pece et al., 1986). In Table 2 these samples are compared with the new gas analyses from Roccamonfina volcano (3, 5, 10, 12 and

Table 2
Chemical composition of gas samples (in vol.%) from Campania

Sample No.	Name	CO_2	H_2S	H_2	CH_4	C_2H_6	C_3H_9	N_2	$O_2 + Ar$
3	Acqua Inferno	99.14	0.42	<0.001	0.075	0.002	<0.001	0.751	0.004
5	Codecchia	98.09	0.24	<0.001	0.043	0.001	<0.001	1.599	0.029
10	Mondragone 3	98.11	1.685	<0.001	0.006	0.001	<0.001	0.198	0.005
12	Valogno	93.41	<0.001	<0.001	<0.001	<0.001	<0.001	5.506	1.089
29	Mefite	97.4	0.324	<0.001	0.248	0.003	0.001	2.02	0.008
33	Capaccio 2	5.39	<0.001	<0.001	<0.001	<0.001	<0.001	87.97	6.64
34	Capaccio 3	3.07	<0.001	<0.001	<0.001	<0.001	<0.001	93.34	3.58
42	Contursi 2	79.39	<0.001	<0.001	1.15	0.007	<0.001	20.18	0.08
50	Bolle Malvizze	0.87	1.48	<0.001	92.68	0.43	<0.001	3.83	0.69
61	Garigliano	96.81	<0.001	<0.001	0.042	0.001	<0.001	3.09	0.05
	Bocca Grande (1)	98.2	0.99	0.22	0.034	<0.001	nd	0.32	nd
	Pisciarelli (2)	97.19	0.83	0.12	0.001	nd	nd	1.32	0.081
	Pozzuoli sea (3)	98.6	0.1	0.005	0.161	nd	nd	0.68	0.04

The numbers refer to the associated water sample in Table 1.
nd = not determined.
(1) = Bolognesi et al. (1986); (2) = Martini et al. (1984); (3) = Pece et al. (1986).

61), Paestum (33 and 34), Contursi (42), Mefite (29) near S. Angelo dei Lombardi and Bolle Malvizze (50). The latter turned out to be a CH_4 manifestation ($CH_4 > 92\%$) clearly derived from some small oil fields embedded in the synorogenic Tertiary formations, which evidently contain layers rich in organic material (Ippolito et al., 1973).

The Paestum samples (33–34) show compositions strongly influenced by atmospheric components ($N_2 > 85\%$), probably due to the shallowness of the hydrological circuits in association with highly aerated aquifers (Cestari, 1969). Samples from Suio (3, 5, 61), Mondragone (10), the foot of Roccamonfina volcano (12) and Mefite (29) in Irpinia, are CO_2-rich gas samples associated with minor H_2S and CH_4. This type of manifestation is commonly found in the west coastal sector of central-northern Italy associated with both thermal and cold springs (Panichi and Tongiorgi, 1976). Their origin, at least in the northern Apennines, is related to metamorphism of carbonate layers embedded in the Paleozoic crystalline metamorphic basement beneath the Mesozoic carbonate series (Duchi and Minissale, 1994).

The Pozzuoli samples, particularly from Solfatara volcano (''Bocca Grande''), are associated with steam and are regarded as derived from a 236°C shallow dry-steam geothermal reservoir (Cioni et al., 1984) that contains H_2, which is an indicator of high temperature at depth. All the other CO_2-rich samples (3, 5, 10, 12, 29, 42 and 61) have no detectable H_2 (about 0.001%). These low H_2 concentrations suggest cool equilibration temperatures for the gas phase at shallow depth.

7. Relation between deep and shallow fluids

Calculation of calcite saturation indices according to the WATEQ 4F program (Ball and Nordstrom, 1991) suggests that all the thermal springs in the region, whether they are from the active volcanic areas of Ischia and Pozzuoli or from non-volcanic areas, are saturated in $CaCO_3$ or are near the saturation limit. This phenomenon of calcite saturation in thermal springs, already reported in other regions of central Italy (i.e., Duchi et al., 1992), is mainly due to the ascent from depth of CO_2, which is dissolved in both the aquifer waters in the Mesozoic carbonate formations and in the more superficial aquifers reached by the system of active fractures. Once the solutions reach the surface they tend to release CO_2, thus favouring $CaCO_3$ precipitation and/or the formation of CO_2-rich springs. All this is predominantly caused by the decrease of hydraulic heads before emergence.

Hydrogeochemically, many thermal springs around Pozzuoli, Ischia and Roccamonfina (Mondragone) show Na-Cl-rich compositions, which might be due to the ascent of deep brines of magmatic origin that get mixed with less saline waters of meteoric origin. This type of mixing between deep brines and shallow waters has already been ruled out isotopically for the thermal waters of Ischia and Campi Flegrei; although influenced by shallow evaporation, thermal waters seem to be derived from the mixing of local meteoric waters and water of marine origin (Fig. 4).

There also seem to be geological reasons to assume that the Na-Cl component of these thermal waters is of ''superficial'' origin. In fact, the circulation model of Mesozoic carbonate aquifers suggests the presence of deep $Ca\text{-}HCO_3$ or $Ca\text{-}HCO_3\text{-}SO_4$-rich waters, like all the springs emerging at the eastern border of the Campana plain, which circulate in the carbonate mountains of the Campanian Apennine. The same is true for Suio thermal waters (1, 5, 6) despite the nearby Roccamonfina volcano. It can therefore be assumed that the Na-Cl component for the thermal systems around the volcanic areas of Ischia, Pozzuoli and Roccamonfina, and for the circuits of Bolle Malvizze, Mondragone, Contursi and Paestum, is derived from fossil waters trapped, either in the synorogenic Miocene sediments or in the Plio-Quaternary sediments and volcanics that are ubiquitous at the borders of carbonate outcrops in the area. The enrichment of Na with respect to Cl ions above the seawater ratio (Fig. 3) for most of samples investigated is probably caused by the interaction of rising CO_2 with clay minerals, which tend to exchange Na ions for Ca ions (Drever, 1982). As described in the next paragraph the presence of shallow saline waters strongly affects the interpretation of samples from a geothermometric point of view.

8. Geothermometry

The Mesozoic carbonate formations have been regarded as the main potential reservoir in central-southern Italy. Neither the Campi Flegrei drillings (De

Table 3
Temperature (in °C) calculated with the main liquid phase geothermometers

Sample No.:	6	10	26	42	51	62	63	64	65	66
emergence temp.	58	52	27	40	29	71	51	57	65	99
Na-K (1)	355	195	239	235	−43	11	135	193	84	100
Na-K (2)	375	203	250	245	−44	11	140	201	86	102
Na-K (3)	339	223	257	254	7	61	174	222	130	143
Na-K (4)	343	238	269	266	29	83	192	237	150	163
Na-K (5)	351	203	245	240	−31	24	146	201	96	111
Na-K-Ca[a] (6)	227	180	163	198	56	99	199	211	155	173
Na-K-Ca[b] (6)	115	117	40	128						
Ca-K (2)	146	137	81	148	108	136	245	209	185	217
Ca-Na (2)	57	97	11	96	498	343	368	215	306	366
Mg-Li (7)	61	33	6	123	47	145	76	54	74	112
K-Mg (4)	86	84	43	89	51	90	115	114	100	128
Na-Li (8)	390	148	191	770	42	269	168	144	150	202
Na-Li (9)	218	99	124	344	31	164	111	97	100	130
Na-K-Ca-Mg[a] (10)	50	63		53		91	21	48	22	76
Na-K-Ca-Mg[b] (10)	47	64		52		91	46	52	25	102
Quartz nsl (11)	112	91	58	65	33	169	157	102	131	164
Quartz msl (11)	111	93	64	70	42	159	149	102	127	155
Chalcedony (12)	83	60	26	33	1	146	132	104	104	140
α-Cristobalite (13)	61	41	9	16	−13	119	106	80	80	114
Opale (13)	14	−9	−34	−28	−55	68	57	32	32	64
Amorph. silica (13)	−5	−23	−50	−44	−69	46	34	11	11	41

nsl = no steam loss; msl = maximum steam loss.
(1) = Truesdell (1975); (2) = Tonani (1980); (3) = Fournier (1979); (4) = Giggenbach et al. (1983); (5) = Arnorsson (1983); (6) = Fournier and Truesdell (1973); (7) = Kharaka and Mariner (1989); (8) = Fouillac and Michard (1981); (9) = Kharaka et al. (1982); (10) = Fournier and Potter (1979); (11) = Fournier and Rowe (1966); (12) = Fournier (1973); (13) = Fournier (1991).
[a] $\beta = 1/3$.
[b] $\beta = 4/3$.

Vivo et al., 1989) nor the Roccamonfina well (Watts, 1987) intersected carbonate rocks, although at Campi Flegrei fluids in volcanic rocks were found with temperatures over 420°C. This means that the reservoir for high-enthalpy fluids is larger than the carbonate reservoir.

Table 3 reports temperatures calculated from chemical geothermometers described by Fournier (1991). Some of the geothermometers in Table 3 re-equilibrate rapidly as temperature decreases [all SiO_2 geothermometers (Fournier and Rowe, 1966) and all those based on Mg concentration (Ellis, 1971; Giggenbach, 1988)]. Others are not dependent on cooling phenomena and shallow re-equilibration, such as those based on the Na/K ratio and, more generally, all geothermometers based on the alkaline elements. Geothermometers dependent on Ca concentration are strongly affected by CO_2 partial pressure (Paces, 1975). To avoid this problem, Fournier and Potter (1979) introduced a factor (R), based on Mg concentration, into the Na-K-Ca geothermometer, whereas Tonani (1980) introduced a Ca/Na geothermometer to check the reliability of the Na/K geothermometer.

All the above drawbacks limit the reliability of most geothermometers. Consequently, the different values calculated for each spring are not consistent. For Pozzuoli (62–63) and Ischia (64–66) samples, the calculated temperatures are not only variable for a given sample, but also between samples from the same area. Pozzuoli sample 62 and Ischia samples 65 and 66 yield temperatures from the different Na/K geothermometers that are lower than for sample 63 and 64, respectively, but also lower than their emergence temperatures. On the contrary, at Roccamonfina, Na/K temperatures in samples 6 and 10 are much higher than the temperature measured in the deep well. These inconsistent values, recorded in areas where waters circulate prevalently in volcanic rocks, should discourage

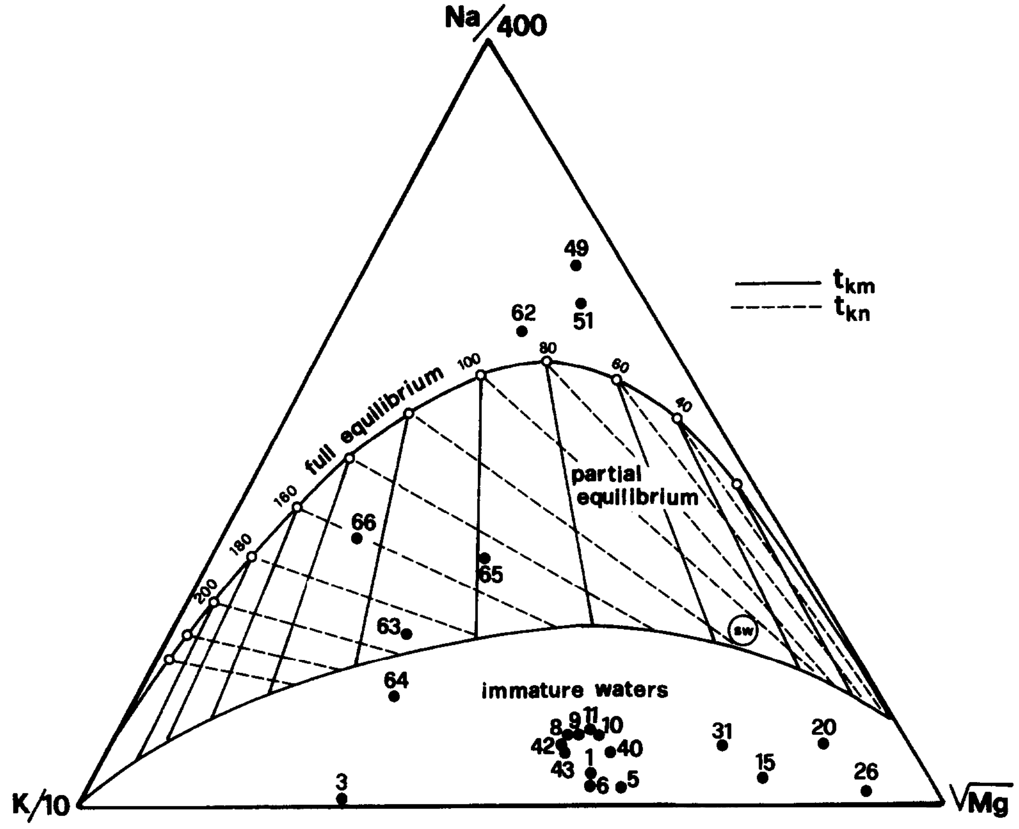

Fig. 6. Graphical evaluation of water–rock equilibration temperatures in thermal springs (Giggenbach, 1988; Giggenbach and Corrales, 1992) using relative Na, K and Mg concentration (in mg/kg).

the use of these geothermometers in areas where thermal waters circulate in sedimentary formations (Minissale and Duchi, 1988), and also in K-rich volcanics similar to those in the study area, where K ions tend to be easily soluble even at low temperature (Dall'Aglio et al., 1994). The different quartz and silica geothermometers give calculated temperatures lower than those measured in Pozzuoli and Ischia and higher than the one measured at Roccamonfina.

Recently, Giggenbach (1986, 1988) developed a technique to correlate fast (K^2/Mg) and slow (Na/K) re-equilibrating geothermometers. It allows evaluation of both the degree of water–rock equilibration at given temperatures with crustal material of average composition (Taylor, 1964) indicated by the Na/K ratio, as well as the degree of shallow re-equilibration given by the K^2/Mg ratio. The graphical resolution of this combined geothermometer for the samples of this study is reported in the $Na/400–Mg^{1/2}–K/10$ (Giggenbach and Corrales, 1992) diagram of Fig. 6. This figure suggests that the samples from Suio and Mondragone (1, 5, 6, 10 and 11) are immature waters that resulted from dissolution of rocks and did not reach equilibrium at high temperature. For Pozzuoli (62–63) and Ischia (64–66), Fig. 6 suggests that these samples were only partially equilibrated with deep high-enthalpy fluids, very likely because of mixing with superficial waters. Thermal samples from Contursi (40, 42, 43) and San Teodoro (26) also lie in the field of immature waters and do not seem to be derived from high-temperature systems, but rather from leakage of rocks in areas with normal thermal gradients. The thermal springs from Bolle Malvizze (49–51) have equilibration temperatures on the order of 60–80°C, probably because the concentration of Mg in these waters is equilibrated with the aquifer itself owing to the long residence time underground before emergence. Geothermometers based on Na/Li (Fouillac and Michard, 1981) and

Mg/Li (Kharaka and Mariner, 1989) ratios are both unreliable, particularly the latter, which gives very low temperatures for Pozzuoli and Ischia.

9. Discussion

The isotopic compositions of thermal waters from Pozzuoli and Ischia suggest that they are not of deep origin and, particularly the deuterium values, are very different from those recently reported by Giggenbach (1992) for geothermal and volcanic systems along convergent plate boundaries. On the other hand, their positions on Fig. 6 suggest the presence of a deep high-temperature (> 200°C) fluid component. Geologically, however, these waters are very likely the result of mixing between low-salinity, deep, hot waters and more superficial marine waters. Paradoxically, the contrary hypothesis is also viable: deep hot marine waters heated at depth by the high thermal gradient in the area, mixed with more superficial low-salinity waters of meteoric origin. Log $a(Na^+/H^+)$–log $a(K^+/H^+)$ diagrams at 150, 200 and 250°C for the system Na_2O–K_2O–Al_2O_3–SiO_2–H_2O are shown in Fig. 7 and used to decide which model is more probable. The activities of Na^+, K^+ and H^+ were determined through WATEQ 4F. This program does not supply different activity values at different temperatures, so that although the stability fields of minerals change with temperature on Fig. 7, the positions of individual samples at 150, 200 and 250°C remain the same. In spite of this limitation (acceptable if we consider the many uncertainties related to data obtained from spring samples), the diagrams show that the samples from Pozzuoli (62–63), Ischia (64–66) and Mondragone (8–11) lie near the border between the albite and K-feldspar fields at 150°C. They would therefore seem to be in approximate equilibrium with these phases and suitable for geothermometric evaluation with the many Na/K geothermometers reported in Table 3. As discussed earlier, however, the results from the Na/K geothermometers are unsatisfactory. The seawater point (SW) is marked on the diagrams of Fig. 7 and thermal samples of Pozzuoli, Ischia and Mondragone are located on a "mixing" line between seawater and superficial samples (dots) equilibrated with low-temperature minerals in the kaolinite-muscovite-paragonite fields. As a consequence, the different Na/K and Na-K-Ca geothermometers and those that use Li^+ (an element that is highly enriched in connate waters) are not reliable when used

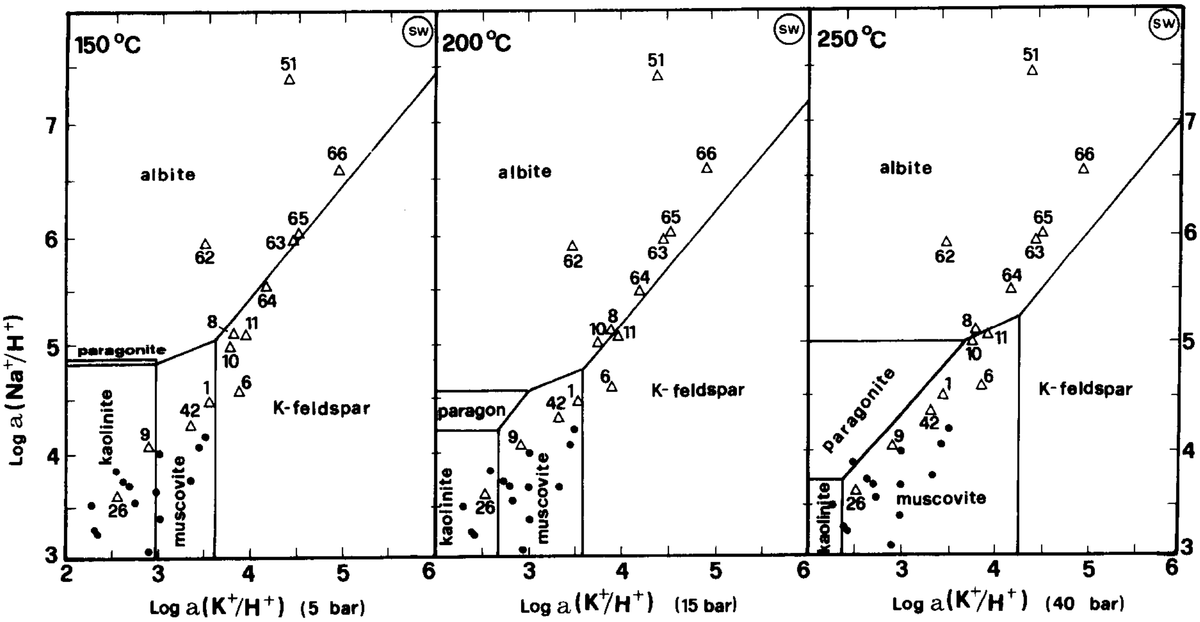

Fig. 7. Activity diagrams at 150, 200 and 250°C in the system Na_2O–K_2O–Al_2O_3–SiO_2–H_2O. ● represent cold samples; △ represent hot samples; *SW* = seawater.

on thermal springs whose Na/K ratios are not derived from the equilibration at depth of the reaction:

$$\text{albite} + K^+ = K - \text{feldspar} + Na^+$$

on which the different Na/K geothermometers are empirically based. Therefore, the presence of a strong marine (connate) component prevents the use of these cations for geothermometric purposes. This is a common situation for the thermal springs of central-northern Italy (i.e., Duchi et al., 1987) and it has often been reported for thermal springs in different geothermal areas of the world, especially where spring waters have interacted with organic-rich sediments (Fournier, 1991). One might suspect that, on a global scale, magmatic Cl-rich solutions formed near plate boundaries could often undergo the same non-equilibration effect at depth for many other reasons. Possibilities include deep equilibration with alkali-feldspar-free lithologies, short-term residence of the waters in hot deep aquifers, or boiling of deep brines (Truesdell et al., 1984). All of these mechanisms seem likely because magmas produced along convergent plate boundaries, such as western Italy, recycle most of their water from the oceanic crust and their sedimentary cover, which is dominantly seawater (Peacock, 1990).

Whether the mixing at Pozzuoli and Ischia occurs between deep, hot, saline waters (marine or connate) and shallow low-salinity fresh cold waters or vice versa can also be ascertained chemically. Although they have high Na and Cl ion concentrations, the Pozzuoli, Ischia and Mondragone samples show low concentrations of SO_4 and Mg ions, two of the main components of seawater. This implies that the hot endmember is "old" Mg-re-equilibrated connate water, whereas the cold endmember is low-salinity water very likely of meteoric origin. This interpretation is supported by the isotopic signatures of cold and hot samples in the area.

10. Conclusions

Although the pattern of temperatures at depth from Pozzuoli, Ischia and Roccamonfina is well known, the thermal springs emerging in these areas do not seem to originate from high-enthalpy systems. At Pozzuoli and Ischia they have a rather superficial origin. In contrast, the thermal waters near Roccamonfina originate at a greater depth (over 1000 m deep), as suggested by the low bottom-hole temperature measured in the 880-m-deep well drilled by UNOCAL.

From a regional point of view the bicarbonate springs of Suio and Mondragone circulate mostly in the Mesozoic carbonate formations, whereas those at Ischia and Pozzuoli circulate within superficial Quaternary volcanic units containing connate waters.

Like the thermal waters around Roccamonfina volcano, those emerging in the non-volcanic areas of San Teodoro (Irpinia) and Contursi (Sele valley) in the Apennine range circulate deeply in the carbonate formations. However, these waters do not seem to arise from high-temperature systems but are rather the result of fast ascent along the main seismically active faults bordering the carbonate nuclei. This occurs in areas where the high hydraulic heads allow the artesian ascent of these deeply seated thermal waters.

The weakly thermal waters of Bolle Malvizze do not seem to come from the Mesozoic carbonate formations but rather have a shallow circuit in the Tertiary clastic synorogenic formations. Their high saline contents likely stem from brines associated with hydrocarbons, as supported by the high CH_4 concentrations in the gas phase associated with the spring.

Like the waters, the CO_2-rich gas phase associated with the thermal springs of Suio, Mondragone and Mefite is likely to have a deep origin. In particular, the large gas manifestation at Mefite, located near the epicentral zone of the large ($M_s = 6.9$) earthquake that occurred in Irpinia in November 1980, is likely related to one of the important deep regional active faults whose movement caused the seismic event. As suggested by Chelini and Marini (1994) following studies by Barnes et al. (1978, 1988), CO_2 may even originate in the mantle.

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