ANNALI DI GEOFISICA, VOL. XXXVIII, N. 2, May 1995

Geochemical evolution of groundwater of the Iblean Foreland (Southeastern Sicily) after the December 13, 1990 earthquake (M = 5.4)

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Abstract
Geochemical surveys were performed by the Istituto Nazionale di Geofisica (ING), between December 1990 and July 1991, in the framework of an interdisciplinary task study throughout the Siracusa epicentral area: these studies were aimed at collecting specific information on the geochemical patterns of fluids, in relation to the geodynamic and seismic evolution of the northern Iblean Foreland area, starting from the December, 13, 1990 Syracuse earthquake (M = 5.4). The results of the hydrogeochemical surveys, discussed in this paper, were in part unexpected. In particular, a steady decrease of the PCO_2 values, after the earthquake, in groundwaters of the epicentral area, along a NNW-SSE fault bordering the Augusta Graben (*Brucoli Sulphureous Spring*), was observed. This observation enabled us to reconstruct the geochemical processes triggered by the earthquake: a sudden and strong release of CO_2 of deep origin, probably related to a pore pressure uprising and/or to a water/rock interaction changes in the vicinity of the seismogenic structure. The existence of deep-fluid uprising (CO_2, ^{222}Rn, NH_3, H_2S), as well as the variation in time of geochemical flows accompanying seismic activity along this NNW-SSE anomalous-sites line, within the whole Iblean Foreland, witness the activity (as concern as fluidodynamic and geochemistry) of the NNW-SSE stricking Ibleo-Maltese Escarpment fault system. This fact can be taken into account in locating the seismogenic structure responsible for the 1990 earthquake, like a contribution of the geochemical methods applied to seismotectonics. During June 1992, a more complete analysis of the Iblean Foreland groundwaters was performed, collecting data on the geochemical features of the different aquifers in aseismic period. Multivariable statistics, chemical equilibria studies and mapping with our geochemical data, were also performed.

Key words *earthquake geochemistry – earthquake prediction – Iblean Foreland (Sicily, Italy)*

1. Introduction

Immediately following the December 13, 1990 Syracuse earthquake (M = 5.4) the Istituto Nazionale di Geofisica (ING) developed a series of studies in the area surrounding the city of Syracuse, including historical seismicity, macroseismic patterns, aftershock activity and other geophysical and geochemical phenomena (Boschi and Basili, 1991). These initiatives offered the opportunity to start with hydrogeochemical studies, in cooperation with the Earth Science Department of «La Sapienza» University in Rome.

The work performed in Eastern Sicily was part of a research program on geochemical earthquake precursors (Dall'Aglio *et al.*, 1988, 1991a). The preliminary phase of this research consisted in selecting significant groundwater sites connected with specific seismotectonic structures and thus suitable for geochemical monitoring (Dall'Aglio *et al.*, 1992, 1993).

Due to the almost complete lack of other hydrogeochemical data on the Iblean Foreland before the earthquake, the 1991-1992 monitoring of the Syracuse epicentral area was also aimed at establishing the *aseismic geochemical conditions* of the aquifers, with respect to the variations triggered by the 1990 earthquake.

The methodological approach used in Eastern Sicily aimed to stress the importance of using a huge number of geochemical parameters either to define the seismic area, together with geological and geophysical data, or to evaluate the feasibility of earthquake prediction experiments. Our further purpose was to evaluate the reliability of some geochemical parameters as seismic forerunners.

In recent decades, a large number of hydrogeochemical precursor phenomena, in different seismotectonic regions, have been found and observed. Reviews of such observations can be found in a series of publications (Hauksson, 1981; Barsukov *et al.*, 1985; King, 1986; Roeloffs, 1988; Thomas, 1988). Till early 1991, only four of the multitude of papers existing on hydrogeochemical changes were submitted as nominations for inclusion in the list of potentially reliable precursors by the IASPEI subcommission on earthquake prediction (Wyss, 1991); but only one (Wakita *et al.*, 1988) was accepted: it regards a ^{222}Rn precursor.

The reliability of earthquake prediction may be increased by an understanding of the basic physical phenomena of the earthquake fracturing processes. A number of studies have been published (Scholz, 1990; Thomas, 1988; Kumbel, 1991; Dubinchuk, 1991), in which an attempt has been made to explain the hydrogeochemical anomalies on a theoretical model, such as dilatance, IRSA, WIZ, hydro-geodeformational field. Not pretending an overview, it is worthwhile noting the following hypothesis and processes discussed by models proposed until now: rock dilatation and water diffusion, direct strain influence on emission of precursor component from solid matrix into porous fluids with special reference to the gaseous ones (^{222}Rn, He, H_2, CH_4, CO_2, H_2S, etc..), activation of convection-diffusion transport, ultrasonic phenomena and shaking, mixing of fluids from deeper layers, stress-strain related variation of physico-chemical conditions (activation energy, rate of soluting, diffusion velocity, etc..), decay and recoil effects.

The available geochemical data suggest either non-linear relationships between amplitude, shape and precursor times of the anomalies and epicentral distance, magnitude and source mechanism of an earthquake or a strong influence of local effects (such as aquifer geometry, chemistry, relation with the fault systems, etc..). Migration of trace elements, changes in the contact surface area due to cracking, and pore pressure variations are thought to strongly depend on the local conditions of fluid-flow, pore-pressure gradient and *in-situ* geochemical framework.

Often the papers reported in literature failed to insert the geochemical time series, related to only one or two parameters as precursor components, in the geochemical, geodynamical and seismological framework of the area taken in consideration: this lack should be overcome either by full preliminary geochemical investigations or by an interdisciplinary approach.

Until now no significant progress in this field has been made: the strategy towards earthquake prediction would be to continue to rely on empirical evidence, possibly with continuous monitoring devices (for imminent and short-term precursors), such as the drastic increase in observed anomalies in different types of hydrogeochemical parameters from representative seismic regions. A very few test-site task studies on earthquake prediction, also with geochemical tools, have been carried out (*i.e.* Parkfield, Tokai GAP, Turkish NAFZ): our geochemical and interdisciplinary approach could be considered a new methodological one.

The geochemical informations in the framework of a seismogenetic area can also be useful for the seismic-risk maps, due to its intrinsic link with short-term prediction and with the active faults recognition methods.

2. Geodynamical framework and methodological approach

The area of our studies is located at the intersection between the Apenninic-Magrebide chain and the African Foreland (fig. 1); it underwent an intense basaltic volcanic activity related to the Pliocene-Pleistocene extensional tectonics (Bianchi *et al.*, 1987; Ghisetti and Vezzani, 1980), which is also responsible for the present volcanic activity of Mt. Etna.

The area is characterized by volcanites and calcarenites outcropping in the typical sequence of the Iblean Foreland (Carbone *et al.*, 1987) and by Pliocene-Pleistocene clayey rocks of the Lentini and Brucoli-Augusta

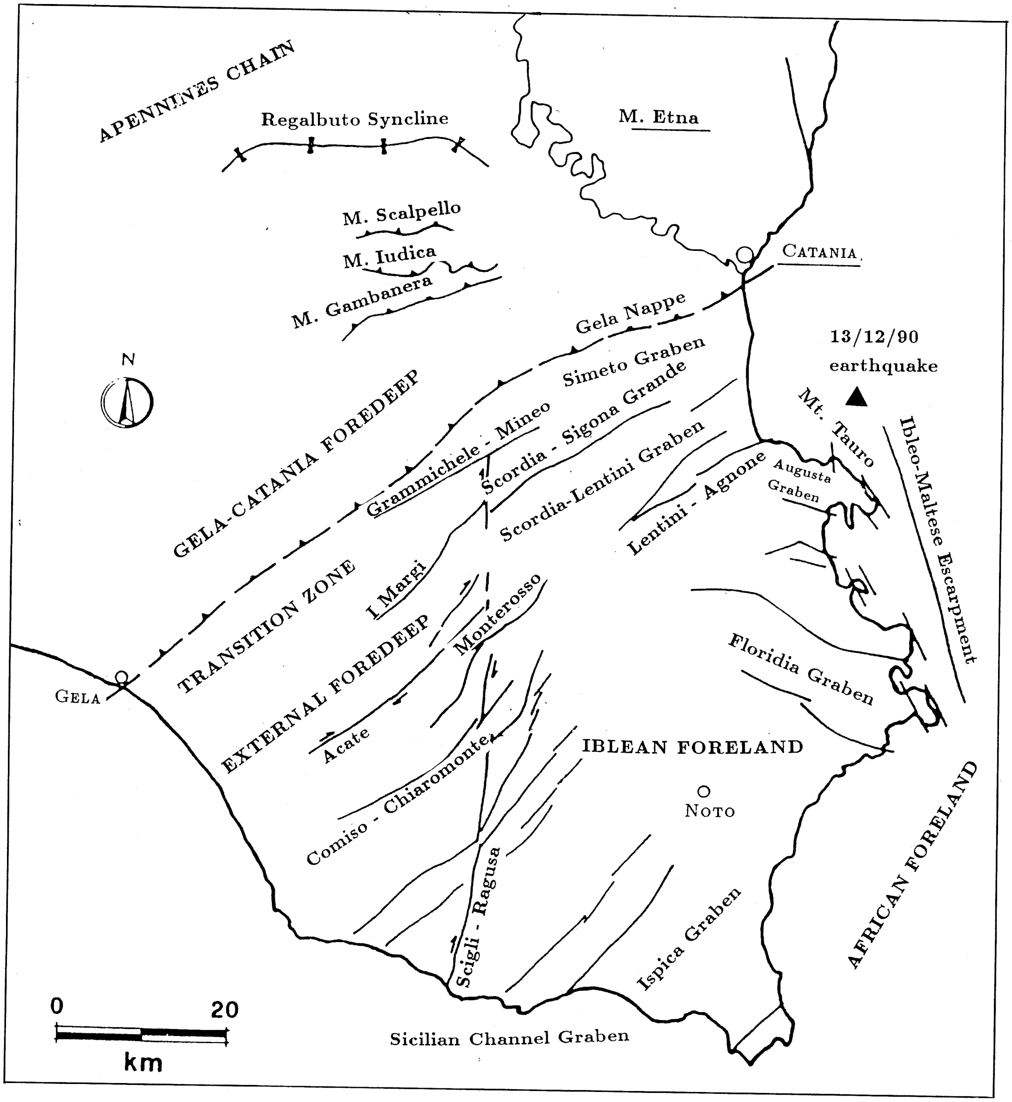


Fig. 1. Main structural frameworks in the Iblean Foreland (Eastern Sicily). Modified from Bianchi *et al.*, 1987.

Graben. The most important hydrogeological units are the fractured basalts and the calcarenites, while the *aquiclude* is constituted by a sequence of cemented tuffs and basalts and by the Pliocene Blue Clays.

The December 13, 1990 earthquake ($M = 5.4$) occurred in the northern Iblean Foreland and the epicenter was located slightly offshore Brucoli: the aftershocks were accurately localized by the ING's Mobile Network, installed immediately after the mainshock (Amato *et al.*, 1991).

Historically, this area experienced large earthquakes, such as the January 1693 event, that produced 60000 casualties. The seismic activity of this area is characterized by strong energy releases, followed by long periods of quiescence (Mulargia *et al.*, 1985). Although the highest concentration of earthquakes is found in the area of the Simeto-Scordia-Lentini Graben and along the NE-SW strike-slip structures, the largest earthquakes were located close to the Ibleo-Maltese Escarpment fault system (from De Rubeis *et al.*, 1991).

Based on the seismological data, the hydrogeochemical survey, performed immediately after the earthquake, was extended to an area spanning a large longitude range (from Vizzini-Palagonia to Brucoli-Augusta: see fig. 2). Therefore the sampling sites of the first survey in December, 1990 were selected considering the position of neotectonic structural lineaments (Di Geronimo *et al.*, 1980), macroseismic data and aftershock hypocenters.

The purpose of the first survey was to collect information on fluid geochemistry and on possible anomalies in the aquifers (*i.e.*, fracture relating gas-leak in soils and groundwaters, etc.); we also took into account geochemical and hydrogeological data found in the literature (Aureli *et al.*, 1989; Battaglia *et al.*, 1991): these data are very helpful for a hydrogeochemical reconstruction of the area, but insufficient for our research, due to the lack of analytical data concerning some minor and trace elements (^{222}Rn, He, NH_3, $S^{=}$, As, Fe, Mn, etc..), closely related to the upwelling of deep fluids along tectonic structures.

During the next surveys (January 1991 to July 1991), we collected new data concerning either the sites which were sampled right after the earthquake, or new sites belonging to aquifers of geodynamic relevance. In particular, the study and collection of data were focused on the sulphureous aquifer of the Augusta Graben, on the thermal aquifer of the

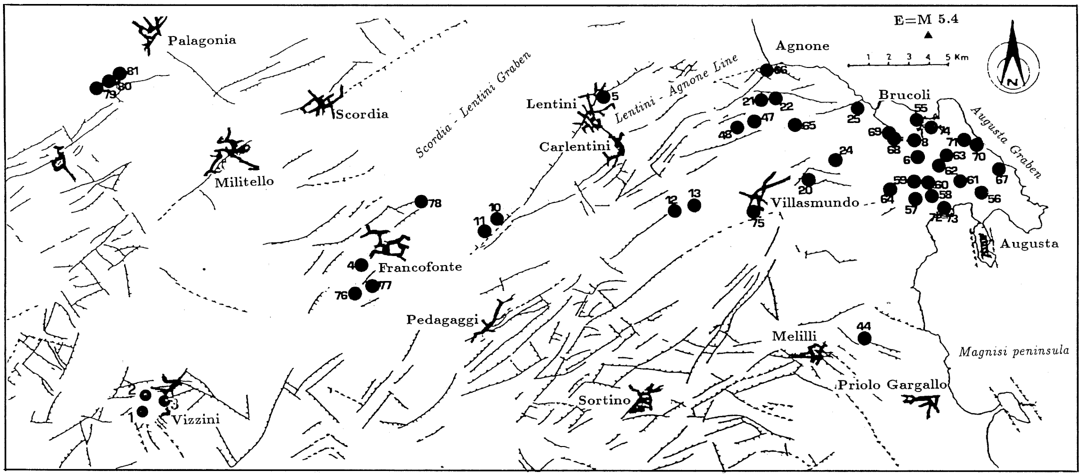


Fig. 2. Groundwater samples map with the main faults of the NE Iblean Foreland. Modified from *Carta della Sicilia Orientale 1:100000, Università di Catania.*

Scordia-Lentini Graben and on the thermal aquifer of the Mineo geothermal field. The last hydrogeochemical survey was performed in June 1992, including all the previously identified sites.

During the different surveys, we monitored sites belonging to different hydrogeological basins because our purpose was also to construct a map of anomalies relatively to the regional *background values*. Although this approach should require a larger number of samples than we used, it allowed us to observe the links between deep fluids (CO_2, H_2S, ^4He, ^{222}Rn, NH_3, etc..) and tectonic patterns of the area. On the field we measured the physico-chemical parameters (temperature, pH, Eh, electrical conductivity), the ^{222}Rn content (α – detector EDA) and the NH_3 concentration (ORION selective electrod). All the analytical studies of the groundwaters were performed in the Laboratory of Environmental Geochemistry of the ENEA (Ente Nazionale Energia e Ambiente) using thoroughly tested methods (Brondi *et al.*, 1986), also considering some of the minor and trace elements revealing some interaction with deep fluids (*i.e.*: He, Li, B, Sr, As, Fe, Mn). The He measurements were taken with a leak detector (mass spectrometry). Then the analytical data were processed using SOLMINEQ88 (Kharaka, 1988) to study the chemical equilibria (computation of the PCO_2, saturation indices, chemical geothermometers, etc.). Finally we used Factor Analysis and Cluster Analysis statistical techniques to investigate both the geochemical processes connected to each of the groundwater families, and the relation between the different aquifers in the earthquake zone.

3. Data description

Table I shows the analytical results obtained on a total of 66 samples, which were collected during the hydrogeochemical surveys performed between December 1990 and June 1992. The Chebotarev diagram (fig. 3) shows the general chemism of the Iblean Foreland groundwaters, and on the triangular diagram (fig. 4) we distinguished different groundwater groups belonging to different basins. The geochemical processes which influenced the different evolutionary trends will be discussed later. Different types of groundwater may be also grouped based on their geo-structural location: the surveys are carried out in three peculiar areas to understand the different geochemical patterns, also in relation to the 1990 seismogenic structure. The structural areas are:

1) *Vizzini fault system (E-W and NE-SW)* – 40 km far from the 1990 epicentral zone: groundwaters (No. 1-2-3) mixing between sulphate waters probably interacting with oil deposits (Vizzini I Well, AGIP), and superficial bicarbonate waters; the electrical conductivity reaches 1.5 mS/cm. This fault system was not involved in the 1990 earthquake and our studies did not show a possible implication with some stress-field variation.

2) *Lentini Graben and Mineo geothermal field* – 25-30 km far from the 1990 epicentral zone: thermal waters of Na-HCO_3 type related to the CO_2 rich Mineo geothermal field. The groundwater shows a strong water-rock interaction with clayey minerals, in presence of high PCO_2 at depth, but no anomalies were pointed out with the earthquake.

The samples No. 4-10-11-15-16-76-77 were collected in the plain of the Lentini Graben and indicate the presence of a thermal artesian aquifer, while sample No. 78 and those collected close to the village of Lentini (No. 5-23) belong to cold surface aquifers. The samples No. 10-15-16-11, collected in the *Paparone* and *Buongiovanni* wells, along the fault system bordering the graben to the east, are the most representative of the thermal aquifer. They exhibit a purely bicarbonate-alkaline chemism with a high pH (≥ 8.0). Although all the other samples are characterized by high reaction values for Na^+-HCO_3^- and by the almost total disappearance of bivalent cations (ionic exchange processes in the clayey sediments of the graben), their chemism changes depending on the degree of mixing with surface aquifers. This geochemical evolution is favoured by lo-

Table I. Analytical data for 66 samples: December 1990-May 1991 surveys and June 1992 survey.

No.	Date d/m/y	Site	Temp. °C	*pH*	*Eh* mV	*Cond.* mS/cm	*Ca* meq/l	*Mg* meq/l	*Na* meq/l	*K* meq/l	HCO_3 meq/l	SO_4 meq/l	*Cl* meq/l	SiO_2 ppm	*B* ppm	*Sr* ppm	*Li* ppb	*As* ppb	*Rn* pCi/l	*He* ppb v/v
I Survey																				
1	18-12-90	W. Balada 1	16.8	7.26	495	1.149	6.86	2.50	1.72	0.150	5.90	3.04	1.62	20.15	0.20	1.80	8.80	n.d.	163	152
2	18-12-90	S. Balada	14.3	7.25	500	1.095	8.28	1.70	1.23	0.032	6.50	2.85	1.10	47.54	≤0.05	1.00	3.10	n.d.	131	n.d.
3	18-12-90	W. Balada 2	17.4	7.58	494	1.150	4.54	3.92	3.95	0.184	4.90	5.52	1.62	16.21	0.322	2.35	8.50	n.d.	23	n.d.
4	19-12-90	W. Cozzarelle 1	28.9	7.95	496	0.681	1.32	2.17	3.20	0.292	2.70	2.74	0.99	31.35	≤0.05	0.70	4.40	0.16	128	131
5	19-12-90	W. Mulinelli	18.7	7.24	471	1.130	3.65	2.00	5.03	0.160	5.42	1.99	4.15	32.54	0.41	n.d.	1.05	4.1	157	339
6	20-12-90	W. Trovato	18.8	7.39	457	0.706	1.35	3.29	2.43	0.171	5.53	0.56	1.83	28.23	≤0.05	1.95	6.70	n.d.	156	n.d.
7	20-12-90	S. Sulfurea Brucoli	19.8	7.00	282	24.600	9.36	52.50	187.00	5.800	4.24	25.00	218.00	20.13	2.09	2.65	73.00	0.36	689	72
8	20-12-90	S. Sampieri	18.6	7.02	506	1.690	6.85	0.82	2.37	0.080	5.24	2.03	1.90	20.03	≤0.05	0.50	2.20	n.d.	148	n.d.
9	20-12-90	W. Mangiamele	18.8	7.07	517	0.811	4.36	0.75	1.37	0.080	4.95	0.71	1.35	24.91	≤0.05	0.45	1.40	n.d.	874	49
10	20-12-90	W. Paparone	27.1	8.38	491	1.207	0.09	0.01	10.60	0.158	4.40	3.18	3.87	34.13	0.50	≤0.20	4.70	0.88	222	n.d.
11	20-12-90	W. Buongiovanni	24.8	8.45	498	0.892	0.05	0.06	8.50	0.125	6.10	1.55	1.83	13.16	0.83	≤0.20	3.40	3.10	162	n.d.
II Survey																				
12	22-01-91	W. Murabito	19.1	6.74	456	0.512	2.25	1.78	0.62	0.034	3.84	0.16	0.42	23.33	≤0.05	0.80	1.5	n.d.	50	45
13	22-01-91	W. Buda	18.8	6.78	460	0.479	2.25	1.50	0.72	0.038	4.26	0.19	0.48	26.07	≤0.05	0.80	1.6	n.d.	161	54
14	23-01-91	W. Cozzarelle 1	28.5	7.40	426	0.654	1.32	2.17	3.25	0.290	3.20	3.00	0.77	32.06	≤0.05	0.60	4.8	1.52	131	131
15	23-01-91	W. Paparone	27.3	8.42	388	1.189	0.07	0.01	10.70	0.154	4.39	3.38	4.01	33.77	0.52	≤0.20	4.7	0.66	164	n.d.
16	23-01-91	W. Buongiovanni	22.3	8.82	383	0.919	0.04	0.015	9.10	0.175	6.08	1.92	1.72	12.50	0.83	≤0.20	1.6	1.06	243	222
17	24-01-91	S. Sulfurea Brucoli	20.1	7.34	295	11.960	3.34	24.50	92.80	0.272	3.82	10.65	106.00	10.35	1.02	1.75	31	0.40	696	772
18	24-01-91	W. Trovato	19.2	8.10	515	0.907	1.60	3.00	3.40	0.148	4.82	0.83	1.69	27.28	≤0.05	1.90	6.8	n.d.	198	258
19	24-01-91	S. Sampieri	18.9	7.00	475	1.074	7.80	0.95	2.38	0.061	5.38	2.30	1.65	19.56	≤0.05	0.60	1.9	n.d.	113	655
20	24-01-91	W. La Ferla	17.3	7.42	465	0.498	2.09	2.67	0.68	0.021	4.30	0.21	0.70	10.96	≤0.05	0.25	0.6	n.d.	77	82
21	24-01-91	W. S. Calogero	19.9	7.41	440	0.526	1.55	1.50	2.05	0.268	4.44	0.26	1.13	23.10	≤0.05	0.30	5.3	n.d.	235	52
22	25-01-91	W. S. Calogero rom.	16.6	7.56	455	0.636	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	59	n.d.
23	25-01-91	W. Mulinelli	19.1	7.43	448	1.113	3.43	1.85	5.64	0.171	4.86	1.92	4.44	33.11	0.48	1.05	5.3	n.d.	283	n.d.
24	25-01-91	W. Pagliaro	16.2	7.05	464	1.018	6.40	2.60	1.66	0.118	5.70	2.18	1.76	24.30	≤0.05	0.70	2.5	n.d.	325	34
25	25-01-91	W. Frandanisi	18.4	7.19	460	0.849	4.10	2.24	1.78	0.150	5.00	2.11	2.11	31.94	≤0.05	1.00	5.6	n.d.	188	n.d.
26	25-01-91	W. Mangiamele	18.5	7.15	465	0.703	4.66	1.00	1.46	0.100	4.78	0.75	1.72	24.58	≤0.05	0.50	1.6	n.d.	388	184

Table I *(continued)*.

No.	Date d/m/y	Site	Temp. °C	*pH*	*Eh* mV	*Cond.* mS/cm	*Ca* meq/l	*Mg* meq/l	*Na* meq/l	*K* meq/l	HCO_3 meq/l	SO_4 meq/l	*Cl* meq/l	SiO_2 ppm	*B* ppm	*Sr* ppm	*Li* ppb	*As* ppb	*Rn* pCi/l	*He* ppb v/v
III Survey																				
28	27-02-91	S. Sulfurea Brucoli	19.8	7.26	141	25.500	11.48	48.00	188.75	7.39	4.65	27.50	275.00	9.93	1.98	3.35	n.d.	0.46	515	100
29	27-02-91	Sea Brucoli Bay	15.6	8.08	364	58.000	28.70	115.00	490.00	11.40	2.84	76.00	632.00	0.12	4.40	6.35	n.d.	n.d.	n.d.	n.d.
30	28-02-91	S. Sampieri	18.5	7.01	n.d.	1.130	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	147	n.d.
31	28-02-91	W. Pagliaro	16.6	6.88	n.d.	1.070	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	252	n.d.
32	28-02-91	W. Andolina	18.3	7.40	n.d.	0.707	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	219	n.d.
33	28-02-91	W. Eras 7	19.3	7.28	n.d.	0.678	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	190	6 (°)
34	28-02-91	W. Mangiamele	18.7	7.44	n.d.	1.127	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	517	n.d.
35	28-02-91	S. Mangiamele	18.3	7.07	n.d.	0.975	6.25	0.95	18.00	0.075	4.57	1.50	1.24	25.12	≤ 0.05	0.60	n.d.	n.d.	299	n.d.
IV Survey																				
36	30-04-91	W. Mangiamele	20.0	6.95	469	0.747	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d	n.d.	508	88
37	30-04-91	S. Mangiamele Int.	17.7	7.10	441	0.907	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	266	n.d.
38	30-04-91	S. Mangiamele	18.8	7.08	495	0.875	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	281	n.d.
39	01-05-91	S. Sulfurea Brucoli	20.3	7.37	−25	17.100	6.75	22.25	98.00	3.60	4.60	14.50	n.d.	35.35	1.46	1.60	n.d.	8.00	987	37
40	01-05-91	Sea Brucoli Canal	19.9	8.08	226	53.700	18.50	104.40	390.00	9.50	2.90	84.00	n.d.	0.89	3.80	n.d.	n.d.	n.d.	n.d	n.d.
41	01-05-91	S. Sampieri	18.7	7.07	391	1.167	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	207	n.d.
42	01-05-91	W. Trovato	21.3	7.95	367	0.797	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	180	n.d.
43	01-05-91	W. Pagliaro	16.5	7.21	404	1.077	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	391	n.d.
44	01-05-91	S. San Cusimano	17.9	7.29	354	0.535	3.53	1.11	0.645	0.04	3.83	0.56	0.98	14.68	0.05	0.60	n.d.	n.d.	243	n.d.
45	03-05-91	S. Mangiamele Int.	18.5	7.36	396	0.911	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	183	n.d.
46	03-05-91	S. Sulfurea Brucoli	20.1	7.40	−32	23.500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	911	n.d.
47	03-05-91	W. Castro di Sotto	17.5	7.16	411	0.984	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	409	n.d.
48	03-05-91	W. Luogo Grande	16.5	7.33	394	1.063	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	108	n.d.

Table I (*continued*).

No.	Date d/m/y	Site	Temp. °C	*pH*	*Eh* mV	*Cond.* mS/cm	*Ca* meq/l	*Mg* meq/l	*Na* meq/l	*K* meq/l	HCO_3 meq/l	SO_4 meq/l	*Cl* meq/l	SiO_2 ppm	NH_3 ppm	*Sr* ppm	*Li* ppb	*Fe* ppm	*Mn* ppm	*As* ppb	*Rn* pCi/l	*He* ppb v/v
1992 Survey																						
55	10-06-92	S. Sulfurea di Brucoli	19.8	7.46	–94	24500	8.62	46.43	177.38	4.200	4.94	23.500	210.60	8.93	0.958	2.68	59.50	≤ 0.02	0.11	9.020	644	38
56	10-06-92	W. Cimitero Augusta	21.7	8.51	–36	1401	0.56	2.26	9.95	0.490	5.79	0.350	7.45	23.00	1.689	1.70	6.90	≤ 0.02	≤ 0.02	0.242	276	32
57	10-06-92	W. S. Giorgio Com.	22.9	8.04	320	894	0.65	2.06	5.60	0.270	5.00	0.880	2.73	18.38	0.215	0.70	5.50	≤ 0.02	≤ 0.02	n.d.	279	27
58	10-06-92	W. Reitano Com.	21.9	7.79	305	674	1.25	3.62	2.72	0.210	5.23	0.810	1.46	22.06	0.064	2.50	7.00	≤ 0.02	≤ 0.02	0.374	213	n.d.
59	10-06-92	W. Vignali I Com.	21.2	7.67	320	649	0.68	3.42	2.85	0.214	4.61	0.650	1.42	20.57	0.159	1.31	5.65	≤ 0.02	≤ 0.02	n.d.	248	21
60	10-06-92	W. Vignali II Com.	21.2	7.92	335	659	0.49	2.98	3.48	0.220	5.08	0.570	1.63	18.65	n.d.	1.15	5.90	≤ 0.02	≤ 0.02	n.d.	235	n.d.
61	11-06-92	W. Villa Salus	24.3	8.48	–74	1880	0.60	2.65	16.00	0.570	5.79	0.370	11.40	27.18	2.231	2.90	6.50	≤ 0.02	≤ 0.02	0.440	103	49
62	11-06-92	W. Serena Com.	24.4	8.27	–5	1093	0.54	2.28	7.60	0.390	4.89	0.550	4.59	19.70	0.492	2.10	5.90	≤ 0.02	≤ 0.02	0.132	271	26
63	11-06-92	W. Giummo Com.	23.1	8.26	60	1032	0.55	2.88	6.25	0.360	4.63	0.600	3.96	17.42	0.386	2.10	5.85	≤ 0.02	≤ 0.02	n.d.	319	23
64	11-06-92	W. 87 Com.	22.9	7.58	365	810	1.45	2.96	3.75	0.170	5.38	0.990	1.56	20.80	0.016	0.75	4.80	≤ 0.02	≤ 0.02	n.d.	168	11
65	11-06-92	W. Mangiamele	19.6	7.06	417	709	4.30	0.91	1.39	0.085	4.57	0.785	1.15	22.12	0.027	0.60	1.40	≤ 0.02	≤ 0.02	n.d.	386	11
66	11-06-92	W. Acqua Tre Stelle	23.4	7.71	391	1870	4.25	8.08	6.80	0.496	3.97	1.870	13.30	34.38	0.115	5.51	22.00	≤ 0.02	≤ 0.02	n.d.	448	63
67	12-06-92	W. Riera	20.7	7.11	463	626	1.55	2.66	1.33	0.028	4.35	0.310	0.98	13.73	0.025	0.20	6.00	≤ 0.02	≤ 0.02	n.d.	161	69
68	12-06-92	W. B Valtur	19.8	7.40	367	842	2.72	3.36	2.48	0.130	5.16	1.110	1.64	31.04	0.020	1.55	6.30	≤ 0.02	≤ 0.02	n.d.	406	92
69	12-06-92	W. A Valtur	19.3	7.27	447	969	3.52	3.80	2.47	0.300	5.74	1.650	1.80	31.30	0.019	1.05	4.80	≤ 0.02	≤ 0.02	n.d.	244	n.d.
70	12-06-92	W. Europa Club	20.7	7.50	471	886	1.20	2.74	5.00	0.200	5.01	0.900	2.55	18.81	0.023	0.60	4.90	≤ 0.02	≤ 0.02	n.d.	79	28
71	12-06-92	W. Monteamara	20.7	7.49	513	636	1.95	3.20	1.74	0.060	4.85	0.340	1.12	15.34	0.020	≤ 0.20	6.50	≤ 0.02	≤ 0.02	n.d.	272	5
72	13-06-92	W. Genio Marina I	24.6	7.99	384	1015	0.75	1.60	6.34	0.300	5.21	1.075	2.84	16.78	0.117	0.65	7.25	≤ 0.02	≤ 0.02	1.056	226	34
73	13-06-92	W. Genio Marina II	24.1	8.04	312	1098	0.55	1.71	8.00	0.330	5.43	0.950	3.29	17.72	0.353	0.75	7.30	≤ 0.02	≤ 0.02	n.d.	261	35
74	13-06-92	S. Puzzillo Brucoli	21.0	7.30	–72	1317	5.19	4.53	2.78	0.510	4.99	1.375	5.88	23.51	0.039	2.10	8.40	≤ 0.02	0.065	n.d.	83	22
75	13-06-92	S. Villasmundo	19.6	8.12	465	525	2.20	1.75	1.13	0.029	4.18	0.325	0.55	61.05	0.005	≤ 0.20	2.10	≤ 0.02	≤ 0.02	n.d.	25	n.d.
76	14-06-92	W. Serra Pagliaccio	28.0	7.94	446	641	1.90	2.85	2.13	0.180	3.51	3.080	0.49	36.92	0.015	1.79	6.00	≤ 0.02	≤ 0.02	2.992	119	42
77	14-06-92	W. La Fanusa	25.8	8.00	378	693	1.23	2.21	4.10	0.250	4.33	1.200	1.58	27.88	n.d.	≤ 0.20	2.50	≤ 0.02	≤ 0.02	n.d.	72	45
78	14-06-92	W. Porta Chiusa	20.9	7.53	366	1221	4.25	7.35	2.53	0.174	5.48	5.630	1.62	27.85	0.005	3.78	9.00	≤ 0.02	≤ 0.02	1.892	279	n.d.
79	15-06-92	W. Donizella Mineo I	24.0	7.49	417	1920	4.33	8.95	11.65	0.277	7.58	12.200	3.23	28.20	0.005	0.55	10.50	≤ 0.02	≤ 0.02	0.572	184	536
80	15-06-92	W. Donizella Mineo II	23.0	8.31	414	1038	1.47	2.20	6.72	0.160	5.02	3.320	1.71	29.18	0.005	0.75	3.20	≤ 0.02	≤ 0.02	n.d.	n.d.	n.d.
81	15-06-92	W. Poggio Pizzuti (A)	23.2	9.16	357	1320	0.40	0.41	10.44	0.280	6.26	4.170	1.38	25.29	0.010	≤ 0.20	2.50	0.10	≤ 0.02	1.914	569	342
82	26-09-92	W. Poggio Pizzuti (B)	33.0	7.12	–67	2930	13.45	6.25	12.00	0.460	22.41	4.540	3.56	44.30	0.067	6.68	n.d.	3.20	0.065	0.440	n.d.	316
67A	16-01-92	W. Riera	32.0	n.d.	n.d.	n.d.	3.80	2.75	1.42	0.040	6.69	0.325	1.00	15.83	n.d.	≤ 0.20	1.20	≤ 0.02	≤ 0.02	0.484	n.d.	n.d.
67B	16-01-92	W. Riera	32.0	n.d.	n.d.	n.d.	3.80	2.83	1.42	0.040	6.75	0.315	1.03	15.76	n.d.	≤ 0.20	1.20	≤ 0.02	≤ 0.02	n.d.	n.d.	n.d.
67C	25-01-92	W. Riera	25.0	n.d.	n.d.	n.d.	2.50	2.91	1.37	0.035	5.47	0.272	1.08	14.21	n.d.	≤ 0.20	0.90	≤ 0.02	≤ 0.02	n.d.	n.d.	n.d.
67D	25-01-92	W. Riera	25.0	n.d.	n.d.	n.d.	1.55	2.75	1.37	0.032	4.35	0.302	1.05	13.86	n.d.	≤ 0.20	1.20	≤ 0.02	≤ 0.02	n.d.	n.d.	n.d.
67E	06-02-92	W. Riera	21.0	n.d.	n.d.	n.d.	1.55	2.66	1.37	0.032	4.28	0.248	1.08	14.27	n.d.	≤ 0.20	1.00	≤ 0.02	≤ 0.02	n.d.	n.d.	n.d.
67F	06-02-92	W. Riera	21.0	n.d.	n.d.	n.d.	1.65	2.75	1.37	0.032	4.44	0.250	1.11	13.63	n.d.	≤ 0.20	1.00	≤ 0.02	≤ 0.02	0.231	n.d.	n.d.

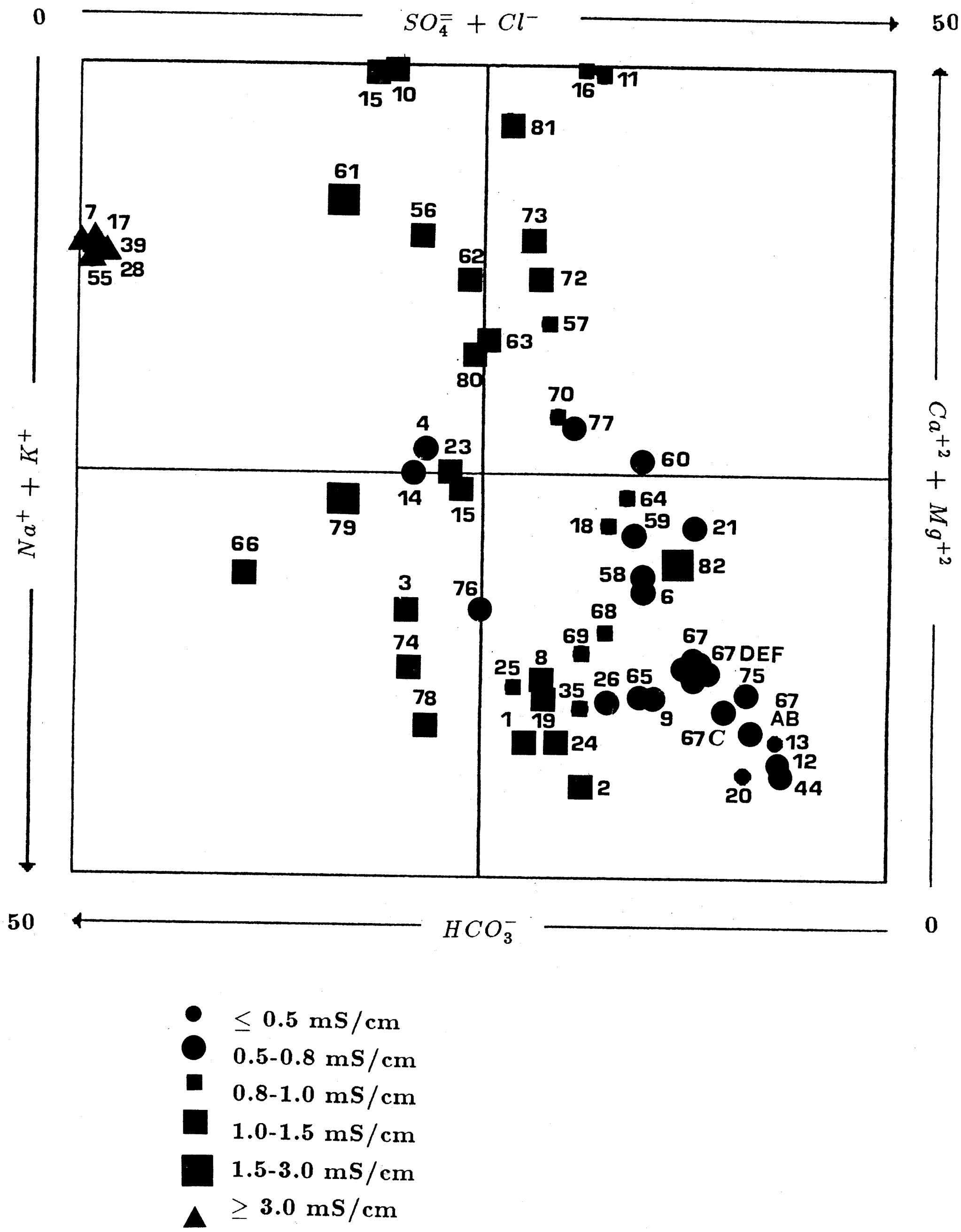


Fig. 3. Chebotarev diagram for the Iblean Foreland groundwaters. Six groups are distinguished considering electrical conductivity (mS/cm).

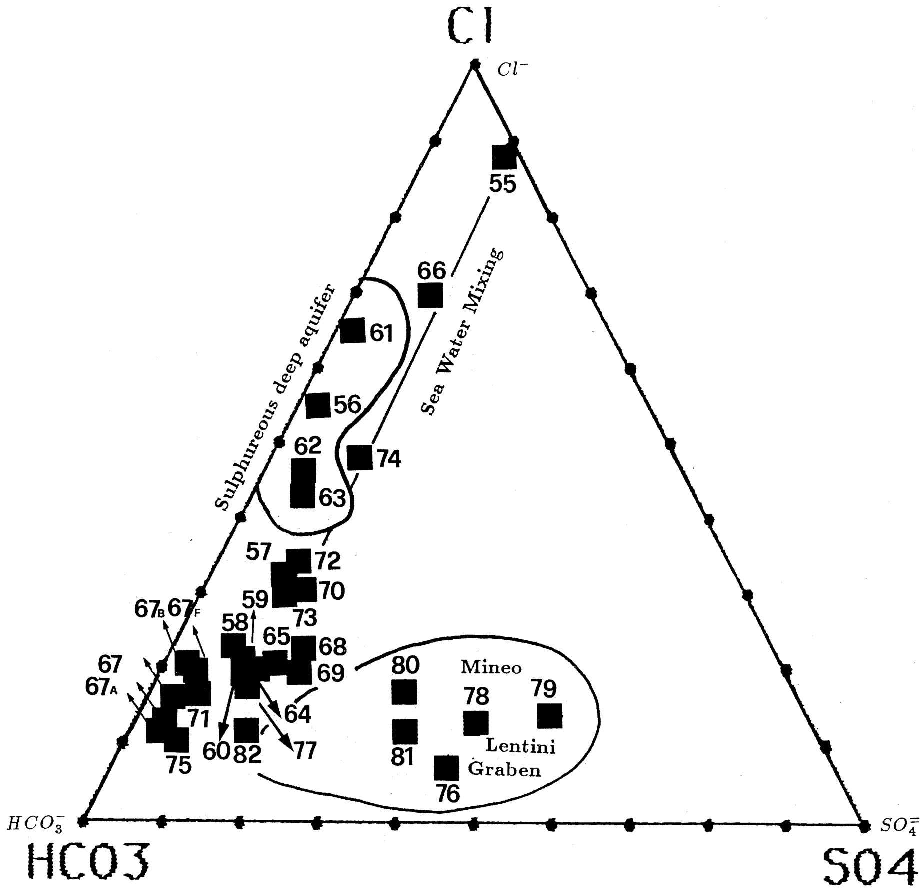


Fig. 4. HCO_3-SO_4-Cl triangular diagram: it is possible to discriminate the mixing between superficial waters and chloride-sulphureous deep groundwaters of the Augusta Graben. The Lentini Graben-Mineo groundwaters show an SO_4 input from a geothermal reservoir.

cal geologic structures (*i.e.*, deep anticlines folds and/or fault planes with slow fluids circulation). Indeed, based on hydrogeologic investigations (Ferrara Vincenzo, personal communication, 1992), a hydraulic continuity between this thermal aquifer, the geothermal anomaly of Mineo, and the deep thermal basins in the Catania-Simeto plain should be excluded. The geothermal Mineo anomaly is discussed later.

3) *Brucoli-Augusta Graben* – 5-10 km far from the 1990 epicentral zone: cold groundwaters contaminated by sea water infiltrating along the graben faults. Discharges of He, ^{222}Rn, H_2S, NH_3 and CO_2 were observed, particularly in the area of the Brucoli, that shows space-time anomalies in concomitance with the 1990 seismic activity (see later).

In this area purely chloride-alkaline waters are found: this group includes all the samples collected in *Brucoli Sulphureous Spring* (No. 7-17-28-39-55) and the seawater samples from Brucoli (No. 29 and 40); their electrical conductivity exceeds 10 mS/cm (fig. 5).

In fig. 4 the triangular diagram of the main anions, including all of the most representative samples, clearly shows two water families with an evolutionary trend (No. 61-56-62-63): a deep sulphureous artesian aquifer with chloride-bicarbonate alkaline chemism is mixing with superficial waters. In this deep aquifer, reducing species (H_2S, NH_3) are found, that decrease the redox potential values with a specific geo-structural meaning, as discussed later.

4) *Superficial aquifers in the Iblean Foreland* – The superficial aquifers of the Iblean Foreland show different water chemism.

i) Purely bicarbonate earthy-alkaline waters (el. cond. $\simeq$ 0.5 mS/cm); the most representative samples are those collected at the high flow (≥ 1 m^3/s) San Cusimano spring (No. 44). The spring carries the groundwater that circulates in the volcanites-calcarenites sequence typical of this portion of the Iblean Foreland. This group includes samples No. 12-13-20-24 and samples No. 67 A-F.

ii) Bicarbonate earthy-alkaline waters (No. 8-9-19-21-24-25-26-35-65) exhibiting a small content of Mg and Cl, which can be attributed to a slight mixing with seawater, as shown by the electrical conductivity values reaching 1.5 mS/cm.

iii) Superficial groundwaters with a mixing of seawater in the Brucoli-Augusta area. It is possible to identify two subgroups, based on the different degree of seawater mixing:

- bicarbonate-chloride earthy-alkaline and alkaline waters (No. 6-18-68-69-70), with electrical conductivity slightly higher than that of the average superficial groundwaters (0.8-1.6 mS/cm);
- chloride-bicarbonate earthy-alkaline and alkaline waters exhibiting a considerable content of seawater: *Acqua Tre Stelle* (No. 66) and *Acqua Puzzillo* from Brucoli (No. 74) are representative; the latter also exhibits an H_2S input. Because of the content of Mg and Cl, the electrical conductivity of these waters is in the range 1.3-1.8 mS/cm.

4. Data discussion

In this section, we discuss the geochemical processes and the anomalies in space and in

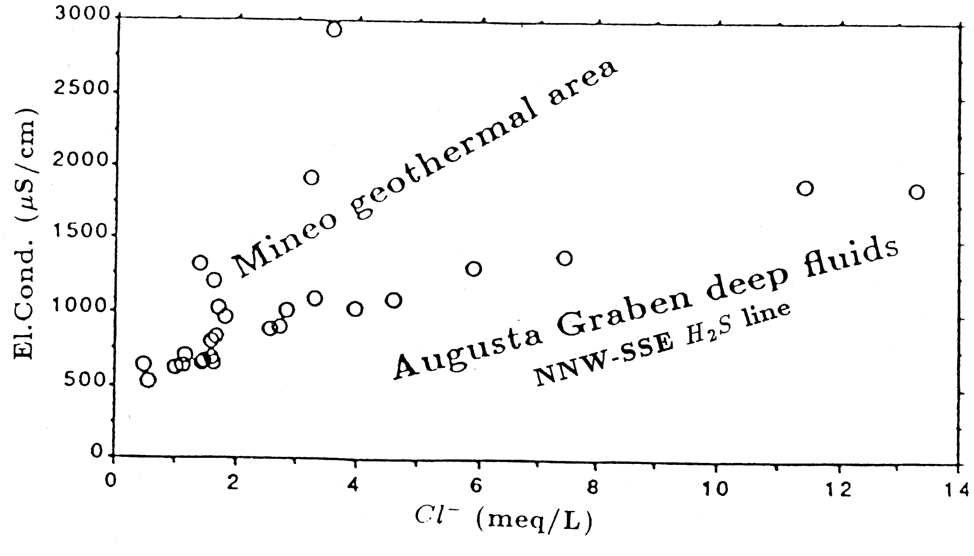


Fig. 5. Correlation diagram of Cl (meq/L) versus electrical conductivity (μS/cm), for the all Iblean Foreland samples. It is possible to distinguish the two deep circulations in the Augusta Graben and in the Mineo areas.

time, in relation to the geodynamic events and with the geostructural setting of the studied area. However, the extent and type of the performed geochemical prospecting permit the dataset (table I) to be used also for hydrogeology and environmental geochemistry.

4.1. *Hydrogeochemical anomalies of the north-eastern portion of the Iblean Foreland*

The differences between the investigated aquifers are not only related to their general chemism and physico-chemical parameters, but also to their content of some minor and trace elements, which are closely related to the geostructural and hydrogeological settings. We discovered spatial anomalies for some of the parameters related to the flow of deep gases (CO_2, H_2S, NH_3, ^{222}Rn). In the attempt to find a possible correlation between these anomalies, the structural setting, and seismotectonic evidence, especially for the 1990 earthquake, we drew up contour line maps of the PCO_2 values computed by SOLMINEQ88, and of the Eh and ^{222}Rn values.

The contour line maps (fig. 7a-c) show two main anomalous areas: Brucoli-Augusta and Mineo. Both these anomalies are located close to important neotectonic structures. In particular, the former is located at the intersection between regional fault systems trending NNW-SSE (Ibleo-Maltese Escarpment) and ENE-WSW Lentini-Agnone line, while the location of the latter coincides with the geothermal area of Mineo, which is characterized by the mainly ENE-WSW fault system that border the Lentini-Scordia Graben crossing the N-S system (fig. 1).

4.2. *The sulphureous aquifer in the Augusta Graben and its geostructural meaning*

Immediately after the December 13, 1990 earthquake, we collected information concerning the presence of H_2S in deep wells drilled along the NNW-SSE fault bordering Mt. Tauro. This information lead us to the detailed identification (table II) of a sulphureous artesian reservoir, buried in sandy sediments. The top of these sediments is located at a depth of approximately 340 m, considerably below sea level, and underlying 300 m of Pleistocene clays. Although the artesian aquifer extends along the whole Augusta area, H_2S and NH_3 were only found in the wells drilled along the above-mentioned NNW-SSE fault (figs. 6 and 7a-c).

The gaseous uprising along this fault is a peculiar and unique feauture throughout the Iblean Foreland; this fact should witness that

Table II. Sulphureous sample sites within the *Augusta Graben*, that are aligned in a NNW-SSE line along the direction of the Ibleo-Maltese Escarpment: they are interesting for geochemical monitoring in seismic surveillance due to the presence of deep-fluids (H_2S, NH_3, CO_2, ^{222}Rn).

Site	Lat.N	Long.E from M.M.	Altit. m	Stat.lev. m	Depth m	Discarge *L*/s
Sulfurea Brucoli	37°16′56″	02°43′59″	0	1	–	3
Acqua Puzzillo	37°16′49″	02°44′25″	0	4	6	–
Pozzo Valtur C	37°16′02″	02°43′48″	55	–	300	–
Pozzo Serena	37°15′50″	02°44′39″	47	185	320	18
Pozzo Giummo	37°15′54″	02°44′51″	47	200	285	15
Pozzo Villasalus	37°15′33″	02°45′25″	22	280	315	20
Pozzo Cimitero Augusta	37°15′04″	02°46′01″	5	260	290	3
Pozzo Cittadella	37°14′02″	02°46′12″	5	–	300	25
Pozzo SO.CO.VA	37°13′14″	02°46′20″	10	70	456	30

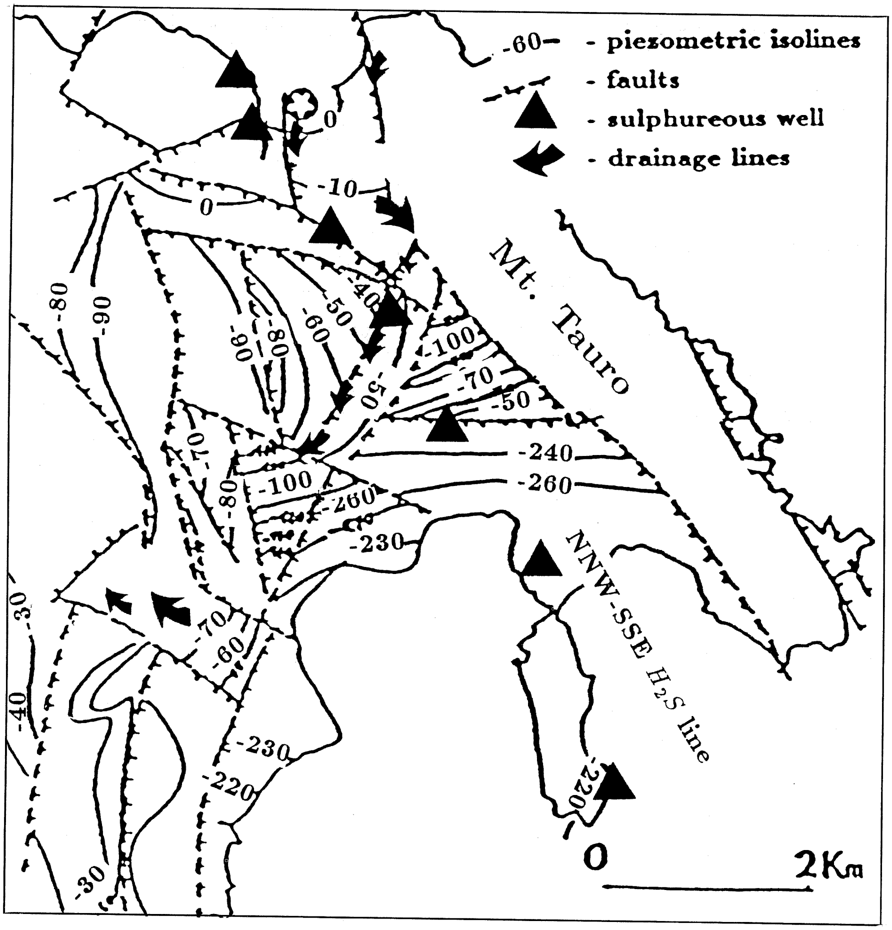
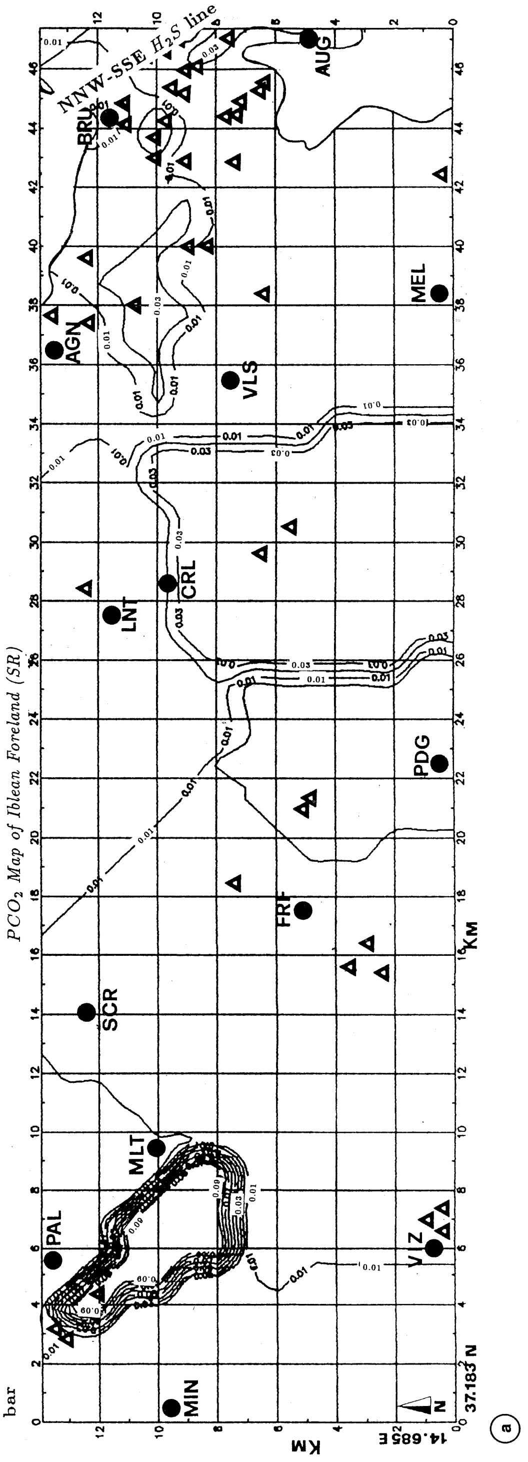


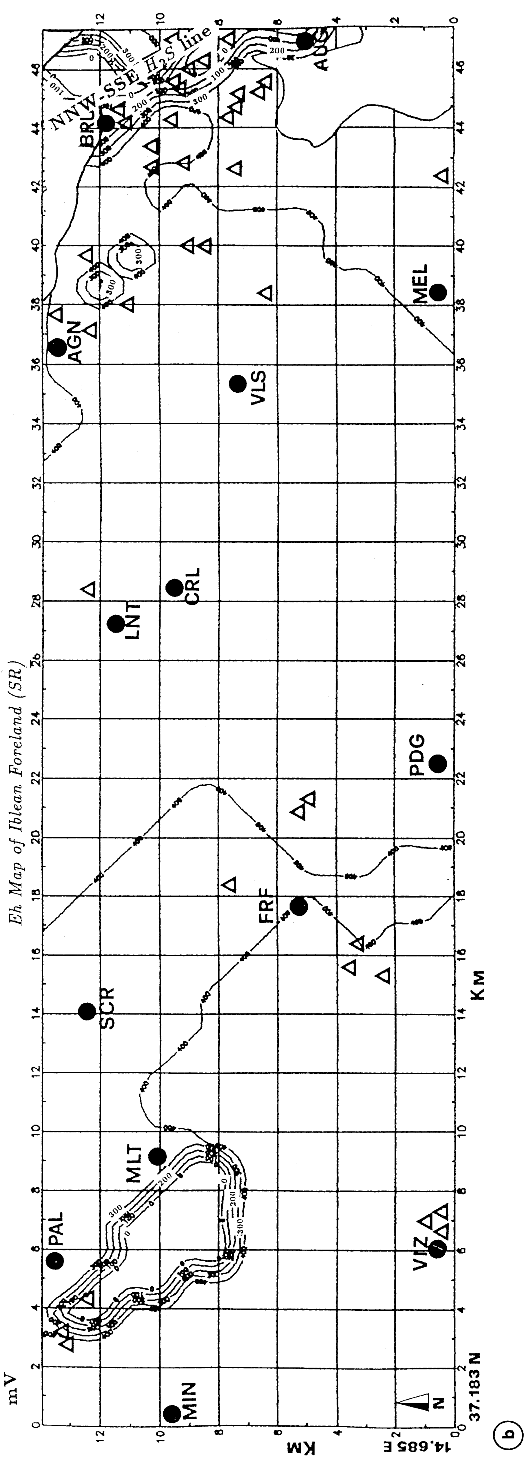
Fig. 6. Piezometric contouring map of the deep aquifer (mt. from s.l.) and sea-water contamination channels along the faults of the Augusta Graben. The stars indicate the sulphureous deep sites along a NNW-SSE line. Modified from Aureli, 1989.

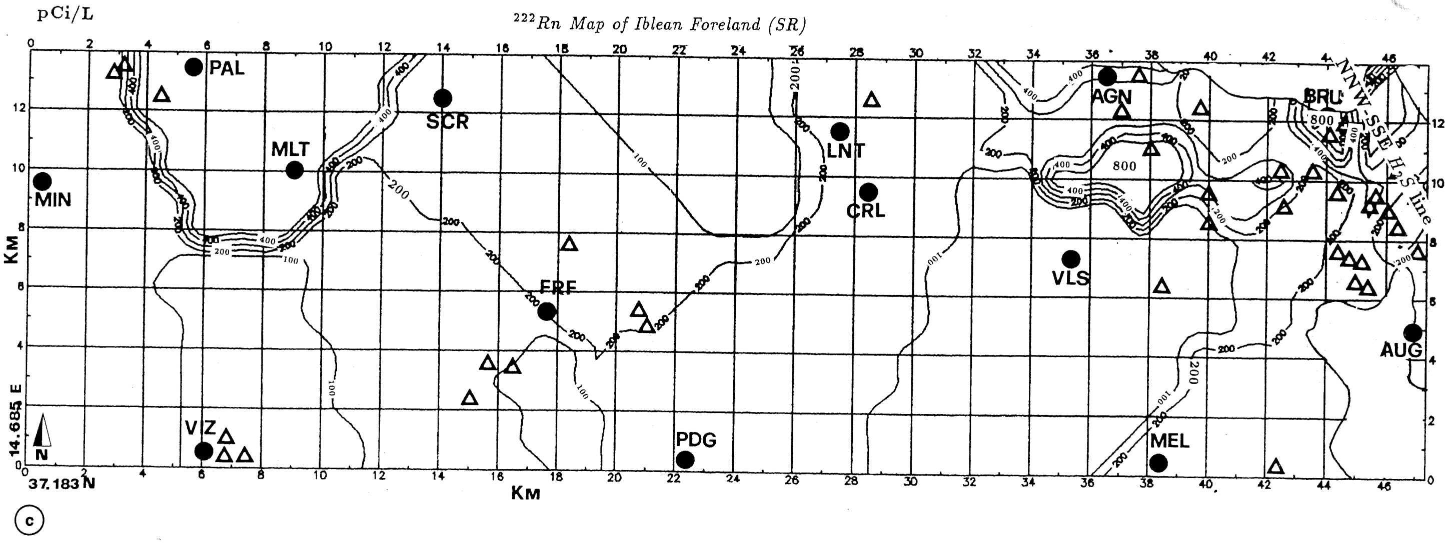
this fault is active (not sealing, high permeability to deep-fluids, linear geometry, variation in time of gaseous flow, etc..).

In particular, the existence of anomalous reducing gaseous flows and other geochemical characteristics such as a low redox potential, high pH values, chlorides chemism, relatively high content of ^{222}Rn, as well as the variation in time of geochemical flows accompanying seismic activity (see next section), are all possible evidence of deep-fluid activity correlated with the actual seismotectonic activity along the NNW-SSE stricking fault system (Ibleo-Maltese Escarpment). This hypothesis should be considered when locating the seismogenic structure responsible for the 1990 earthquake.

The geochemical characteristics of the sulphureous basin in the Augusta Graben are summarized in the results of the Factor Analysis (table III), which were performed on all the samples collected in the area of Augusta-Brucoli. These results reveal a relation between


PCO₂ Map of Iblean Foreland (SR)
bar
NNW-SSE H₂S line
MIN
PAL
MLT
SCR
FRF
LNT
CRL
PDG
VLS
AGN
MEL
BRU
AUG
VIZ
KM
14.685 E
37.183 N
N
a


Eh Map of Iblean Foreland (SR)
mV
NNW-SSE H₂S line
MIN
PAL
MLT
SCR
FRF
LNT
CRL
PDG
VLS
AGN
MEL
BRU
AUG
VIZ
KM
14.685 E
37.183 N
N
b



MIN = MINEO
VIZ = VIZZINI
PAL = PALAGONIA
MIL = MILITELLO
SCR = SCORDIA

FRF = FRANCOFORTE
PDG = PEDAGAGGI
LNT = LENTINI
CRL = CARLENTINI
AGN = AGNONE

VLS = VILLASMUNDO
BRU = BRUCOLI
AUG = AUGUSTA
MEL = MELILLI

Fig. 7a-c. Contouring maps of Eh, PCO_2 and ^{222}Rn values in the north-eastern Iblean Foreland. The *Surfer* code (kriging method) was used with kilometric coordinates computed from geographical coordinates (50 × 20 km grid from a starting point). The PCO_2 values (computed by SOLMINEQ88 code) contouring map (a) show that the highest value is concentrated in the Mineo area (up to 0.9 bar), with regard to the regional background value (0.1 bar). In the Eh contouring map (b), the main negative anomalies (reducing conditions) are located within the Augusta Graben (near the 1990 epicenter) and in the Mineo area. The Eh negative anomaly in the graben follows a NNW-SSE direction, along the Ibleo-Maltese Escarpment fault system. This structure is considered seismogenic and it is probably responsible for the December, 13, 1990 earthquake (Amato *et al.*, 1991). With regard to the ^{222}Rn values (c), positive anomalies, especially in the Brucoli area, can be distinguished; the highest values (up to 1000 pCi/L) were recorded suddenly after the earthquake, probably due to a stress-strain variation. These ^{222}Rn anomalies are located where the NNW-SSE fault system cut across the WSW-ENE system (Agnone-Carlentini line). Here, the fit hydrodynamic patterns allows the ^{222}Rn higher flow to be related to the stress-field conditions. The triangles correspond to the sampling sites.

Table III. Factor analysis related to the Brucoli-Augusta groundwaters sampled in June 1992 (asismic period). The data processing was performed with the Varimax Method (18 variables); scoring coefficients are listed for each sample, regarding the factor identified. The same data processing was applied to both 20 samples and 19 samples without the *Brucoli Sulphureous Spring*. In both the data managing, the deep sulphureous aquifer in the Augusta Graben is well characterized in a factor that includes temperature, pH, negative redox potential, HCO_3, NH_3, and also electrical conductivity, Cl, Na, K, testifying the deep circulation.

Variables	FACTOR1	FACTOR2	FACTOR3	No.	Site	FACTOR1	FACTOR2	FACTOR3
		Factor analysis					*Scoring coefficient*	
Temp.	−0.27249	**0.70634**	−0.01227	1	Sulfurea di Brucoli	**4.19765**	−0.05290	−0.40162
pH	−0.15258	**0.93231**	−0.01367	2	Cimitero Augusta	−0.12449	**1.76634**	0.14237
Eh	−0.46168	**−0.71145**	−0.07146	3	S. Giorgio Com.	−0.30378	0.22448	−0.62006
Cond.	**0.99269**	0.02964	−0.05079	4	Reitano Com.	−0.28764	0.07972	0.08630
Ca	**0.78437**	−0.40789	0.27160	5	Vignali 1 Com.	−0.29216	−0.33927	−0.34738
Mg	**0.99178**	−0.03850	0.01027	6	Vignali 2 Com.	−0.31306	−0.01557	−0.62562
Na	**0.98586**	0.07023	−0.07548	7	Villa Salus	−0.18920	**2.48284**	0.90605
K	**0.98971**	0.11560	−0.01690	8	Serena Com.	−0.20762	**1.13829**	−0.08244
HCO_3	−0.09180	**0.50536**	−0.10596	9	Giummo Com.	−0.16025	**0.74490**	−0.22079
SO_4	**0.99023**	−0.04165	−0.04470	10	Pozzo 87 Com.	−0.37389	−0.06467	−0.79481
Cl	**0.99317**	0.02903	−0.04775	11	Mangiamele	−0.17088	−1.45124	−0.26275
SiO_2	−0.38312	0.00802	0.86050	12	Acqua Tre Stelle	0.16741	−0.41183	2.94664
NH_3	0.25261	**0.82089**	0.13155	13	Riera M. Tauro	−0.33050	−1.30691	−0.43326
Sr	0.31974	0.31461	0.74901	14	Valtur B	−0.21847	−0.98629	1.72277
Li	**0.96989**	0.00769	0.11414	15	Valtur A	−0.27278	−1.01600	1.21783
^{222}Rn	**0.69964**	−0.17105	0.27688	16	Europa Club	−0.39401	−0.63784	−0.78570
^{4}He	0.04220	−0.16990	0.71784	17	Monteamara	−0.27362	−0.84928	−1.22702
Mn	**0.92327**	−0.04070	−0.07551	18	Genio Marina 1	−0.34354	**0.36913**	−0.72898
				19	Genio Marina 2	−0.29827	**0.59872**	−0.59265
Variance	9.406496	3.15201	2.032848	20	Acqua Puzzillo	0.18909	−0.27262	0.10113
		Factor analysis					*Scoring coefficient*	
Temp.	**0.74440**	−0.00847	−0.25017	1	Cimitero Augusta	**1.65782**	−0.42269	0.28599
pH	**0.91205**	−0.18043	−0.21429	2	S. Giorgio Com.	0.13061	−0.49980	−0.49759
Eh	**−0.75031**	0.01228	−0.46666	3	Reitano Com.	−0.26250	−0.09761	−0.17051
Cond.	**0.74618**	**0.58827**	0.18564	4	Vignali 1 Com.	−0.43041	−0.30987	−0.41904
Ca	−0.47597	**0.65931**	0.44949	5	Vignali 2 Com.	−0.20870	−0.58444	−0.33327
Mg	−0.04003	**0.88694**	0.01120	6	Villa Salus	**2.64018**	−0.09018	0.70160
Na	**0.96576**	0.02343	−0.02201	7	Serena Com.	**0.98380**	−0.36097	−0.36533
K	**0.80604**	0.41313	0.34424	8	Giummo Com.	**0.63705**	−0.25416	−0.59997
HCO_3	0.40093	−0.37100	0.35493	9	Pozzo 87 Com.	−0.33591	−0.50757	0.16613
SO_4	−0.25320	**0.76547**	0.17004	10	Mangiamele	−1.33017	−0.28430	0.02840
Cl	**0.72280**	**0.63228**	0.07937	11	Acqua Tre Stelle	0.38487	**3.63637**	−1.33481
SiO_2	0.10892	**0.79735**	0.12461	12	Riera M. Tauro	−1.11279	−0.54219	−0.39876
NH_3	**0.87602**	−0.11500	0.11024	13	Valtur B	−0.92656	**0.76686**	−0.40978
Sr	0.46065	**0.81042**	−0.05713	14	Valtur A	09.95327	**0.74273**	0.76014
Li	0.22987	**0.85141**	−0.20762	15	Europa Club	−0.48335	−0.50962	0.32415
^{222}Rn	−0.14306	0.43366	−0.61124	16	Monteamara	−0.89956	−0.63599	−0.48068
^{4}He	−0.05072	0.49533	−0.09875	17	Genio Marina 1	**0.28960**	−0.46957	−0.45850
Mn	−0.08255	0.21828	0.87146	18	Genio Marina 2	**0.56019**	−0.47841	−0.39701
				19	Acqua Puzzillo	−0.34087	**0.90139**	3.59869
Variance	6.137720	5.406495	2.059938					

geochemical variables and the clustering of samples belonging to the two different aquifers. Previous hydrogeological studies (fig. 6), aimed at the reconstruction of the deep aquifer (Aureli, 1989) pointed out the presence of deep and buried faults, leading to the identification of seeping seawater channels. However, the increase in the Cl content in the Augusta sulphureous aquifer is not only to be attributed to the possible seawater contamination along the fractures of the graben: we can relate the increase in chlorides (from Mg/Cl) to the deepening of the sulphureous circuit and to the long residence time in the reservoir; isotopic analyses could confirm this hypothesis. We exclude deep thermal anomalies in the area of the graben (constant and normal values of Li and B and the SiO_2 geothermometry.

We wish to point out a rather peculiar and isolated event. In January 1992, the water temperature of the *Pozzo Riera* (No. 67, 67a-f), located on Mt. Tauro, increased from 20 °C to 32 °C. The first two samples collected immediately after the event (January 16, 1992), exhibited no anomalies in any other physico-chemical parameters, nor in the content of $S^{=}$, NH_3, NO_3. They were characterized by a strong smell of hydrocarbons and a higher concentration of some elements compared to the following samples collected (January 25, 1992-June 12, 1992). In particular, we found in the first two samples an increase in HCO_3, SO_4, Ca, As and SiO_2, which was closely related to the temperature variation. Our hypothesis is that the surface aquifer of Mt. Tauro (overlying the sulphureous artesian basin) was subjected to an extraordinary supply of hot deep fluids, presumably involving an input of CO_2, which resulted in an increase in the bicarbonate content.

This phenomenon occurred in coincidence with the opening of the second eruptive fracture of Mt. Etna (1991-1992 eruption). The hypothesis that a structural continuity exists between the northeastern Iblean Foreland and Mt. Etna (*i.e.*, Patanè and Imposa, 1987; Ferrari, 1991), along the the Ibleo-Maltese Escarpment fault system, leads us to believe that the anomalous supply of fluids may be related to the current volcanic activity of Mt. Etna. The uprising of deep fluids could have been induced by the same stress field that resulted in the Mt. Etna eruption. Therefore, in concomitance either with the December, 1990 Syracuse earthquake or of the December, 1991 Etna eruption, the NNW-SSE Augusta Graben deep-fluid alignment was activated, witnessing the seismotectonic relevance of this fault system. However, this hypothesis should be confirmed by other theoretical and experimental studies.

4.3. *The monitoring of Brucoli Sulphureous Spring*

The Brucoli Sulphureous Spring is the only sulphureous mineral spring throughout this portion of the Iblean Foreland. The location of the spring within the Augusta graben, characterized by the NNW-SSE fault system, is the best argument that supports the hypothesis of upward deep fluids (H_2S, CO_2, NH_3, ^{222}Rn, He), which mix with local meteoric waters and seawater located overlooking the spring. For these reasons, we started to monitor the spring waters on the days following the 1990 earthquake, the epicenter of which was only a few kilometers away from Brucoli (Amato *et al.*, 1991).

The results obtained by analyzing the time series of the parameters connected to the supply of CO_2 (fig. 8a-d) lead us to consider the following:

i) the pH and PCO_2 (computed by SOLMINEQ88) trend values suggest an increase in the flow of CO_2 to the spring in concomitance with (or before ?) the mainshock. A slight PCO_2 decrease, in the months that followed, was observed (fig. 8a,b), progressively returning to *normal values* (June 1992). This supply of CO_2 may also have induced an increase in HCO_3 ions in solution;

ii) the flow of CO_2 may have induced a stripping of H_2S resulting in an increase in Eh (fig. 8c) up to + 300 mV on the days immediately following the earthquake, which then returned progressively to *normal values* ($\simeq -100$ mV);

iii) the results obtained using SOLMINEQ 88 show that this anomalous flow of CO_2 may

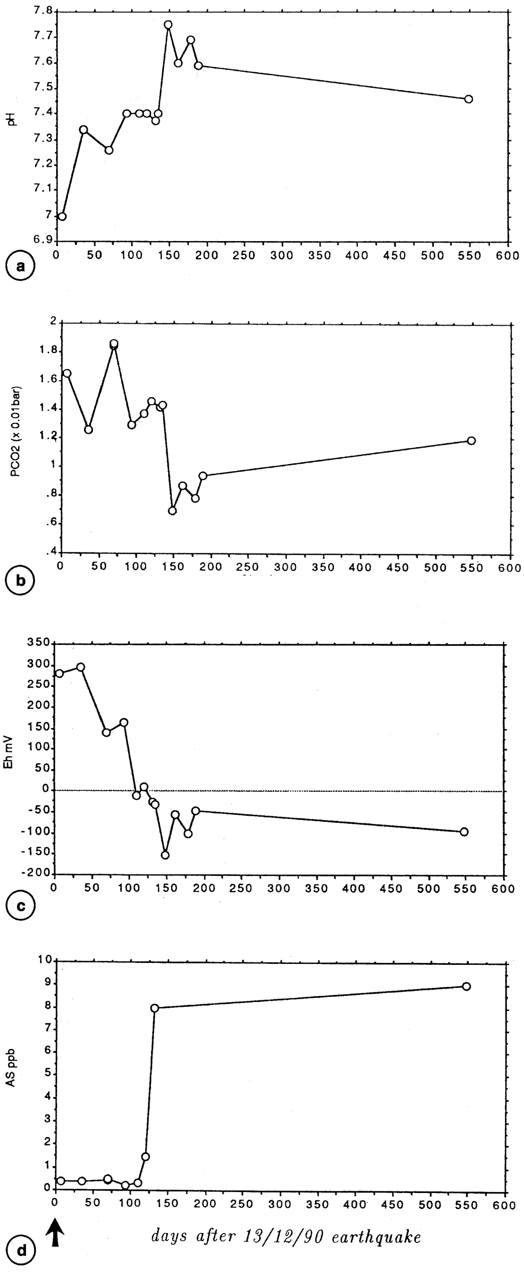


Fig. 8a-d. Temporal trends (December 1990-June 1992, starting from the Syracuse earthquake, M = 5.4) of some geochemical parameters in the *Brucoli Sulphureous Spring*: pH (a), CO_2 (b), Eh (c), As (d).

have produced a variation of the saturation indices of some carbonatic and silicatic phases (fig. 9a-c).

These three geochemical temporal trends enable us to put forward a very convincing and challenging hypothesis for the relation between fluid-geochemistry and seismogenic structure: a pore-pressure uprising could be generated in the core-proximity of the Syracuse, 1990 seismogenic fault, by a combination of processes including coseismic dilatancy, fracture permeability increase and fault-valve behavior (recharging fault with a deep CO_2 rich-fluid). It is during cosismic slip that most of the fracture porosity and permeability uprising should be generated near the principal slip-surface (Chester *et al.*, 1993.) The post seismic CO_2 decreasing could be explained because healing and sealing of fractures (also with $CaCO_3$ observed precipitation) are most important in the post-seismic period when dissolution and alteration within the fault-core are promoted.

iv) The relatively high content of B and Li witnesses a small contribution from a thermal reservoir. The anomalous gaseous flow was probably characterized by a thermal anomaly at depth, which could be related to a delay-variation of arsenic between December 1990 and June 1992 (fig. 8d).

4.4. *The geothermal anomaly of Mineo*

After drilling a deep well in the village of Poggio Pizzuti (near Palagonia), we found a thermal artesian aquifer (temperature reaching 65 °C) in the area of Palagonia-Mineo. It is common knowledge that this area is characterized by a low enthalpy geothermal anomaly, of which the main surface evidence is the lake of *Naftia* and the *Mofeta dei Palici* (Catalano *et al.*, 1988). In this area, we sampled three very close wells (No. 79-80-81-82), finding significant differences in their physico-chemical parameters as well as in their composition. These differences can be explained by taking into account the hydrogeological setting of the area (Ferrara Vincenzo, personal communication,

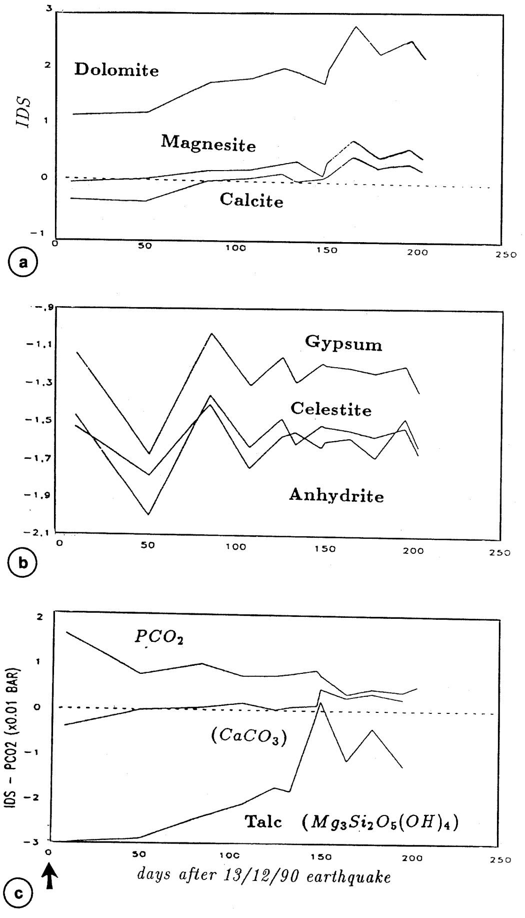


Fig. 9a-c. Temporal trends from December, 1990 to July, 1991 of saturation index computed by SOLMINEQ88 in the *Brucoli Sulphureous Spring*: carbonatic phases (a), sulphates (b), Talc-PCO_2-$CaCO_3$ (c).

1992), as well as the existence of a deep geothermal anomaly with a considerable release of CO_2. We hypothesize that ionic exchange processes occur at the bottom of the layer with minor permeability ($\simeq$ 200 m), separating the surface aquifer in the plio-pleistocene volcanites from the thermal deeper basin. In these processes the role of CO_2 is critical for the evolution of bicarbonate-alkaline waters. The high PCO_2 value (fig. 7a) in the thermal artesian aquifer also suggests the precipitation of $CaCO_3$ in the impervious layers. In June 1992, a purely Na-HCO_3 Lake of Naftia sample, in which the content of HCO_3 and Na exceeds 25 meq/L, was collected (Brozzo Giampiero, personal communication, 1992). The content of SO_4 found also in the purely Ca-sulphate River Caldo water, near Mineo, is high ($SO_4 \simeq 33$ meq/L), even if compared to values found in all the other waters sampled in the Iblean Foreland.

This kind of geochemical evolution of circulating fluids is commonly observed in geothermal areas (Dall'Aglio, 1991c; Duchi *et al.*, 1987), where thermal reservoirs with a high content of CO_2 are covered by impermeable rocks of considerable thickness, undergoing self-sealing processes. Therefore this area is particularly interesting for geochemical surveillance for earthquake prediction because the monitoring of these peculiar stratified aquifers may yield information on the possible fluido-dynamic variations of the hydrothermal confined reservoir, related to the stress field variations of this portion of the Iblean Foreland.

5. Conclusions

Two different conclusions emerge from the geochemical studies performed in the northern Iblean Foreland after the December 13, 1990 Syracuse earthquake.

1) Among the different aquifers investigated within the Iblean Foreland, only the anomalies found in groundwaters collected along the Augusta-Brucoli Graben are a clear sign of the interaction with deep-source fluids. Although an artesian aquifer was found throughout the whole Augusta area, H_2S, NH_3 ^{222}Rn and relatively high PCO_2 values, were only found in the wells drilled along the NNW-SSE fault system, bordering M. Tauro ($\simeq$ 10 km from epicentral area).

In the *Brucoli Sulphureous Spring*, the 1990-1992 temporal trends of the physico-chemical parameters and of the chemical equilibria lead us to set forth some hypotheses on the processes triggered by the 1990 earthquake.

In particular, the evidence of a strong release of CO_2 in concomitance with the mainshock, supported by our experimental data, gives an original and challenging indication for the seismogenic fault recognition, and it may be taken into account in the geophysical modeling of the earthquake source. Indeed the CO_2-related temporal trends enable us to avail a very convincing hypothesis for the relation between fluid-geochemistry and seismogenic fault: a pore-pressure uprising could be generated in the core-proximity of the seismogenic fault, by a combination of processes including coseismic slip-dilatancy, fracture permeability increase and fault-valve behavior, followed by healing and sealing processes in the fracture zone.

The increase in the flow of CO_2 at the spring, in concomitance with the mainshock, was probably due either to a pore-pressure variation or a permeability pattern and fracturing modification in the vicinity of the seismogenic structure. Due to the lack of geochemical data before the mainshock, we cannot hypothesize whether this process began before the earthquake.

The variations in space and time of geochemical flows accompanying the 1990 seismicity constitute possible evidence of the activity (fluidodynamic and geochemistry in the tectonic framework), along the NNW-SSE fault system (the Ibleo-Maltese Escarpment). Thus, we argue that the Ibleo-Maltese Escarpment can be the fault activated during the 1990 Syracuse earthquake.

These results could clarify the contribution of fluid geochemistry to seismotectonics, in recognizing active tectonic structures, together with geological and geophysical methods (paleosismology, neotectonics, stress-strain studies, remote-sensing, etc...).

2) Based on the hydrogeochemical studies carried out in the Iblean Foreland, we can single out a few sites which may be of interest for seismic surveillance. The following is a list of the most suitable sites for monitoring:

in the Augusta Graben:

- Brucoli Sulphureous Spring;
- Villa Salus Well and Serena Comunale Well;

in the area of the Lentini-Mineo Graben:

- Cozzarelle Comunale Well;
- Poggio Pizzuti Well.

Bearing in mind the geochemical characteristics directly related to the deep-source gaseous input, the parameters to be considered in continuous monitoring are the following: temperature, electrical conductivity, pH, Eh, PCO_2, static level, simple environmental parameters, ^{222}Rn, He, H_2S, H_2 and other gas-related parameters in deep wells.

Finally, this study shows the importance for future developments of the knowledge of proper aseismic-seismic and post seismic hydrogeochemical patterns, in those areas selected for surveillance, as a significant contribution to understanding the different phases of the seismogenic process.

Acknowledgements

We wish to thank M. Brondi, E. Ghiara and Dr. R. Gragnani of the Laboratory of ENEA (AMB-SAF), for the chemical analyses carried out, and Dr. G. Venanzi for the statistical analyses. We are also grateful to Prof. G. Lauretta of ITIS of Syracuse. We wish to thank, finally, the very helpful technician, I. Settembrini.

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