

## THERMAL FLUID DISCHARGES FROM SUBMARINE SPRINGS AT THE FORMICHE DI GROSSETO ISLETS (TYRRHENIAN SEA, TUSCANY, ITALY) AND THEIR RELATION WITH REGIONAL ANTI-APENNINE TECTONIC LINEAMENTS

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**Abstract** - The Formiche di Grosseto (southern Tuscany, Italy) islets are a reef system of about 1,500 m<sup>2</sup>, 9 nautical miles offshore the outfall of the Ombrone river and are constituted by Liassic carbonate rocks of the Tuscan Series (Calcare Massiccio) and are part of the Giannutri-Formiche di Grosseto (GFR) ridge separating Neogene basins of the Tuscan Shelf.

In 2005, during a monitoring survey several thermal springs discharging from the sea bottom close to Formiche islets were noticed. Thermal fluids discharge from several points mainly located along the N-NE scarp bordering the main reef at depths varying from 6 to 32 m. and an outlet temperature of about 41 °C was measured.

Accordingly, continental Tuscany is characterized by a large amount of Ca-SO<sub>4</sub> thermal water discharges, such as Bagni Osa and Roselle located inland in the proximity of the Formiche di Grosseto area, whose chemistry is to be related to mixing of fluids from different sources, i.e. hydrothermal and seawater (Bagni Osa) and/or hydrothermal and meteoric (Roselle).

For these considerations, the occurrence of CO<sub>2</sub>-rich submarine thermal discharges at Formiche di Grosseto may conveniently be related to the regional anti-Appennine tectonic lineaments.

**Riassunto** – Le Formiche di Grosseto sono un insieme di piccoli isolotti, nell’Arcipelago toscano, di circa 1.500 m<sup>2</sup> di superficie a 9 miglia nautiche dalla costa toscana di fronte alla foce del Fiume Ombrone. Fanno parte di un sistema di reef costituito da rocce carbonatiche liassiche della Serie Toscana. Sono un alto strutturale che si congiunge all’Isola di Giannutri separato dalla piattaforma costiera da un bacino neogenico.

Nel 2005 durante un monitoraggio sottomarino dello stato della flora e dei fondali, furono notate, a profondità variabili fra 6 e 32 m fuoriuscite di fluidi caldi che una successiva misura della temperatura stabilì a circa 41 °C.

L’analisi geochimica successiva dei fluidi e dei gas ha evidenziato una composizione ricca in CaSO<sub>4</sub> in accordo con le misure effettuate alle Terme dell’Osa (principalmente acqua di mare) e a Roselle (fluidi più meteorici).

Per questo motivo possiamo considerare, le emissioni fluide alle Formiche di Grosseto, strettamente correlate con i lineamenti tettonici anti-Appenninici, lineamenti evidenziati da precedenti indagini geofisiche.

## Introduction

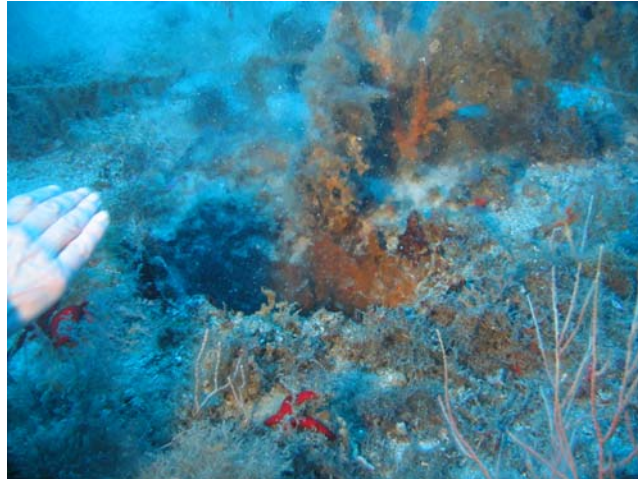
The Formiche di Grosseto (southern Tuscany, Italy) islets are a reef system of about 1,500 m<sup>2</sup>, 9 nautical miles offshore the outfall of the Ombrone river. They are constituted by Liassic carbonate rocks of the Tuscan Series (Calcare Massiccio, [8]; [6] and are part of the Giannutri-Formiche di Grosseto (GFR) ridge separating Neogene basins of the Tuscan Shelf [7].

In 2005, during a monitoring campaign aimed to investigate the effects of polluted sea water on local submarine vegetation several thermal springs discharging from the sea bottom close to the Formiche di Grosseto were noticed (Slide 1). Thermal fluids discharge from several points mainly located along the N-NE scarp bordering the main reef (Fig. 1; Slide 2), at depths varying from 6 to 32 m.



Figure 1 - Map of southern Tuscany and Formiche di Grosseto with the location of the sampling sites and the anti-Appennine lineations

*Figura 1 –Mappa del Sud della Toscana e delle Formiche di Grosseto con la posizione dei punti di campionamento e l'indicazione delle lineazioni anti-Appenniniche*



Picture 1 - Submarine thermal emission at Formiche di Grosseto (Tuscany, Italy).  
*Foto 1 – Emissione termale sottomarina alle Formiche di Grosseto (Toscana – Italia)*



Picture 2 - Formiche di Grosseto (Tuscany, Italy) main reef.  
*Foto 2 – Formica grande di Grosseto (Toscana, Italia)*

## **Methodology and data analysis**

During the first recognition an outlet temperature of about 41 °C was measured. In 2007, a second scuba expedition was organized to collect water and dissolved gas samples for chemical analysis (Slide 3a,b). The main aim of the present work is to assess the origin of discharged fluids and their relation with local and regional tectonics.

The results show that the chemical compositions of the water samples are quite similar to that of seawater, although marked by significant enrichments of  $\text{SO}_4$ , Ca and B and Mg depletion (Table 1).

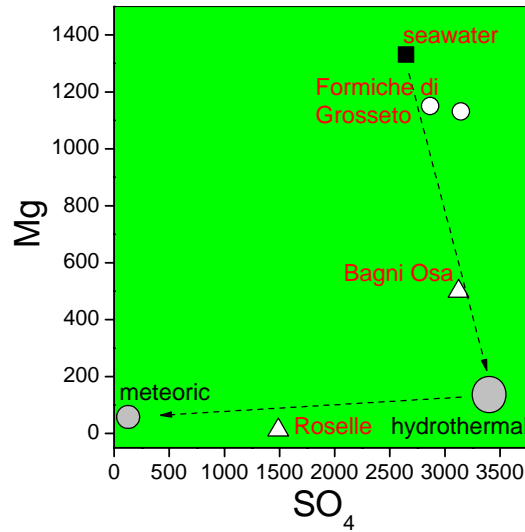


Figure 2 - Mg vs.  $\text{SO}_4$  binary diagram for the Formiche di Grosseto submarine fluid discharges. Hydrothermal and meteoric end-members are also reported, as well as the composition of seawater and Bagni Osa and Roselle springs.

*Figura 2 – Diagramma binario Mg/ $\text{SO}_4$  delle fuoriuscite termali sottomarine: Sono riportati i membri idrotermali e meteorici, prettamente a composizione marina per i Bagni dell’Osa e meteorici per Roselle.*

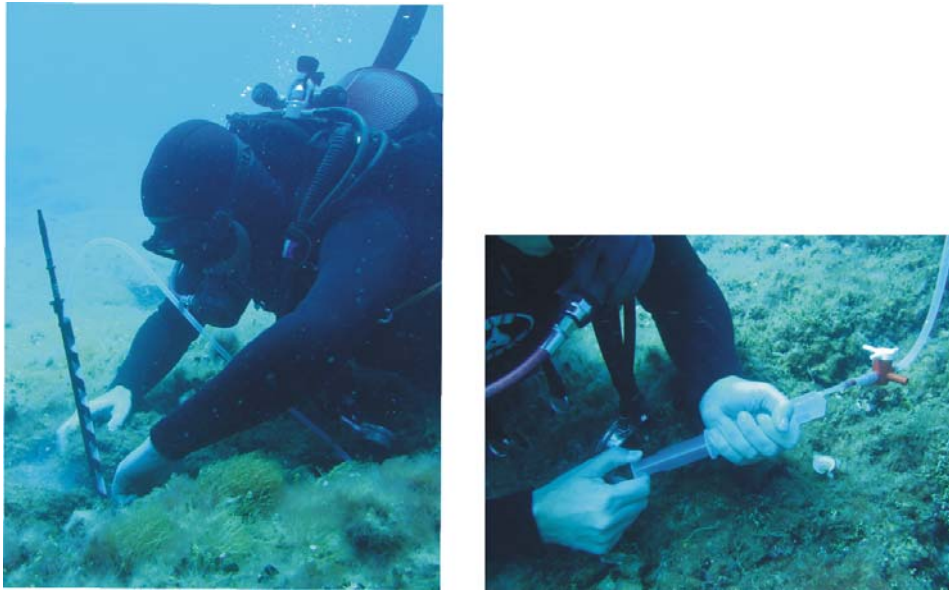
These compositional characteristics are likely to be ascribed to the mixing of seawater with hydrothermal fluids, the latter reaching the sea bottom through a long hydrological pattern.

Actually, in the Mg vs.  $\text{SO}_4$  binary diagram (Fig. 2) Formiche di Grosseto samples plot close to an hypothetical mixing line between seawater and a  $\text{SO}_4$ -rich hydrothermal end-member, which is typically depleted in Mg [4] due to water-rock interaction at relatively high temperature [2].

Accordingly, continental Tuscany is characterized by a large amount of Ca- $\text{SO}_4$  thermal water discharges, such as Bagni Osa and Roselle (Table 1) located inland in the proximity of the Formiche di Grosseto area (Fig. 1), whose chemistry is to be related to mixing of fluids from different sources, i.e. hydrothermal and seawater (Bagni Osa) and/or hydrothermal and meteoric (Roselle) (Fig. 2).

The chemical features of the hydrothermal end-member are derived by rock-water interactions processes involving carbonate-anhydrite rocks, such as those of the quite thick Mesozoic limestones of the Tuscan Series with intercalated anhydrite layers (Burano Formation). A significant contribution from an hydrothermal system may also explain the composition of the Formiche di Grosseto dissolved gas sample, showing relatively high  $\text{CO}_2$  concentrations (up to 90 % by vol.), similar to those measured at the inland springs

(Table 1). The C-CO<sub>2</sub> isotopic signature (-2.3 ‰ V-PDB) of Bagni Osa spring [5] suggests a deep origin for the CO<sub>2</sub> of the thermal emissions discharging in this area.



Picture 3a,b - Water and dissolved gas sampling from submarine fluid discharge.

*Foto 3a, b – Campionamento dell'acqua e dei gas in prossimità della fuoriuscite dei fluidi tremali sottomarini*

## Conclusions

It is worthy of noting that the spatial distribution of the thermal springs of Tuscany is generally governed by regional tectonics and corresponds to the boundaries of the carbonate formation outcrops, which represent the main aquifer [5].

According to these considerations, the occurrence of CO<sub>2</sub>-rich submarine thermal discharges at Formiche di Grosseto may conveniently be related to the regional anti-Appennine tectonic lineament passing through Torre Cannelle, which runs sub-parallel to the Follonica-Rimini line (Fig. 1). Its presence was already suggested on the basis of offshore geophysical investigations carried out by mono and multichannel seismic reflection profiles [1]; [3].

sample	North	East	T°C	pH	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	Na	K	Ca	Mg	NH <sub>4</sub>	NO <sub>3</sub>	B	F	Br	Li
1	42°34'94"	10°52'53"	41	6.20	144	21686	2866	11700	418	1141	1150	0.61	4.7	64.00	1.51	63	0.19
2	42°34'69"	10°52'79"	40	5.36	145	21640	3145	12620	415	1251	1131	0.55	16	66.00	1.23	65	0.21
Bagni Osa	42°33'07"	11°10'34"	30	6.77	535	6873	3125	3885	142	1250	499	9.30	0.21	39.00	3.1	24	0.39
Roselle	42°48'32"	11°08'36"	38	6.83	92	32	1490	35	10	621	12	1.00	0.07	1.10	0.44	0	0.04
seawater				8.15	135	18952	2648	10468	348	411	1331	0.11		4.60	1.3	65	0.17

sample	CO <sub>2</sub>	N <sub>2</sub>	Ar	CH <sub>4</sub>	O <sub>2</sub>	Ne	He	δ <sup>13</sup> C-CO <sub>2</sub> *
mmol/L	9.202	0.911	0.022	0.0014	0.082	0.00001	0.0001	
% by vol	90.051	8.920	0.212	0.0135	0.803	0.00011	0.0010	
Bagni Osa	91.213	7.439	0.278	0.0761	0.162	0.00016	0.0000	
Roselle	83.029	14.299	0.370	0.0001	2.301	0.00019	0.0000	-2.3

Table 1. Water and gas composition of the thermal discharges at the islets of Formiche di Grosseto. Concentration of dissolved solutes are in mg/L. Concentrations of the gas compounds are in mmol/L (first row) and % by vol. (second row). Chemical composition of seawater and water (in mg/L) and gas (in % by vol.) samples from Bagni Osa and Roselle thermal springs are also reported.

\* The δ<sup>13</sup>C-CO<sub>2</sub> value is from [5].

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