

Geochemical and hydrogeological characterization of thermal springs in Western Sicily, Italy

R. Favara^a, F. Grassa^b, S. Inguaggiato^{a,*}, F. D'Amore^c

^a *Istituto di Geochimica dei Fluidi C.N.R. Via Ugo La Malfa, 153, Palermo, Italy*

^b *Dipartimento C.F.T.A., Università di Palermo, Via Archirafi, 36, Palermo, Italy*

^c *Istituto Internazionale Ricerche Geotermiche C.N.R., P.zza Solferino, 2, Pisa, Italy*

Accepted 10 April 1998

Abstract

Thermal and cold waters from Castellammare–Alcamo (Western Sicily-Italy) were collected between May 1994 and May 1995 and studied for their chemical and isotopic composition. During the same period, mean monthly samples of meteoric water were also collected and measured for their isotopic composition. The main purpose of this study was the characterization of the aquifers and, if possible, of their recharge areas. According to the results obtained, the aquifers were divided into three main groups: (a) selenitic waters, (b) cold carbonatic waters, and (c) deep thermal waters resulting from the mixing of the other two types. Besides a mixing process between carbonatic and selenitic waters, contamination processes of thermal waters by seawater take place during their ascent. The water temperature of the aquifer feeding the thermal springs was estimated by means of various geothermometers to range between 60°C and 97°C. Isotope data on rainwater samples show a wide seasonal variation of both $\delta^{18}\text{O}$ and δD values. The fairly constant values of thermal waters through time and the lack of an apparent correlation with the isotopic values of rainwater suggest the existence of a deep circuit determining an almost complete homogenisation of the seasonal variations of the isotopic values. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: selenitic waters; cold carbonatic waters; aquifers

1. Introduction

Hydrothermal systems are quite common throughout Sicily and the islands lying off it. They can be found on active volcanic islands such as the Aeolian Islands and Pantelleria as well as in the north-eastern (Alì, Acireale, Castoreale), central (Termini Imerese,

Trabia, Cefalà Diana, Chiusa Sclafani, S.G. Gemini) and western sections of the main island.

The Sciacca–Montevago thermal springs on the southern coast of Sicily and the Castellammare–Alcamo springs on the northern coast are among the most important systems in Western Sicily. The first studies on Sicilian thermal waters date back to the first half of the last century. More recently Gino and Sommaruga (1953) discussed the location of the springs and their classification in terms of temperature. Later on, Dall'Aglio (1966, Dall'Aglio and Tedesco (1968), Carapezza et al. (1977), Dongarrà

* Corresponding author. Fax: +39-91-6809449; e-mail: inguagg@igf.pa.cnr.it

and Hauser (1982), Alaimo et al. (1978, 1990) and Fancelli et al. (1991), studied these waters from the geochemical point of view.

The thermal springs in the Castellammare–Alcamo area are of particular interest for the potential use of their low enthalpy fluids because of their temperature ($\sim 50^{\circ}\text{C}$) and their flow (~ 200 l/s).

The aim of this study is the chemical and isotopic characterization of these thermal springs, locating their recharge areas and tracing the hydrogeological circuits as far as possible.

Between May 1994 and May 1995 three thermal springs were sampled monthly. Besides the thermal springs, 34 water samples were also collected in

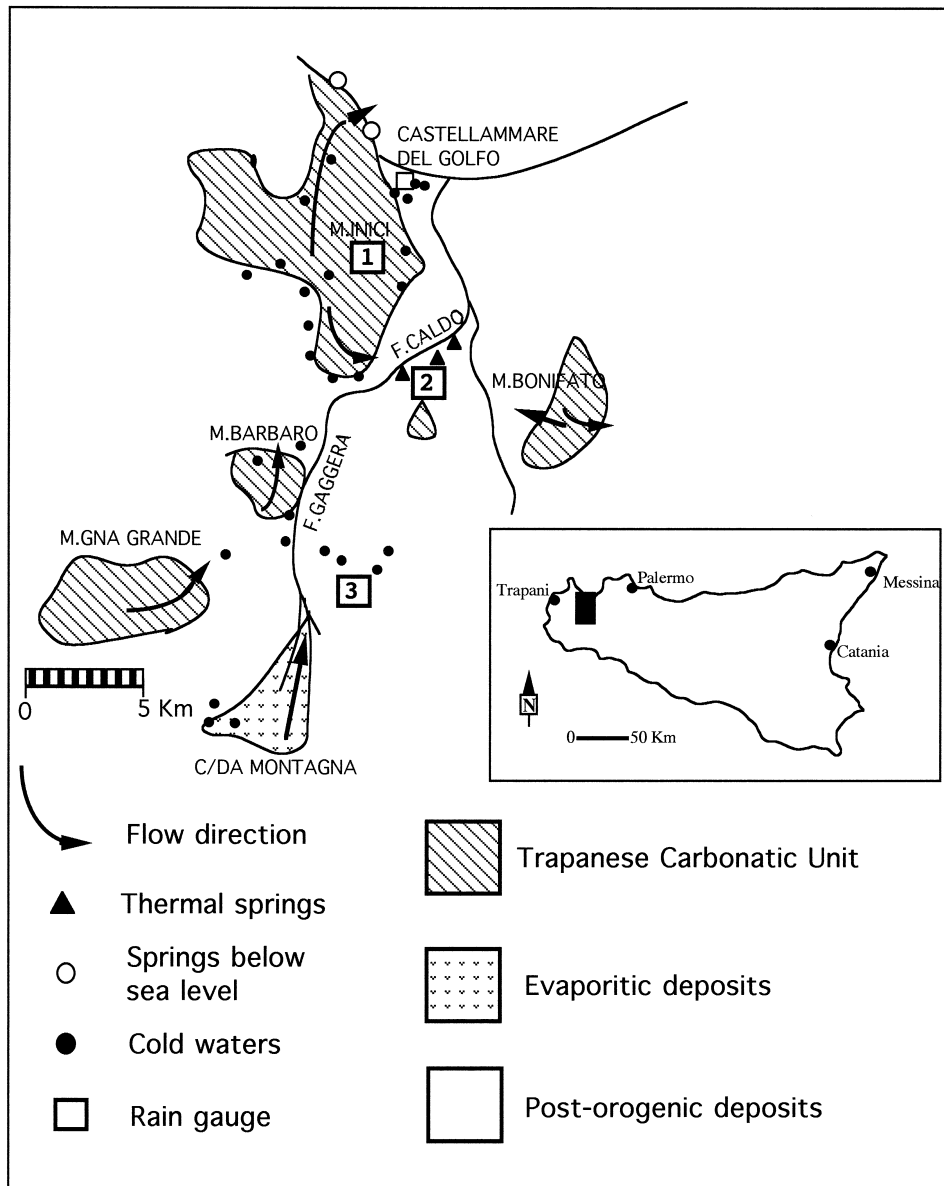


Fig. 1. Location map of rain gauges, cold and thermal water samples.

October 1994 from a selection of cold springs in the same basin. Mean monthly rainwater samples were also collected from three rain gauges during 1994–1995. These gauges were located on Mt. Inici at different elevations: 1060 m a.s.l. (no. 1), 60 m a.s.l. (no. 2) and 375 m a.s.l. in the town of Calatafimi, (no. 3). The location of the sampling points and of the rain gauges is shown in Fig. 1.

2. Geological and hydrological setting

Sicily can be considered as the southernmost section of the alpedic orogene in the Mediterranean Basin. It consists mainly of two sections: (1) the Hyblaean upland with the characteristics of a foreland and crustal similarities with Africa; (2) the chain formed by the south-verging, piling-up of layers, located in the northern part of the island and in the zone going from the Palermo mountains to the Sciacca mountains (Catalano and D'Argenio, 1982).

The Caltanissetta and Castelvetro basins (Neogene–Pleistocene in age) are located south of this chain. They have the characteristics of a foregraben and are filled with terrigenous, evaporitic and carbonatic sediments reaching a thickness of more than 1500 m.

The following domains can be distinguished in the area under study on the basis of stratigraphic, structural and hydrogeological data:

(1) The Trapanese carbonatic domain, formed by platform limestones, pelagic and marly limestones ranging in age from middle-upper Trias to Eocene. The carbonatic outcrops cover about 250 km², both inside the drainage basin and outside the surficial watershed. The geological complex of this domain can reach a thickness of about 3000 m, as proven by some wells drilled for hydrocarbon exploration. The sedimentary sequence is deeply fractured and karstified so that its medium-high porosity, close to about 30%, favours the presence of a massive aquifer. According to a map of the hanging wall formation (Catalano et al., 1983), and a geologic section from Inici to Sciacca (Catalano et al., 1982), the buried section of the Trapanese domain spreads over an area considerably greater than the outcropping. A huge deep aquifer may therefore fill up the whole Trapanese domain. The outcropping carbonatic rocks

belonging to the same unit are the recharge area, and the vertical continuity of the Trapanese domain allows the physical continuity of the water circulation.

(2) The terrigenous deposits domain include: (a) the flysch deposits of upper Oligocene-lower Miocene belonging to the Termini Imerese formation (Catalano and D'Argenio, 1982). They are considered to be an impermeable formation except for the limited areas where highly fractured quartzarenites crop out; (b) the late orogenic deposits from the Cozzo di Terravecchia Formation (conglomerates, sands, clays of fluviodeltaic facies) Tortonian to lower Messinian in age. The hydrogeology of these deposits is complex: it is possible, in fact, to distinguish an upper impermeable section (represented by clays and clayey marls) and a lower permeable one (highly porous sands and conglomerates). According to Catalano et al. (1983), the average effective permeation is 10% of the precipitation. The contribution of surface waters flowing on impermeable ground must be taken into consideration in the calculation of total permeation. These waters, due to the morphologic characteristics of the ground, eventually feed the underlying aquifer.

(3) The evaporitic deposits domain formed by organogenic calcarenites (Baucina formation), gypsum of the 2nd cycle and limestones of Messinian age. The marked permeability of these deposits is related to tectonic disturbances and karst processes.

3. Analytical methods

Water temperature, pH and HCO₃ contents were measured directly in the field; HCO₃ was determined by titration with HCl 0.1 N. Water samples were filtered by means of cellulose filters (0.45 μm) and the major and minor constituents determined by Dionex 2000i ion chromatograph (reproducibility within ±2%). A Dionex CS-12 column was used for determining the cations (Li, Na, K, Mg, Ca), whereas a Dionex AS4A-SC column was used for the anions (F, Cl, NO₃, SO₄) (Sortino et al., 1991). D/H water measurements were carried out using the Kendall and Coplen (1985) technique (reaction with zinc at 450°C), while ¹⁸O/¹⁶O measurements were carried out by the CO₂–water equilibration technique (Epstein and Mayeda, 1953). Mass-spectrometer analy-

ses were carried with a Finnigan Mat 250 and a Finnigan Delta S mass spectrometer and the results are reported in δ per mil units vs. V-SMOW standard. The standard deviations of the measurements are about $\pm 1\%$ and $\pm 0.2\%$ respectively for D/H and $^{18}\text{O}/^{16}\text{O}$ measurements (1σ).

4. Analytical results and classification of waters

The analytical results are reported in Tables 1 and 2 for thermal waters and non-thermal waters respectively. Using the Langelier-Ludwig diagram (Langelier and Ludwig, 1942), which considers the rela-

Table 1
Chemical and isotopic composition of thermal springs

Sample	T	pH	Cond	TDS	Na	K	Ca	Mg	Cl	HCO ₃	SO ₄	Li	Br*	F*	SiO ₂	$\delta^{18}\text{O}$	δD
<i>Gorga 1</i>																	
May 94	47.6	6.70	2300	1511	192	11	190	62	331	241	476	n.d.	1278	3171	28.5	-7.6	-41
Jun. 94	47.6	6.60	1970	1430	192	10	181	62	288	244	448	69	1278	3646	28.3	-7.5	n.a.
Jul. 94	48.4	6.68	2240	1457	213	12	189	54	315	201	463	n.d.	1358	5906	29.0	-7.5	-41
Aug. 94	48.4	6.31	2230	1413	190	11	171	59	292	229	445	224	1358	2849	29.5	-7.5	n.a.
Sep. 94	48.2	6.94	1840	1479	174	22	227	56	300	238	456	n.d.	1598	3798	28.5	-7.6	n.a.
Oct. 94	48.4	6.59	2170	1420	197	8	174	56	307	229	446	n.d.	1438	2849	28.5	-7.4	n.a.
Nov. 94	48.2	6.61	2170	1373	181	8	173	50	306	220	447	n.d.	1278	2962	29.0	-7.1	-39
Dec. 94	48.2	6.68	2190	1435	198	11	175	59	304	235	444	n.d.	1358	2469	29.0	-7.2	-40
Jan. 95	48.3	6.59	2080	1494	189	12	189	62	327	241	461	n.d.	1358	2867	29.0	-6.8	-39
Feb. 95	48.3	6.52	2130	1426	185	11	186	58	297	238	447	69	1358	2981	28.5	-7.5	-41
Mar. 95	48.2	6.90	1990	1391	178	10	178	54	310	232	428	56	1438	3000	29.0	-7.7	n.a.
Apr. 95	48.2	6.80	2110	1412	186	8	227	58	381	235	453	n.d.	1039	3779	29.0	-7.4	n.a.
<i>Gorga 2</i>																	
May 94	49.0	6.81	3400	2039	349	18	222	75	624	250	502	n.d.	2477	4539	29.0	-7.6	n.a.
Jun. 94	49.2	6.62	3350	2164	376	17	256	87	674	204	541	91	2876	3817	29.5	-7.4	-39
Jul. 94	50.7	6.70	3320	1964	356	15	211	78	620	168	511	n.d.	2477	2754	29.0	-7.4	-40
Aug. 94	49.6	6.24	3240	2078	382	27	216	65	664	195	514	210	2397	5127	28.5	-7.4	-39
Sep. 94	49.5	6.72	2720	2019	353	23	211	73	608	244	500	n.d.	2397	3798	29.0	-7.6	n.a.
Oct. 94	49.5	6.61	3090	2054	367	13	204	73	643	244	504	n.d.	2397	3038	29.0	-7.4	-40
Nov. 94	49.5	6.62	3060	2041	341	14	207	69	650	235	516	154	2157	2962	29.0	-7.2	-38
Dec. 94	49.4	6.64	3030	2171	357	13	220	74	697	247	554	140	2477	3836	29.5	-6.8	n.a.
Jan. 95	49.5	6.20	2970	2085	337	18	219	77	641	259	528	n.d.	2717	3171	29.5	-7.3	-39
Feb. 95	49.5	6.80	2850	2034	343	17	218	73	613	250	515	70	2477	3057	28.5	-7.4	-40
Mar. 95	49.1	6.93	3120	1885	300	12	214	65	578	238	477	42	2717	4994	29.0	-7.6	n.a.
Apr. 95	49.5	6.70	3200	1956	342	11	258	72	652	259	518	n.d.	2077	3798	29.0	-7.4	n.a.
<i>T. Segestane</i>																	
May 94	43.4	6.70	2550	1695	233	14	209	72	424	238	498	n.d.	1598	3437	24.7	-7.5	n.a.
Jun. 94	43.8	6.80	2590	1658	251	11	205	72	400	241	459	n.d.	1598	3551	24.3	-7.4	n.a.
Jul. 94	43.8	6.83	2550	1576	261	15	172	58	449	153	511	56	1598	399	24.5	-7.2	-41
Aug. 94	44.3	6.40	2570	1502	231	9	164	59	376	214	464	n.d.	1758	3057	24.5	-7.3	-38
Sep. 94	44.0	6.90	n.d.	1664	220	8	238	62	409	244	473	n.d.	1598	5127	25.0	-7.6	n.a.
Oct. 94	44.0	6.60	2460	1598	241	10	177	61	401	235	468	n.d.	1598	3228	25.2	-7.5	-39
Nov. 94	43.7	6.72	2700	1554	234	10	179	61	401	192	469	42	1598	3076	25.0	-6.7	-38
Jan. 95	43.1	6.59	2450	1683	232	13	195	68	420	256	488	n.d.	1998	7463	25.5	-7.3	n.a.
Feb. 95	43.4	6.70	2560	1618	234	14	191	64	385	250	478	49	1678	2792	25.0	-7.3	-41
Mar. 95	43.9	6.88	2480	1554	217	9	202	59	393	226	446	56	1678	2811	24.5	-7.6	n.a.
Apr. 95	44.0	6.90	2590	1655	234	8	232	65	397	238	584	n.d.	1678	2905	25.0	-7.4	n.a.

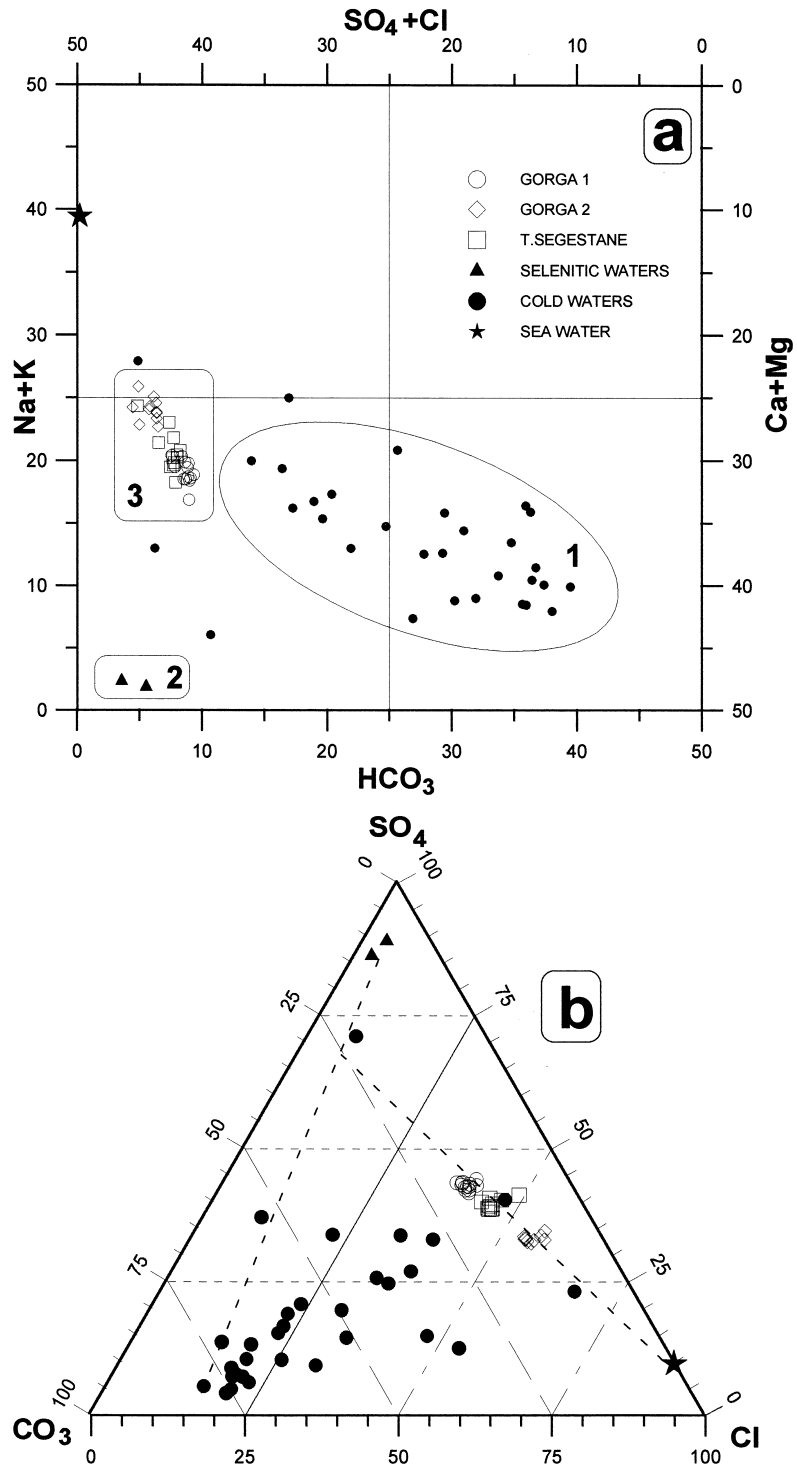
Values are expressed in mg/kg except for Br and F, expressed in $\mu\text{g}/\text{kg}$. Temperature is expressed in $^{\circ}\text{C}$ (accuracy $\pm 0.1^{\circ}\text{C}$), pH in pH unit (accuracy ± 0.01 unit), conductivity in $\mu\text{S}/\text{cm}$ at 25°C . The isotopic compositions of oxygen and hydrogen are reported in δ per mil units vs. V-SMOW standard. n.a. = not analysed; n.d. = not determined.

Table 2

Chemical and isotopic composition of cold water

Sample	Location	Kind	Flow (l/s)	Date	T	pH	Cond	TDS	Na	K	Ca	Mg	Cl	HCO ₃	SO ₄	Br*	Fl*	δ ¹⁸ O	δD
Pozzo D	33SUC134049	W	20	Sep-94	29.1	7.26	1140	812	91	<1	94	44	167	206	157	799	1101	-6.8	n.a.
Maranzano	33SUC119043	W	20	Sep-94	25.4	7.18	1030	695	80	2	69	40	122	203	126	<160	1329	-6.8	n.a.
Angeli	33SUB112994	S	0.25	Oct-94	17.5	7.37	1510	521	33	2	52	34	50	240	46	240	437	-6.5	-34
Salanga	33SUC085027	S	0.1	Oct-94	21.5	7.93	723	472	23	<1	90	6	29	203	38	160	190	-5.4	n.a.
Arancio	33SUB104981	R	n.m.	Oct-94	17.7	8.15	2250	2372	35	1	556	41	43	125	1533	<160	1899	-6.5	n.a.
D'Angelo	33SUB093977	S	6	Oct-94	22.0	7.13	1146	927	66	13	131	31	104	279	211	<160	2659	-6.2	n.a.
T. Acqua 1	33SUB078940	S	0.1	Oct-94	23.2	7.39	622	275	23	<1	67	7	34	186	22	<160	323	-6.1	n.a.
T. Acqua 2	33SUB078938	S	0.1	Oct-94	23.5	7.60	562	459	34	<1	89	7	40	208	20	<160	570	-6.7	n.a.
Roccone	33SUB078948	S	0.5	Oct-94	18.6	6.71	560	461	27	<1	80	10	34	235	16	<160	570	-6.8	n.a.
Fraginesi	33SUC113114	W	15	Oct-94	19.5	8.16	1031	764	91	1	103	34	188	208	80	799	1329	-6.8	n.a.
Scopello	33SUC086160	S	0.2	Oct-94	19.7	7.87	398	318	18	<1	53	7	31	157	10	<160	380	-6.4	n.a.
Baida	33SUC072131	S	0.25	Oct-94	17.4	8.11	410	367	21	<1	77	8	37	159	13	<160	1899	-6.1	n.a.
Guigliardetta	33SUC150089	S	0.2	Oct-94	23.0	7.06	1226	972	53	<1	112	63	101	368	99	<160	950	-5.6	n.a.
Inici	33SUC104070	S	n.m.	Oct-94	22.3	8.00	324	262	13	<1	54	3	28	127	7	<160	190	-6.9	-39
Capo	33SUB094962	S	30	Oct-94	16.0	7.72	2240	2406	29	<1	592	33	29	191	1474	400	760	-6.2	-38
Di Fiume C\da Capo Di Fiume	33SUB093962	S	n.m.	Oct-94	19.1	8.04	2300	2277	216	2	357	111	607	221	701	240	760	-5.0	n.a.
Pioppo	33SUC156067	S	0.7	Oct-94	20.9	7.15	850	616	35	1	97	27	72	245	39	240	190	-6.2	-34
Rio	33SUB113978	W	2.5	Nov-94	17.2	6.65	630	645	50	2	75	36	76	245	90	<160	247	-5.8	n.a.
Enaro	33SUB121976	W	10	Nov-94	17.6	6.70	670	460	44	2	46	21	47	221	22	240	760	-6.0	n.a.
Rudisi	33SUB125979	W	8	Nov-94	17.5	6.70	682	537	48	2	71	13	51	260	27	<160	0	-6.5	n.a.
P3-P3bis	33SUB129974	W	5	Nov-94	18.4	6.60	800	602	49	2	77	25	58	279	41	240	418	-6.4	n.a.
P2-P2bis	33SUB126973	W	6	Nov-94	17.8	6.73	855	701	52	3	92	28	79	284	90	240	152	-6.1	n.a.
Zangara	33SUB122970	W	1.5	Nov-95	16.6	7.50	1430	1194	47	2	188	67	48	186	607	240	703	-6.4	n.a.
Calemici	33SUB113981	S	10	Nov-94	17.8	7.00	713	558	25	1	56	44	26	208	141	<160	1158	-6.5	n.a.
Tre Croci	33SUB121997	W	2	Nov-94	22.3	6.80	760	597	60	2	35	48	96	245	38	320	152	-6.3	n.a.
Carrara	33SUC147998	W	25	Nov-94	19.5	6.90	1295	1135	160	5	99	61	192	397	110	799	589	-6.1	n.a.
Duchessa	33SUC147109	W	70	Nov-94	20.5	7.02	1922	1394	238	12	102	68	399	348	126	1278	437	-6.2	-35
Petrolo	33SUC146111	W	60	Nov-94	19.5	6.97	1537	1229	134	27	123	51	163	221	221	400	437	-6.1	n.a.
Pinco	33SUC146107	W	20	Nov-94	21.2	6.92	1023	820	73	5	86	47	89	336	82	240	475	-6.2	n.a.
Mangiapane	33SUC153053	S	7	Nov-94	19.1	6.70	2040	1665	217	5	204	50	350	343	396	1039	209	-5.8	n.a.
Superiore	33SUC148050	S	n.m.	Mar-95	12.0	8.00	730	670	63	<1	112	12	102	225	88	<160	114	-6.2	n.a.
Forestale	33SUC137053	S	n.m.	Apr-95	12.3	7.39	432	317	11	<1	74	2	46	142	7	<160	1139	-7.1	n.a.
Gerbino	33SUC148096	W	10	Jan-95	38.2	6.62	3900	2478	495	36	219	83	953	191	444	3516	2279	-7.1	n.a.

Values are expressed in mg/kg except for Br and F, expressed in $\mu\text{g}/\text{kg}$. Temperature is expressed in $^{\circ}\text{C}$ (accuracy $\pm 0.1^{\circ}\text{C}$), pH in pH unit (accuracy ± 0.01 unit), conductivity in $\mu\text{S}/\text{cm}$ at 25°C . The isotopic compositions of oxygen and hydrogen are reported in δ per mil units vs. V-SMOW standard. n.a. = not analysed; n.m. = not measured. W = Well; S = Spring; R = River.



tive concentrations of major constituents (Fig. 2a) made a first classification of the sampled waters.

In agreement with previous studies (Carapezza et al., 1977; Alaimo et al., 1978, 1990) it is possible to distinguish three different families of groundwaters:

- (1) cold bicarbonate alkaline-earth waters, similar to these of meteoric carbonatic recharge;
- (2) waters belonging to the chlorine-sulphate alkaline-earth field, rich in sulphates (selenitic waters) and related to waters flowing through gypsum-sulphurous ground;
- (3) thermal waters belonging to the chlorine-sulphate alkaline-earth field, close to the chlorine-sulphate alkaline field.

Using the $\text{HCO}_3\text{--SO}_4\text{--Cl}$ ternary diagram of Fig. 2b three possible end-members of mixing can be identified. One is of marine origin, another one is selenitic and the third is carbonatic. All the studied thermal waters originate from the mixing of these three end-members.

Thermal spring waters show Na/Cl and Br/Cl ratios close to that representative of seawater. This supports the hypothesis that these waters are probably affected by contamination from a cold, shallower component of marine origin. Assuming that the Cl content of thermal waters is almost totally of sea origin, and taking into account the Cl content of the carbonate cold springs (Inici = 27.7 mg/kg) and of the selenitic springs (Capo di Fiume = 29.1 mg/kg), the % of seawater contamination (seawater = 21.600 mg/kg) for the three thermal springs can be evaluated close to 3% (Gorga 2), 2% (T. Segestane) and 1.5% (Gorga 1). Subtracting the contribution from seawater contamination, the average chemical composition of thermal springs yields the basic chemical composition of deep fluids. According to the homogeneity of the calculated compositions a single feeding reservoir for the three sampled thermal springs (T. Segestane, Gorga 1 e Gorga 2) can be suggested. The chemical composition of the deep-system waters, plotted in the Langelier–Ludwig diagram (Fig. 3a), lies on the line connecting selenitic and carbonatic waters, suggesting the existence of a fairly ho-

mogeneous reservoir produced by the mixing of these two water families. This mixing is confirmed by the salinity diagram in Fig. 3b reported according to section A–A' in Fig. 3a. The three waters (carbonatic, selenitic, and deep thermal) are aligned also in this case. According to this diagram the mixing percentages in the thermal reservoir may be estimated to be about 30% selenitic waters and 70% carbonatic waters.

This hypothesis agrees with the conclusions by Dongarrà and Hauser (1982) who found in thermal waters sulphur isotope values consistent with an origin from Messinian evaporites.

The presence of a deep aquifer in which efficient homogenisation processes take place is also supported by the very narrow range of concentration of major constituents exhibited by the measured samples during the whole hydrological year.

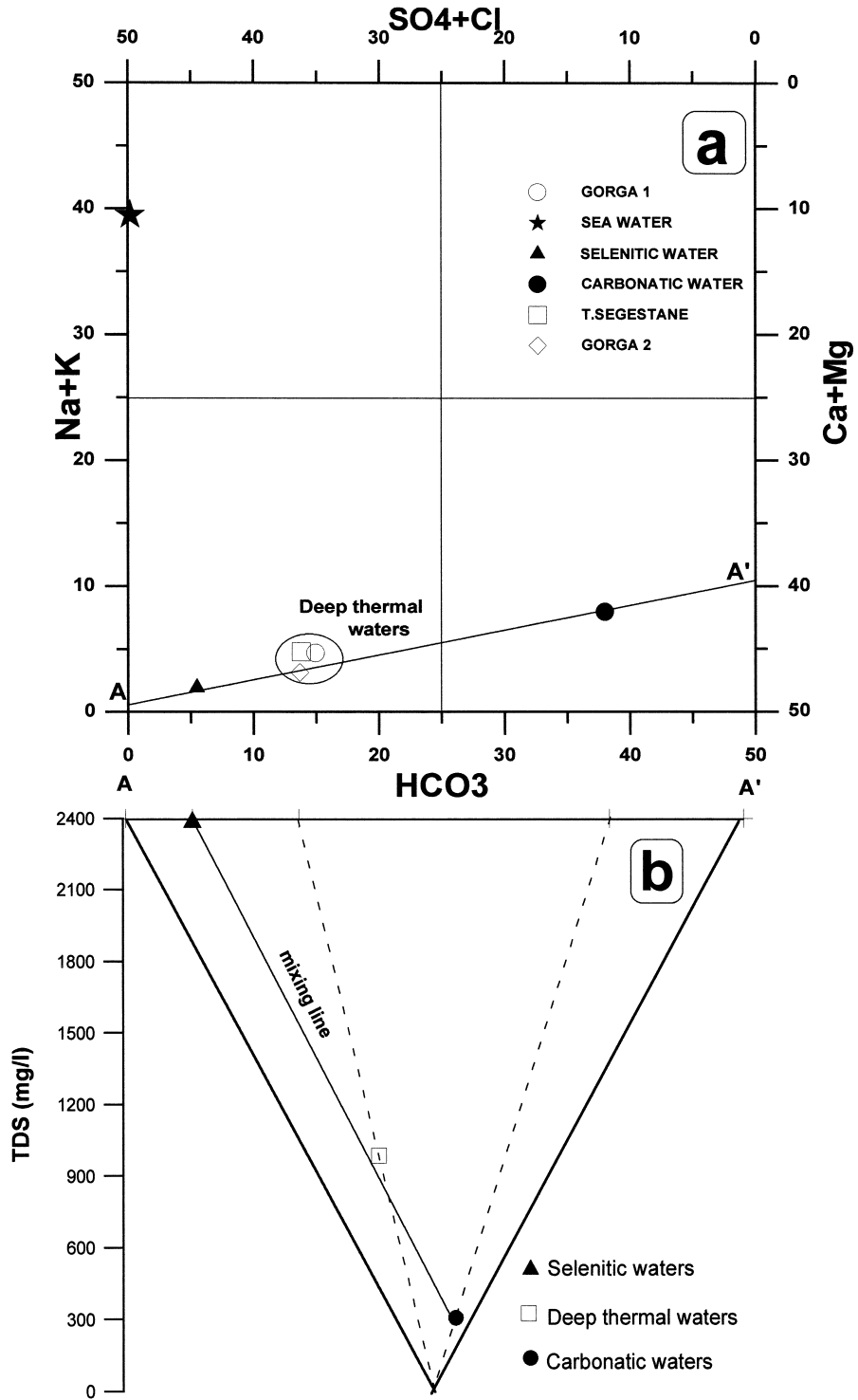
5. Water isotopic composition

5.1. Rainwater

Isotope data of mean rainwater samples collected from the three rain gauges, (Table 3) show a wide range of both $\delta^{18}\text{O}$ and δD seasonal variations.

The heaviest and lightest isotopic values were measured in June–July and in October 1994 respectively. Both these groups of values are rather peculiar since isotopic values close to zero normally result from evaporation processes affecting rainwater droplets during their fall, while very negative isotopic values characterize the coldest months, i.e., December–January. An ^{18}O and D enrichment of rainwater related to evaporation processes has been repeatedly pointed out by various authors, particularly in tropical and subtropical areas. The extremely light isotopic values obtained in October cannot be easily explained since, unfortunately, the mean monthly temperatures at the sites are not available and, consequently, it is not possible to relate the isotopic values to exceptionally low temperatures or to peculiar meteorological conditions.

Fig. 2. (a) Langelier–Ludwig classification diagram. It is possible to distinguish three water families: carbonatic waters (1), selenitic waters (2) and thermal waters (3). (b) Triangular plot $\text{Cl--HCO}_3\text{--SO}_4$ that shows the three water groups and highlights the possible mixing among carbonatic, selenitic and sea water end-members (dashed lines) also reported in the diagram.



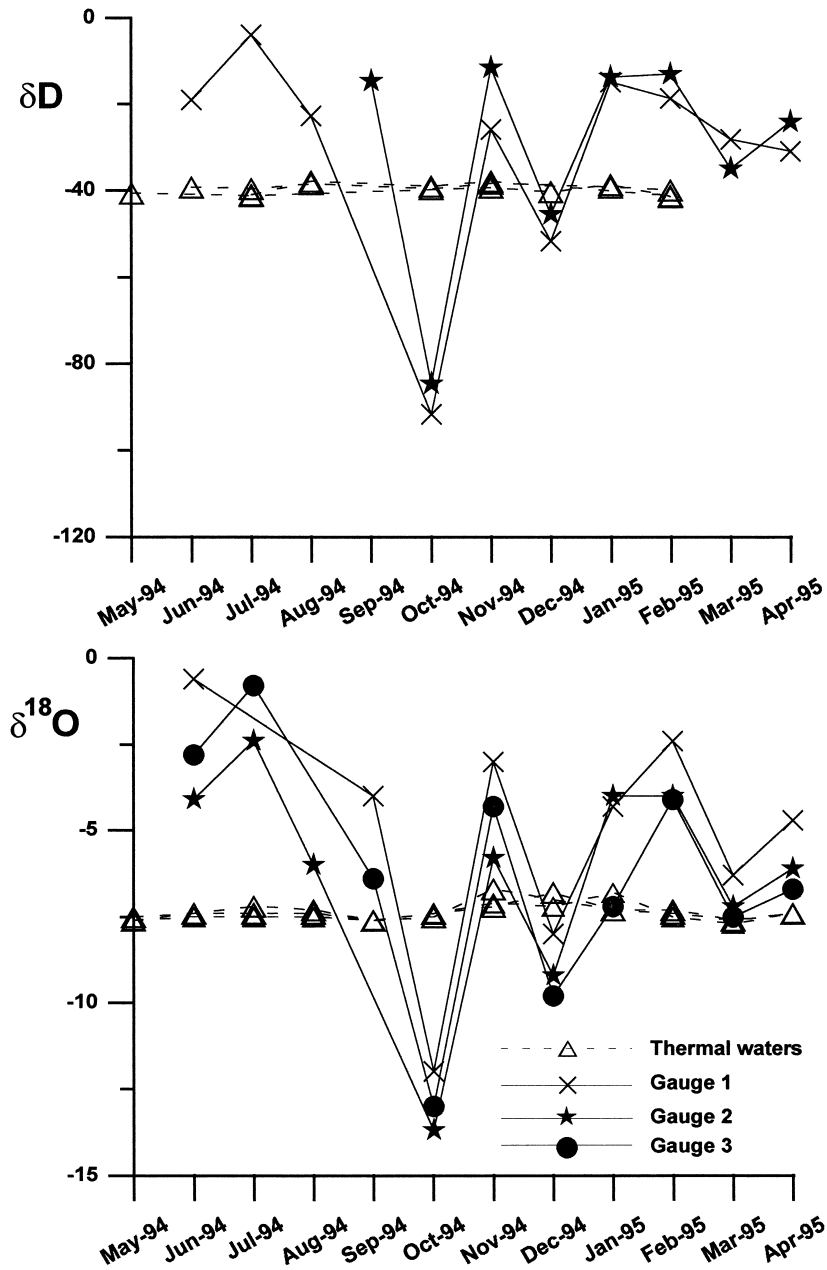


Fig. 4. Isotopic composition of $\delta^{18}\text{O}$ (a) and δD (b) of rain and thermal waters reported over time. The consistency of the isotopic values of thermal waters clearly supports the hypothesis of a deep hydrological circuit with long residence times allowing the homogenisation of the isotope values.

Fig. 3. The values of deep thermal waters restored after subtraction of the sea water contribution, plotted in the Langelier–Ludwig diagram (a) lie on a line that connects selenitic to carbonatic waters (A–A' line), thus suggesting the existence of a reservoir made of a mixing of these two water families. The salinity diagram (b) is reported after the section A–A' of Fig. 3a and also confirm the postulated mixing between carbonatic and selenitic waters.

The isotopic characterisation of these rainwaters is mainly related to two effects:

- an elevation effect, observed between rain gauges 1 and 2 on the slopes of Mt. Inici.
 - a continental effect, observed at rain gauge 3.
- This gauge is 14 km inland, while the other two are located at about 3 km from the coast.

The vertical isotope gradient calculated according to rain gauges 1 and 2 is $0.21 \delta^{18}\text{O}/100 \text{ m}$; this value is quite close both to that calculated by Hauser et al. (1980) ($0.20 \delta^{18}\text{O}/100 \text{ m}$), and to that evaluated by Fancelli et al. (1991) ($0.18 \delta^{18}\text{O}/100 \text{ m}$) in other areas of Sicily. The continental effect calculated between gauges 1 and 3 is $0.2 \delta^{18}\text{O}/\text{km}$. Both δD and $\delta^{18}\text{O}$ values of rainwater and cold and thermal water aquifers fit the local meteoric line very well ($\delta\text{D} = 7.48 * \delta^{18}\text{O} + 14$) (Fig. 4).

5.2. Thermal springs

The isotope data from thermal spring waters are almost identical ($\delta^{18}\text{O} = -7.4, -7.3$ and -7.3‰ , $\delta\text{D} = -40, -39$ and -39‰ respectively for Gorga 1, 2 and T. Segestane), thus confirming the hypothesis of a common source feeding water to these springs. If we take into account, as previously suggested by the chemical composition, that thermal waters result from the mixing of a carbonatic water (Inici spring) with a selenitic water (Capo di Fiume spring) we shall evaluate the isotopic results obtained in the light of this hypothesis.

The catchment area of the carbonatic water component can be located on the carbonatic horsts at a mean elevation of 500 m a.s.l., the yearly mean isotopic composition of rain water in this area being close to -7.1‰ on the basis of a vertical isotopic gradient of about $-0.2 \delta \text{‰}$ per 100 m. The catchment area of the selenitic water, despite its mean elevation of only 400 m a.s.l., is characterized by very light isotopic values (rain gauge no. 3, $\delta^{18}\text{O} = -8.2$), probably related to a continental effect (Table 3).

The percentage of the two components was evaluated to be about 70% carbonate water and 30% selenitic water. According to these percentages, and to the isotopic values previously reported, the mean $\delta^{18}\text{O}$ which may be evaluated for thermal waters is

Table 3
Isotopic values of $\delta\text{D}-\delta^{18}\text{O}$ of rainwater samples

Sample	Date	$\delta^{18}\text{O}$	δD	Rain amount	
Gauge 1	Jun. 94	-4.1	-19	29	
	Jul. 94	-2.4	-4	8	
	Aug. 94	-	-	0	
	Sep. 94	-6.0	-23	30	
	Oct. 94	-13.7	-92	77	
	Nov. 94	-5.8	-26	83	
	Dec. 94	-9.2	-52	222	
	Jan. 95	-4.0	-15	33	
	Feb. 95	-4.0	-19	31	
	Mar. 95	-7.2	-28	30	
	Apr. 95	-6.1	-31	52	
	$\delta^{18}\text{O}$	weighted average -8.2			
	Gauge 2	Jun. 94	-2.8	n.a.	18
		Jul. 94	-0.8	n.a.	8
Aug. 94		-	-	0	
Sep. 94		-6.4	n.a.	10	
Oct. 94		-13.0	n.a.	58	
Nov. 94		-4.3	n.a.	57	
Dec. 94		-9.8	n.a.	260	
Jan. 95		-7.2	n.a.	31	
Feb. 95		-4.1	n.a.	21	
Mar. 95		-7.5	n.a.	31	
Apr. 95		-6.7	n.a.	74	
$\delta^{18}\text{O}$		weighted average -6.1			
Gauge 3		Jun. 94	-0.6	n.a.	11
		Jul. 94	-	-	0
	Aug. 94	-	-	0	
	Sep. 94	-4.0	-15	12	
	Oct. 94	-12.0	-85	40	
	Nov. 94	-3.0	-12	54	
	Dec. 94	-8.0	-46	209	
	Jan. 95	-4.3	-14	22	
	Feb. 95	-2.4	-13	44	
	Mar. 95	-6.3	-35	48	
	Apr. 95	-4.7	-24	59	
	$\delta^{18}\text{O}$	weighted average -8.2			

Their monthly amount and weighted average is also indicated. The isotopic values are reported in δ per ml units vs. V-SMOW standard and the amounts of water are expressed in mm. N.a. = not analysed.

-7.4‰ , coinciding perfectly with the measured mean isotopic composition (Fig. 5).

6. Water-rock interaction

The saturation index in a solution is defined as the logarithm of the ratio between the ion activity relative to a given mineralogical phase and the equilib-

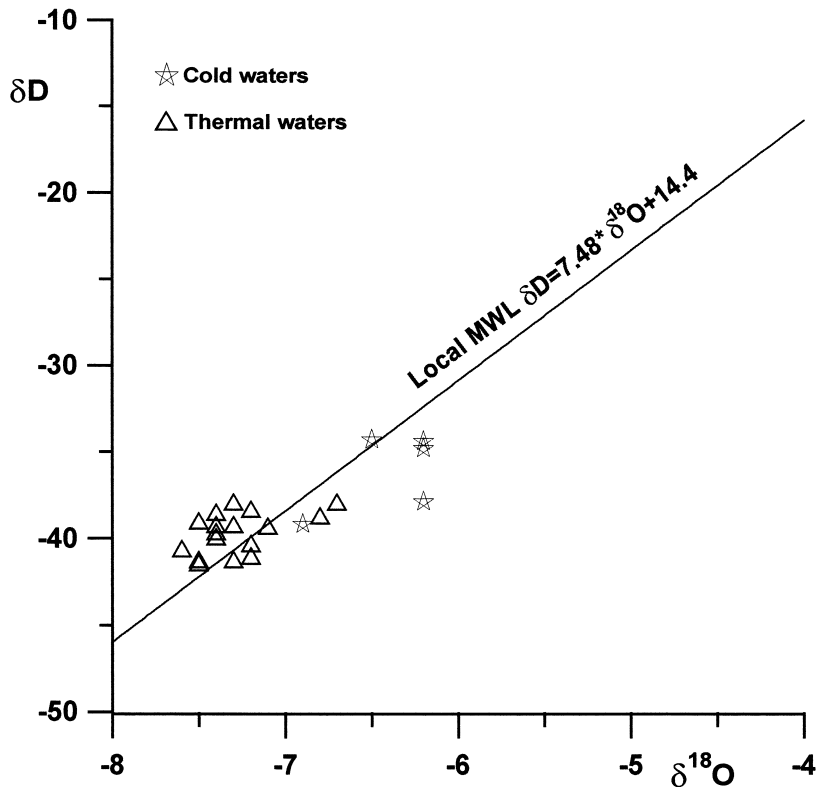


Fig. 5. $\delta\text{D}-\delta^{18}\text{O}$ diagram. The isotopic values of rainwater and the cold and hot spring waters show a good positive correlation. Furthermore, the latter perfectly fit the local meteoric line and do not show any isotopic shift.

rium constant of its solubility product:

$$\text{S.I.} = \log(\text{I.A.P.}/K_{\text{sp}})$$

The saturation index of all the sampled waters, calculated by the WATEQP programme (Appelo, 1988) to an accuracy of 0.05%, is reported in Fig. 6. A solution is usually considered saturated with respect to a given mineralogical phase when S.I. ranges between +5% and -5% of $\log K_{\text{sp}}$ (Jenne et al., 1980). Cold waters are all gypsum-undersaturated, while samples Capo di Fiume and Arancio (selenitic waters), both emerging in the gypsum-sulphurous series (Vita), have a $\text{S.I.} \approx 0$. On the contrary, with respect to the saturation index of calcite and dolomite, the studied samples show a wide variability ranging from undersaturated to oversaturated. The waters from all the hot springs have very similar S.I. values, all being gypsum-undersaturated ($\text{S.I.} \approx -0.8$), whereas they are systematically calcite-saturated. The observed gypsum undersaturation of thermal waters

($\text{S.I.} \approx -0.8$) reflects the absence of this phase in the reservoir rocks. Moreover, the values of calcite saturation rates (always close to zero) confirm both the calcareous-dolomitic nature of the reservoir and equilibrium between the liquid and mineral phases.

Finally, we shall consider the saturation rates of the intermediate terms with respect to gypsum. We will assume that these terms derive from mixing, in various proportions, of carbonatic and selenitic waters having $T = 80^\circ\text{C}$ and $\text{pH} = 6.7$. The temperature considered in these calculations has been evaluated using different geothermometers (see Section 7), while the pH value is the average of repeated measurements of thermal springs. Taking into account the two main terms (carbonate water from Mt. Inici and selenitic water from Capo di Fiume) we calculated the composition of intermediate terms. Using these temperature and pH data we calculated the gypsum saturation index of these intermediate terms by means of the WATEQP programme. These values

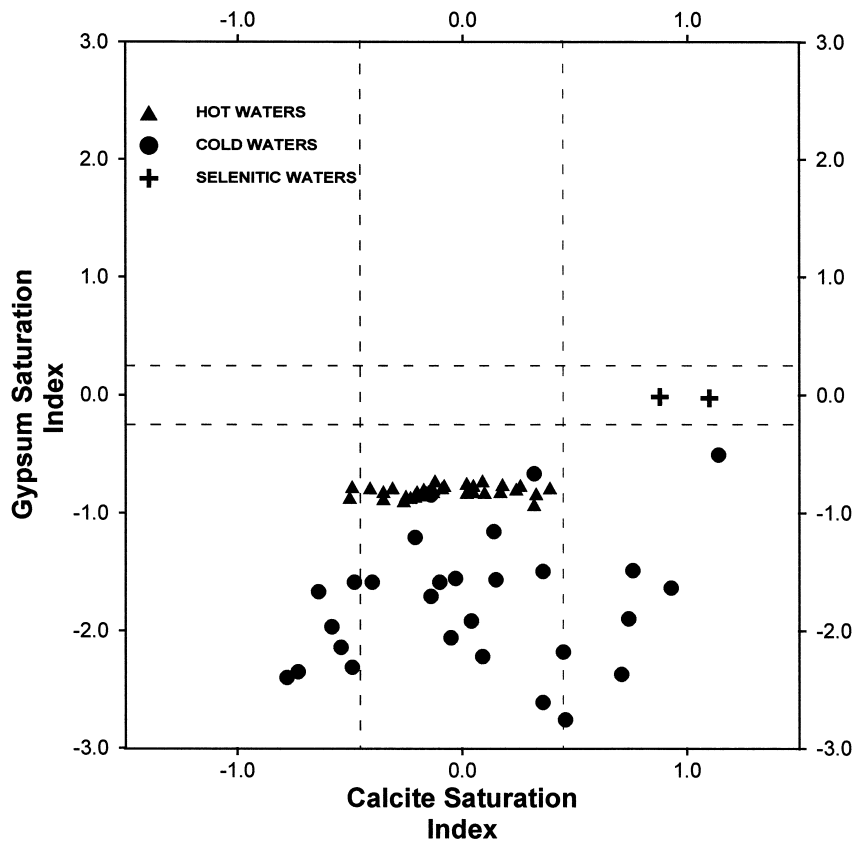


Fig. 6. Saturation indices of calcite and gypsum calculated for all the sampled springs, both cold and hot. Cold waters are all gypsum undersaturated, except the selenitic terms that have an S.I. \cong 0. On the contrary, the samples considered show extreme variability of the calcite saturation index with values ranging from undersaturated to oversaturated. Thermal waters are all gypsum undersaturated (S.I. \cong -0.8), while they are constantly saturated with calcite. Dashed lines represent the saturation range for the mineralogical phases considered.

are reported in Fig. 7 against the percentage contribution of carbonate and selenitic waters. The curve represents these variables in their intermediate terms. For the S.I. value of -0.7 calculated on the average composition of thermal waters, the mixing ratio of 70% and 30% for the carbonate and selenitic terms respectively obtained, confirming the mixing ratios calculated from the salinity diagram (Fig. 3b).

7. Geothermal calculations

The water temperature in the aquifer that feeds the thermal springs was calculated using various geothermometers. Firstly the deep temperatures of

the reservoir were estimated with the K/Mg, Na/K and Na/K/Ca geothermometers, considering a chemical composition of water after correction of Mg and Ca contents for the pollution due to the component of marine origin. The same correction was not made for Na and K contents because the gypsum-sulphurous series (Messinian age) has inclusions of clay containing Na and K salts (Catalano and D'Argenio, 1982) that are rendered soluble during the deep circulation of water. For this reason, the deep Na and K contents in the waters examined could not be distinguished from those coming from the cold shallow source of marine origin. Temperature values obtained with these three geothermometers were about 60°C for all of the three thermal

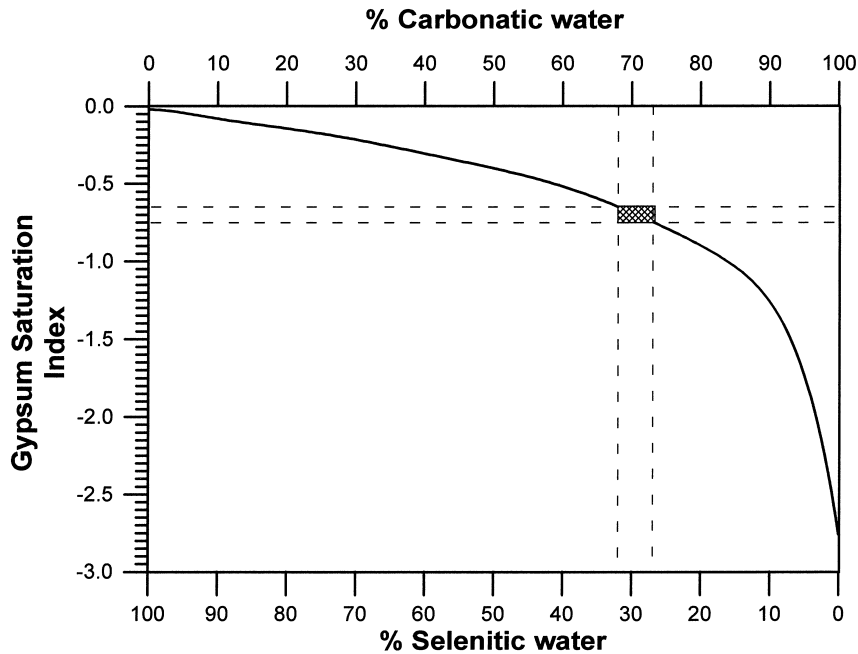


Fig. 7. Variation of gypsum saturation index as a function of hypothetical mixing, in various proportions, between carbonatic and selenitic waters at $T = 80^{\circ}\text{C}$ and $\text{pH} = 6.7$. In this graph we report the value of gypsum S.I. (-0.7) relative to the deep reservoir composition, as calculated from the average chemical composition of the thermal springs. Considering this value we obtain a mixing ratio of 70% and 30% between carbonatic and selenitic waters respectively.

springs (Table 4). In order to verify these temperature values, two additional geothermometers were used. The first one was the geothermometer that considers the calcite–dolomite equilibrium in water solution (TCM, Marini et al., 1986). Both these mineralogical phases are present in the studied reservoir and their saturation rates show the attainment of equilibrium ($\text{S.I.} \cong 0$) at emergence temperatures

(Fig. 6). The other one was the geothermometer that considers quartz solubility in water solution, without any vapour loss (TQC, Fournier, 1973) because of flint insertions as strips and nodules in carbonatic lithotypes (Catalano and D'Argenio, 1982).

The temperature values estimated for the deep term by applying the TCM geothermometer were obtained by eliminating the shallow contamination of

Table 4
Measured and calculated temperature values of thermal springs

Samples	t meas.	t SiO_2 (A)	t Ca–Mg (B)	t Mg (C)	t Na–K (D)	t Na–K–Ca (E)
Gorga 1	48	78	73	54	65	62
Gorga 2	50	78	97	66	60	78
T. Segestane	44	78	79	54	65	63

(A) Fournier, 1973.

(B) Marini et al., 1986—Ca and Mg corrected for sea water pollution.

(C) Fournier and Potter, 1979. Magnesium correction to the Na–K–Ca geothermometer.

(D) Arnosson, 1983, valid for clay minerals.

(E) Fournier and Truesdell, 1973.

Temperature was calculated according to several geothermometers as indicated in the table. Values are expressed in $^{\circ}\text{C}$.

marine origin; falling within a narrow range between 73 and 97°C. These data are in agreement with those obtained with the TQC geothermometer applied to the surface thermal component (~ 80°C; see Table 4). Those estimated temperature values for the three thermal springs further confirm the hypothesis that these springs are fed by a single deep aquifer. Different supplies of a seawater component received during upflow can explain the small differences observed in chemical composition.

The deep temperature data allow an estimate of the theoretical minimum depths of the reservoir by using the equation proposed by Desio (1965):

$$P = (T_w - T_a) / G$$

where: P is the theoretical minimum depth; T_w is the water temperature in the reservoir; T_a is the yearly average air temperature; G is the local geothermal gradient.

The local geothermal gradient was calculated considering an estimated average value of total heat flow between 1.3 and 1.4 HFU (Catalano et al., 1983) in the area examined. In this case the theoretical minimum depths of the reservoir are between 1300 and 1800 m, which are consistent with the thickness of the Trapanese carbonatic domain (Catalano et al., 1983).

8. Water budget

An estimate of the groundwater supplies to the basin was obtained assuming the following water budget:

$$P = I + R + E$$

where: P is the amount of precipitation (mm/year); I is the amount of water infiltration (mm/year); R is the rill coefficient of the basin (mm/year); E is the quantity of water affected by evapotranspiration (mm/year).

On the basis of the data from the local rain gauge network, precipitation was calculated using the method proposed by Thiessen (1911). The pluviometric and thermometric values refer to the 1965–1984 period. The calculation of the evapotranspiration term was carried out using the equation proposed by Turc (1955) subsequently modified by Santoro (1970) for Sicily.

As the data were not sufficient to estimate the rill coefficient, the effective infiltration was calculated using the method of the potential infiltration coefficient (P.I.C.) for the single hydrogeological units, as proposed by Castany et al. (1970). In karst areas, the coefficient of potential infiltration allows a calculation of the percentage of water relative to surface run-off and groundwater outflow, representing the assumed effective infiltration:

$$I_{\text{eff}} = \text{P.I.C.} * D_{\text{tot}}$$

where: I_{eff} is the amount of water infiltration; D_{tot} is the total water rill obtained after subtracting E from the total amount of precipitation (P).

The P.I.C. was defined as a function of a series of parameters such as lithology, fracturation, acclivity, distribution and type of vegetation (herbage or tree), intensity of karst processes. In order to calculate the water budget, both water capacities and the surplus of the most significant hydrogeological units in the assumed hydrogeological basin were estimated. Table 5 reports the data set used to calculate the water budget.

The hydrogeological unit of Mt. Inici has a surface extension of 18.5 km² and consists of dolomites and limestones (Trias–Eocene) belonging to the Trapanese carbonatic platform. The total infiltration is 3.23×10^6 m³, which gives a water capacity of 100 l/s. The surplus (about 70 l/s) was obtained by excluding the known water extraction (30 l/s) from the water capacity. The hydrogeological unit of Mt. Barbaro–Mt. Pispisa has a surface extension of 4.5 km² and consists of calcilutites of the scaglia facies (Cretaceo–Eocene) of the Trapanese domain. The water capacity of this unit is about 25 l/s; the surplus is 20 l/s. The unit of the evaporitic rocks belongs to the Messinian gypsum-sulphureous series and is the recharge area of both superficial and deep selenitic terms. It has a total extension of 16.5 km² and its water capacity is 85 l/s. The springs and the wells of this area extract about 30 l/s, so the water surplus is 55 l/s.

The water budget obtained for the hydrological units considered had a water capacity of about 145 l/s, that is less than the outflow of all the thermal springs (200 l/s). As observed with the chemical data, these thermal waters are the result of a mixing

Table 5

Computation of the contribution of the meteoric recharge to cold and thermal groundwaters

Area	Lithology	km ²	Rainfall	P.I.C	Meteoric recharge	Cold groundwaters	Thermal groundwaters
Mt. Inici	dolomite and limestones	18.5	648	85%	100	30	70
Mt. Barbaro–Mt. Pispisa	calcilutites	4.5	655	80%	25	5	20
C. Da Montagna	gypsum	16.5	685	85%	85	30	55
Mt. Bonifato	calcilutites	8.8	648	80%	50	30	20
Montagna Grande	calcilutites	24.0	655	80%	120	55	65

Rainfall = amount of meteoric precipitation, expressed in mm. Meteoric recharge, cold groundwaters and thermal groundwaters are expressed in l/s.

between two end-members, one carbonatic (about 70%) and one selenitic (about 30%). Therefore, about 140 l/s are to be ascribed to typically carbonatic waters and the remaining part (60 l/s) to selenitic waters. If we assume that the entire surplus reaches the deep aquifer, it is evident that the flow of the selenitic water is sufficient to account for 30% of the total flow of the thermal springs. The carbonatic term, on the contrary, has a water deficiency of about 50 l/s so the hydrogeological basin has to be enlarged so as to include other carbonatic hydrogeological units next to the basin examined.

The carbonatic areas to be considered are:

- (a) Mt. Bonifato,
- (b) Montagna Grande.

The relief of Mt. Bonifato takes up an area of 8.75 km². It is composed of the scaglia of Trapanese domain and has a water capacity of 50 l/s. As the drainage of groundwaters occurs to the west in the basin examined and to the east in Calatubo gorge the contribution to be offered to the deep system must not exceed 20 l/s. The mountain complex of Montagna Grande, about 24 km² wide, consists mainly of the scaglia of the Trapanese domain. Its water capacity can be evaluated at about 120 l/s.

Therefore, the water budget deficiency of the basin studied (\cong 50 l/s) can be balanced assuming that part of the estimated water contributions from Mt. Bonifato and Montagna Grande is allowed to flow into the thermal reservoir.

9. Conclusions

The chemical characteristics and the isotope values of δD and $\delta^{18}O$ of the waters considered, as

well as the geological context where they flow and reside, allowed the identification of three main types of hydrogeological circuits. The first one may be referred to the selenitic water family (rich in sulphates), whose feeding area is in the southern portion of the drainage basin. The second one may be referred to as the cold carbonatic water family, placed under the principal carbonatic reliefs that constitute the recharging area (Mt. Inici, Mt. Barbaro–Mt. Pispisa). The third, deeper than the other two, is characterised by a mixing of the above waters and feeds the thermal springs of the area examined.

The reservoir of this circuit is set in calcareous and dolomitic rocks, as shown by the gypsum and calcite saturation rates of the waters. The compositional ratios in the waters of the thermal springs highlighted the existence of a mixing between three end members: carbonatic, selenitic and marine-derived waters. This mixing occurs in two separate phases:

- (1) mixing between the carbonatic (70%) and the selenitic term (30%) in the reservoir, which determines the hydrothermal term.

- (2) slight contamination of the mixed thermal waters with waters of marine derivation during their upflow. The different percentages of contamination (1.5–3%) are reflected in the small compositional differences between the three thermal springs (Gorga 1, Gorga 2 and T. Segestane).

The temperatures estimated in the thermal reservoir, obtained using various geothermometers, are between 60 and 97°C. The upflow of these thermal waters occurs along structural discontinuities where the loss of load is smaller. In the area studied, in fact, there is an active NW–SE fault, which is

thought to be responsible for the 1968 earthquake of Belice.

From the water budget of the basin it is evident that the feeding areas of the carbonatic term are the carbonatic hydrogeological units of Mt. Inici, of Mt. Barbaro–Mt. Pispisa, Mt. Bonifato and Montagna Grande. The feeding area of the selenitic term, on the contrary, is to be found in the southern section of the basin, where selenitic gypsum of the 2nd cycle crops out. The water capacity of this hydrogeological unit is comparable to the estimated flow of the selenitic portion of the thermal springs. The circulation of selenitic waters occurs at first in shallow circuits, whose limit is represented by the Tortonian clays of the Cozzo di Terravecchia formation. Then, where the impermeable clays are no longer present under the selenitic water reservoir, these waters infiltrate through a network of fractures and reach the deep reservoir, which is assumed to be at a depth ranging from 1300 to 1800 m. In the deep reservoir they mix with the carbonatic waters and reach temperatures ranging between 60 and 90°C. These tem-

peratures are consistent with a geothermal gradient of about 40°C/km.

A model (Fig. 8) that assumes an almost total chemical and isotopic homogenization in the reservoir (as the diffusion velocity is much higher than that of outflow) can represent the schematically hydrogeological circulation into the basin. In fact, depending on the season, the increase of the hydrostatic load produces an increase in the flow of the springs, but it does not produce any significant variation in temperature or in the chemical and isotope compositions.

Acknowledgements

We wish to thank Prof. Antonio Longinelli, Prof. Mariano Valenza and Dr. Salvatore Giammanco for their critical review of an early version of this paper. We also thank Salvatore Francofonte and Dr. Francesco Sortino for their help during the fieldwork.

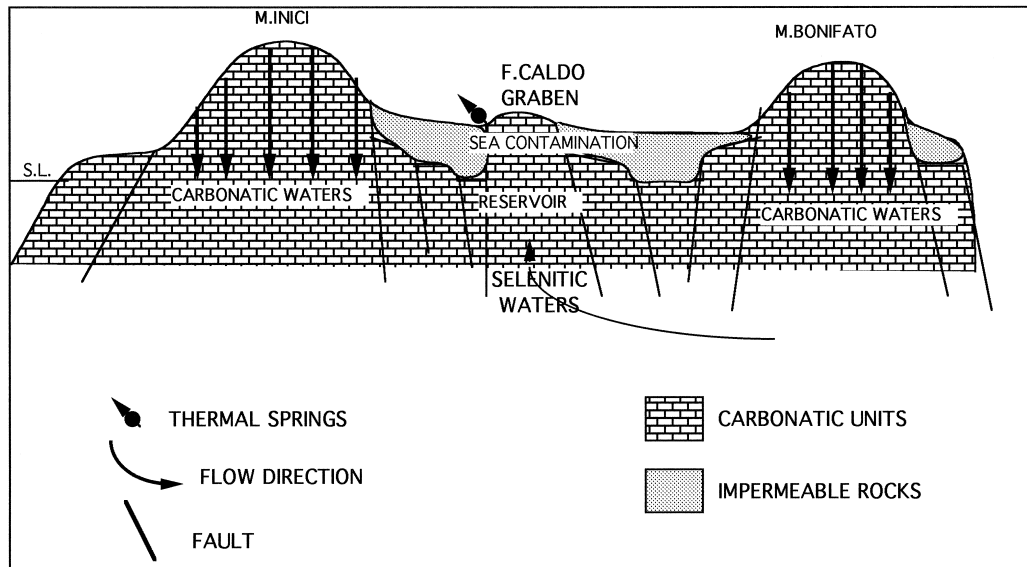


Fig. 8. Schematic model of the hydrogeological circulation in the basin studied (modified by Cusimano et al., 1982). The hydrogeological circulation and the physical–chemical peculiarity of the thermal waters can be explained by the coupling of two models (Richter and Szymczak, 1992). (1) A piston model that causes an increase in the flow of the springs because of the increase in the hydrostatic load. (2) A linear model that causes a diffusion velocity much higher than that of the outflow, this model does not produce any significant variation in the temperature or the chemical and isotopic compositions of waters.

References

- Alaimo, R., Carapezza, M., Dongarrà, G., Hauser, S., 1978. Geochimica delle sorgenti termali siciliane. *Rend. Soc. Chim. Ital.* 34 (2), 577–590.
- Alaimo, R., Calderone, S., Inguaggiato, S., Sortino, F., 1990. Indagine geochimica sull'acquifero termale della Sicilia occidentale. *Geologia ed idrogeologia*, Bari 25, 101–122.
- Appelo, C.A.J., 1988. WATEQP Program. Instituut voor Aardwetenschappen, Vrije Universiteit, Amsterdam.
- Arnosson, S., 1983. The chemistry of geothermal waters in Iceland: I. Calculation of aqueous speciation from 0°C to 370°C. *Geochim. Cosmochim. Acta* 46, 1513–1532.
- Carapezza, M., Cusimano, G., Liguori, V., Alaimo, R., Dongarrà, G., Hauser, S., 1977. Nota introduttiva allo studio delle sorgenti termali dell'isola di Sicilia. *Boll. Soc. Geol. Ital.* 96, 813–836.
- Castany, G., Margat, J., Albinet, 1970. Evaluation rapide des ressources en eaux d'une region. *Atti I Convegno Int. Acque Sotterranee*, Palermo.
- Catalano, R., D'Argenio, B., 1982. Schema geologico della Sicilia occidentale. In: Guida alla geologia della Sicilia occidentale (Ed.), *Soc. Geol. Ital. 1° Centenario della società geologica italiana*.
- Catalano, R., Macaluso, T., Monteleone, S., Calandra, D., 1982. Introduzione allo studio delle potenzialità geotermiche della Sicilia Occidentale. In: Guida alla geologia della Sicilia occidentale (Ed.), *Soc. Geol. Ital., 1° Centenario della società geologica italiana*.
- Catalano, R., Macaluso, T., Monteleone, S., Calandra, D., 1983. Lineamenti geostrutturali ed idrogeologici e geotermici della Sicilia occidentale. *CNR-PFE-RF13*.
- Cusimano, G., Di Cara, V., Liguori, V., Marescalchi, P., 1982. Modello idrostrutturale dell'area termale 'Fiume caldo-Castellammare del Golfo (Trapani)'. *Rend. Soc. Geol. Ital.* 5, 31–34.
- Dall'Aglia, M., 1966. Rilievo geochimico della Sicilia occidentale. *Riv. Min. Sicil.* 100–102, 175–192.
- Dall'Aglia, M., Tedesco, C., 1968. Studio geochimico ed idrogeologico di sorgenti della Sicilia. *Riv. Min. Sicil.* 112–114, 171–210.
- Desio, A., 1965. Il problema delle acque sotterranee in Italia. *Atti Conv. Probl. Acque in Italia, F.A.S.T. Milano*.
- Dongarrà, G., Hauser, S., 1982. Isotopic composition of dissolved sulphate and hydrogen sulphide from some thermal springs of Sicily. *Geothermics* 11 (3), 193–200.
- Epstein, S., Mayeda, T., 1953. Variation of ^{18}O content of water from natural sources. *Geochim. Cosmochim. Acta* 4, 213–224.
- Fancelli, R., Monteleone, S., Nuti, S., Pipitone, G., Rini, S., Taffi, L., 1991. Nuove conoscenze idrogeologiche e geotermiche nella Sicilia occidentale. *Geologia ed idrogeologia*, Bari 26, 25–38.
- Fournier, R.O., 1973. Silica in thermal waters: Laboratory and field investigations. In: *Proceedings, International Symposium on Hydrogeochemistry and Biogeochemistry*, Tokyo, 170, Vol. 1, Hydrogeochemistry, Washington, DC, Clark, pp. 122–129.
- Fournier, R.O., Potter, R.W. II, 1979. Magnesium correction to the Na–K–Ca geothermometer. *Geochim. Cosmochim. Acta* 43, 1543–1550.
- Fournier, R.O., Truesdell, A.H., 1973. An empirical Na–K–Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta* 37, 515–525.
- Gino, G.F., Sommaruga, C., 1953. Le manifestazioni idrotermali della Sicilia. *Riv. Min. Sicil.* 22–23, 172–183.
- Hauser, S., Dongarrà, G., Favara, R., Longinelli, A., 1980. Composizione isotopica delle piogge in Sicilia. Riferimenti di base per studi idrogeologici e relazione con altre aree mediterranee. *Rend. Soc. Ital. Min. e Petr.* 36 (2), 671–680.
- Jenne, E.A., Ball, J.W., Burchard, J.M., Vivit, D.V., Barks, J.H., 1980. Geochemical modeling: apparent solubility controls on Ba, Zn, Cd, Pb and F in waters of Missouri tri-State mining area. In: Heniphill, D.D. (Ed.), *Trace Substances in Environmental Health*, University of Missouri, Columbia. 14, pp. 353–361.
- Kendall, C., Coplen, T.B., 1985. Multisample conversion of water to hydrogen by zinc for stable isotope determination. *Anal. Chem.* 57, 1437–1440.
- Langelier, W.F., Ludwig, H.F., 1942. Graphical methods for indicating the mineral character of natural waters. *JAWWA* 34, 335.
- Marini, L., Chiodini, G., Cioni, R., 1986. New geothermometers for carbonate-evaporite geothermal reservoirs. *Geothermics* 15, 77–86.
- Richter, J., Szymczak, P., 1992. Multis. *Bergakademie Freiberg Lehrstuhl für Hydrogeologie*, pp. 1–46.
- Santoro, M., 1970. Sull'applicabilità della formula del Turc per il calcolo della evapotraspirazione effettiva in Sicilia. *Atti I Convegno Int. Acque Sotterranee*, Palermo-Italy.
- Sortino, F., Inguaggiato, S., Francofonte, S., 1991. Determination of HF, HCl, and total sulphur in fumarolic fluids by ion chromatography. *Acta Vulcanol.* 1, 89–91.
- Thiessen, A.H., 1911. Precipitation average for large areas. *Monthly Weather Rev.* 3, 45–81.
- Turc, L., 1955. Le bilan d'eau des sols. Relation entre les précipitations, l'évaporation et l'écoulement. *Ann. Agron.* 5, 1–131.