

## The mineralised springs of the Adriatic region, central Italy

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### ABSTRACT

In the Adriatic region of central Italy, there are many mineralised (salt and sulphureous) springs, often used for therapeutic purposes. The hydrogeological characteristics of the springs and their tectonic set-up are examined in this paper. The salt springs generally emerge from the Plio-Pleistocene and Messinian deposits. The waters emerging from the Messinian deposits originate from marine waters subjected to evaporation. This leads to the precipitation of gypsum and formation of brines isolated by clayey deposits. Even the salt waters emerging from the Plio-Pleistocene deposits originate from marine waters trapped in the arenaceous Pliocene deposits. The waters are subjected to an ultra-filtration process through the clayey membrane with the formation of brines.

The study reveals that the springs are located in the main thrust fronts, and the springs with higher salinity emerge in the thrusts that squeezed out the brine waters from the post-orogenic Plio-Pleistocene sequence.

The sulphureous springs emerge from the Messinian and Plio-Pleistocene deposits and from the Apennine Meso-Cenozoic limestone ridges. The sulphureous springs emerging from the terrigenous sequence are connected with the Messinian evaporites, while the sulphureous springs emerging from the limestone ridges are related to the Messinian and Triassic evaporite deposits of the Umbrian-Marchean sequence.

In the emergence zones of the salt waters, typical mud volcanoes or puddles are present due to suspended mud in the waters. Generally, the sulphureous springs emerge along streams whose waters are whitish and emit the typical smell because of sulphur precipitation.

### INTRODUCTION

Many mineralised springs are found in the Adriatic region of central Italy where they are often used for therapeutic purposes. These mineralised springs are classified into the salt springs and sulphureous springs. Their tectonic set-up and hydrogeological characteristics are discussed in this paper.

### GEOLOGICAL SETTING

Many salt springs emerge from the deposits of the External Marchean Basin sequence, while the sulphureous springs emerge from the Messinian evaporite deposits in the External Marchean Basin and in the Acqualagna-Visso Depression from the limestone of the Umbrian-Marchean Ridge, in the minor ridges and, sometimes, from the Plio-Pleistocene deposits of the Marchean hilly area. The emergence zones of the salt and sulphureous springs are always connected with structural elements (Fig. 1).

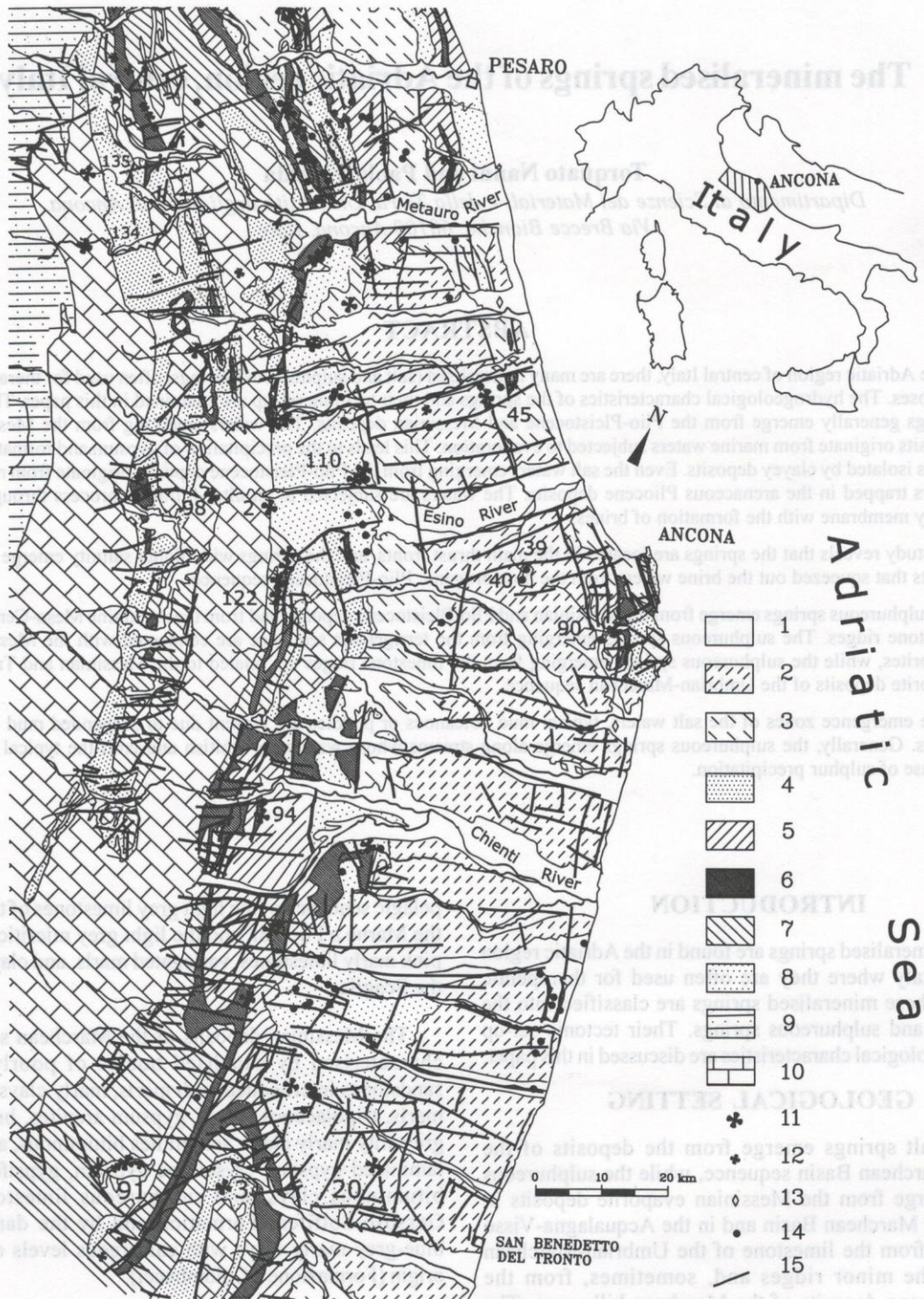
The Meso-Cenozoic sequence present in the Umbrian-Marchean and Marchean Ridges is formed by Jurassic-infra-Cretaceous and Cretaceous-Palaeogene Groups (AA.VV. 1991). The first group is represented by the platform and dolomitic limestones of the Calcare Massiccio and micritic limestones of the Corniola. The second group is represented by the

pelagic sequence of the light grey limestones of the Maiolica, the Marne a Fuocidi, and the light grey micritic limestones, pink marly limestones, variegated marls, and clayey-marls of the Scaglia.

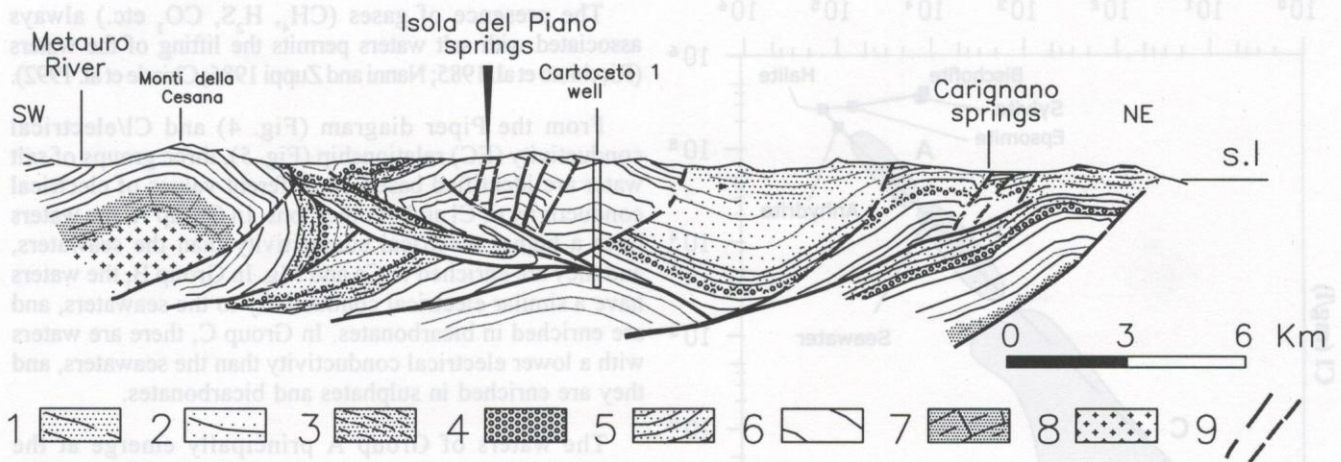
The Messinian deposits of the Marchean sequence are characterised by canalised bodies of poorly cemented sandstones interbedded with marls, marly clays, and clayey marls, tripolaceous levels, gypsum arenites, brownish and grey silty marly clays, sometimes bituminous, and levels of laminated gypsum, crystalline gypsum, gypsiferous clays, bituminous clays, and sulphureous limestones of the Gessoso-Solfifera Formation and by the dark grey and blue-grey marly clays with calcareous levels of evaporite origin (Formazione a Colombacci).

The Plio-Pleistocene lithotypes of the External Marchean Basin crop out in the Adriatic hilly area, and are formed by marly clayey and clayey marly deposits interbedded with arenaceous, silty arenaceous, and arenaceous silty bodies.

Finally, the terraced continental deposits are present, especially in the Pede-Apennine and hilly zones of the External Marchean Basin and they make up the Marchean alluvial plains from the Marchean Ridge to the Adriatic coast (Fig. 2).



**Fig. 1:** Geological and hydrological scheme of the Marche Adriatic foredeep. 1. Alluvial terrace deposits (Pleistocene-Holocene); 2. Clays and marly clays (post-orogenic Plio-Pleistocene); 3 and 4. Marly clays (pre-orogenic lower and middle Pliocene); 5. Marly clays; 6. Bituminous clays and gypsum of Messinian evaporites; 7. Marly clays with arenaceous bodies; 8. Marly limestones, marls, and clayey marls (Serravallian-Tortonian); 9. Marnoso-arenacea Formation; 10. Meso-Cenozoic limestone ridge; 11. Sulphureous springs; 12. Sulphureous springs (not analysed); 13. Mineralised springs in the alluvial plains deposits; 14. Salt springs; 15. Faults. Springs mentioned in the text: 135. Gorgo a Cerbara; 134. S. Nicolò; 45. Filetto-Vallone; 110. Moie; 2. Gorgovivo; 98. Frasassi; 1. Crevalcore; 39, 40. Polverigi; 90. Aspio; 94. Tolentino; 91. Acquasanta; 20. Offida; 3. Casteltronsino.



**Fig. 2:** Geological cross-section through the Marche foredeep in the northern area. 1. Plio-Pleistocene post-orogenic deposits; 2 and 3. Deposits of the lower and middle pre-orogenic Pliocene; 4. Messinian deposits; 5, 6, and 7. Umbrian-Marchean Meso-Cenozoic sequence; 8. Anidriti di Burano Formation; 9. Thrusts and faults.

The Marche region is characterised by the presence of folds and thrusts, and a system of faults with trends due NW-SE, NNW-SSE, NNE-SSW, N-S, and E-W. Several authors (Bally et al. 1986; Lavecchia et al. 1987; Calamita et al. 1990; Calamita et al. 1991; AA.VV. 1991) have stated that the Umbrian-Marchean Ridges were derived from a detachment zone of thrusts in the sedimentary cover that formed a system of concentric folds bordered by thrusts with the Adriatic vergence. The level of the main detachment corresponds to the Anidriti di Burano, while the secondary detachments correspond to the levels of the Scaglia Cinerea, Marne a Fucoidi, and Rosso Ammonitico.

The folds of the western side of the Umbrian-Marchean Ridge are in part overlapped and enveloped in an important thrust that causes their translation to northeast over the Palaeogene and Miocene deposits of the S. Felice-Campodónico Depression. The Marche region is characterised by the presence of an anticline recognisable in the south up to Mt. Vettore, in the Sibillini Complex. In the east and south of the Chienti River, the anticline is delimited by the Sibillini Complex thrust, on which the Apennine structures (corresponding to the thrust upper limit) end. The two ridges lying north of Sibillini originate from the Miocenic deposits of the Acqualagna-Visso Depression, from which the minor ridges emerge. The deposits on the east are probably in thrust contact with the Miocenic deposits.

The Pede-Apennine and the Adriatic hilly zone of the external structural domain is the largest area of the hydrographic basins. It is characterised by folds (near the Marche and minor ridges) interrupted by the Apennine and Antiapennine faults.

In proximity to the coast, the ridges bordered by indirect faults are the main structures involving the Plio-Pleistocene deposits. On the basis of seismic analyses (Calamita et al.

1990; Ori et al. 1991), the presence of a structure buried by the post-orogenic Plio-Pleistocene deposits is evident. The buried structure corresponds to the thrusts that involve the deposits of middle and lower Pliocene.

The alluvial plains are always along the Apennine faults whose neotectonic activity has been very important for their morphogenesis (Nanni and Vivalda 1987).

### SALT SPRINGS

The salt springs in the External Marche Basin emerge from the Plio-Pleistocene and Messinian deposits. Many springs are also located in the continental deposits of the alluvial plains (Fig. 1).

The salt springs of the Messinian deposits derive from the marine water subjected to evaporation up to the same saline concentration of seawater from which gypsum begins to precipitate. The salt waters in the pelitic Messinian sediments have not necessarily been in contact with the Gessoso-Solfifera Formation.

The origin of the Plio-Pleistocene salt waters is not associated with the evaporation of seawater; in fact the Plio-Pleistocene sediments are typical of a deep basin. The salt waters originate from marine waters trapped in sediments and subjected to ultra-filtration processes through a clayey membrane, with the formation of brines. In each case, the enrichment in salinity derives from mixing with the Messinian waters lifted through joints and faults. Therefore, all the salt waters studied originate from basal brines trapped in the sediments at their deposition. This hypothesis is supported by the analysis of the Cl, Na, and Br ions whose values fall close to the seawater dilution-evaporation curve, considered as dilution line of the basal brine (Fig. 3).

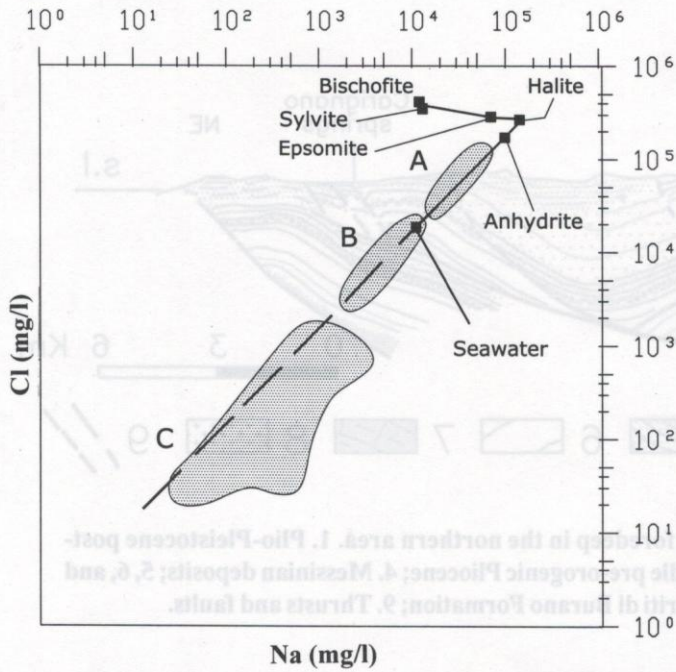


Fig. 3: Plot of Cl versus Na in the salt waters. The analysed springs fall in the hatched areas. The three groups with different salinity (A, B, and C) are indicated.

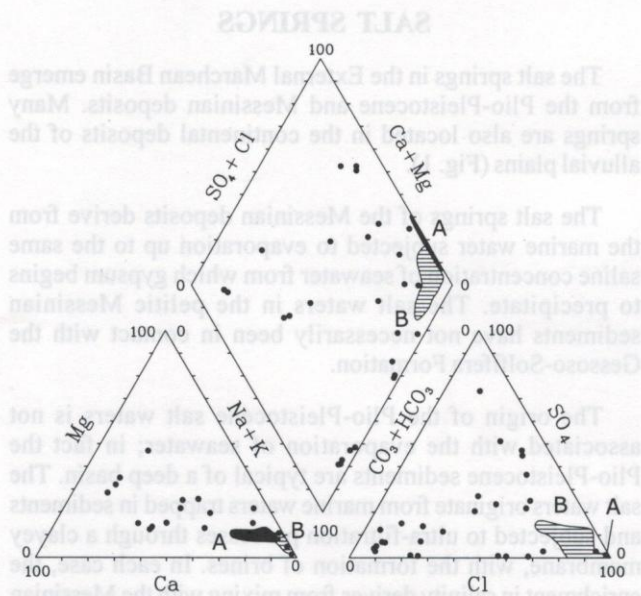


Fig. 4: Piper diagram of the salt waters. Groups A and B of the analysed springs, characterised by homogeneous chemistry, are indicated (black and ruled areas); the waters of Group C (dots) have a variable chemistry.

The presence of gases ( $\text{CH}_4$ ,  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  etc.) always associated with salt waters permits the lifting of the waters (Ricchiuto et al. 1985; Nanni and Zuppi 1986; Chiarle et al. 1992).

From the Piper diagram (Fig. 4) and Cl/electrical conductivity (EC) relationship (Fig. 5), three groups of salt water are identified based on different values of electrical conductivity of Cl and of other ions. In Group A, the waters have a higher electrical conductivity than the seawaters, and they are enriched in Ca and Mg. In Group B, the waters have a similar electrical conductivity to the seawaters, and are enriched in bicarbonates. In Group C, there are waters with a lower electrical conductivity than the seawaters, and they are enriched in sulphates and bicarbonates.

The waters of Group A principally emerge at the Messinian-Pliocene limit (e.g. the Moie Spring, Fig. 1 and 6), and from the Plio-Pleistocene deposits (e.g. the Polverigi Spring, Fig. 1). The waters of Group B mainly derive from the Plio-Pleistocene pelitic deposits, while those of Group C derive from the Plio-Pleistocene, Messinian, and alluvial plain deposits.

The waters with the highest salinity emerge from the Pliocene ridges where the Messinian and lower Pliocene deposits crop out. In the ridges lying in the western part of the External Marchean Basin, the springs are in the eastern

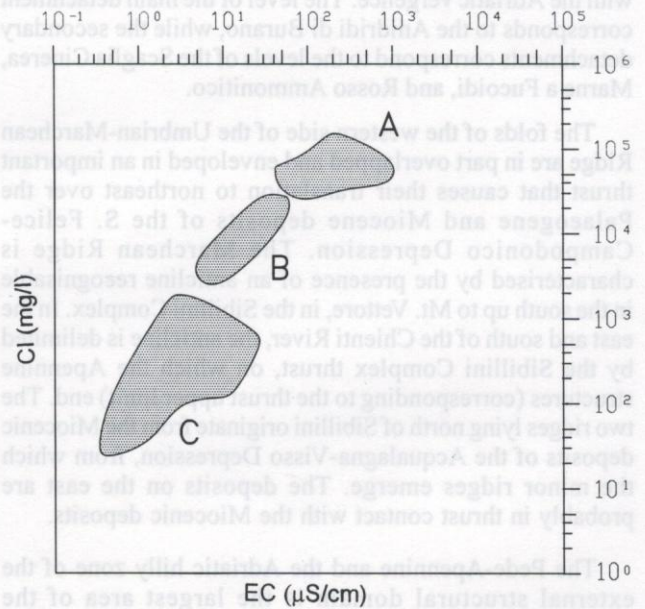


Fig. 5: Plot of Cl versus electrical conductivity relations in the salt waters. The analysed springs fall in the hatched areas. The three groups of water with different salinity (A, B, and C) are indicated.

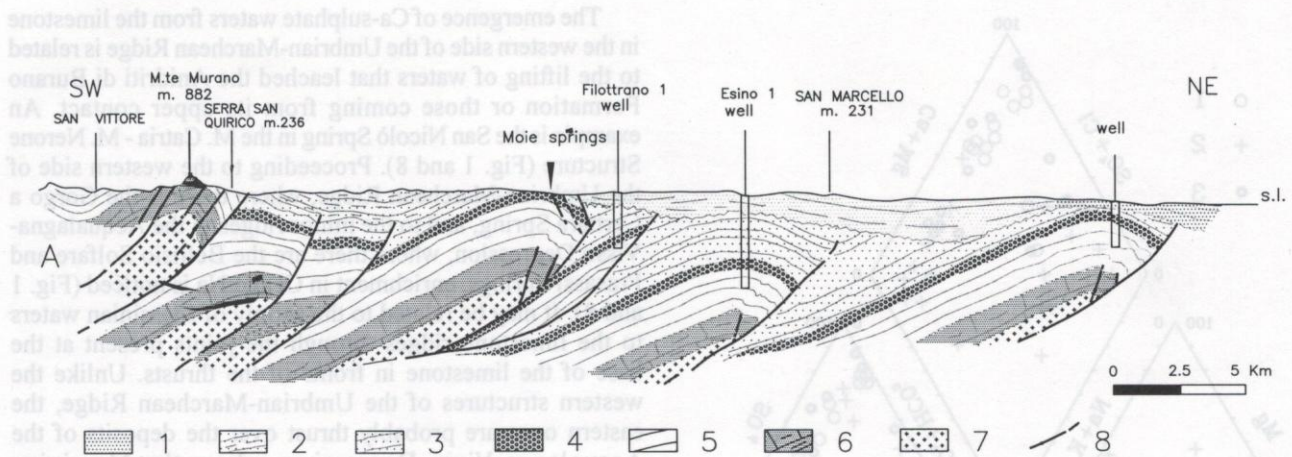


Fig. 6: Geological cross-section through the Marche basin in the central area. 1. Upper Pliocene and Plio-Pleistocene deposits; 2-3-4. Siliciclastic deposits of the lower and middle Pliocene (2 and 3) and Messinian evaporite deposits (4); 5. Siliciclastic pre-evaporite deposits; 6. Umbrian-Marchean Meso-Cenozoic sequence; 7. Anidriti di Burano Formation; 8. Thrusts and faults

front of the structures (e.g. the Tolentino and Moie Springs; Fig. 1). In the coastal ridges (except for the Pleistocene to Recent one) the springs are generally in the western side (e.g. the Filetto-Vallone, Polverigi, and Aspigo Springs; Fig. 1). Here, they are frequently found in the extensive faults connected with thrusts or in the intersection of the Apennine and Antiapennine faults. The compressive tectonics favoured the salt waters squeezing out and their accumulation in the thrust fronts. The high salinity of the waters emerging from the ridges is due to the circulation of waters not in contact with the hydrological circulation ones. This is demonstrated by high  $\text{NH}_4$  values and by low tritium values. It is an indication of hydrogeological conditions typical of a closed system that prevents the deep infiltration of vadose waters (Nanni and Vivalda 1999a).

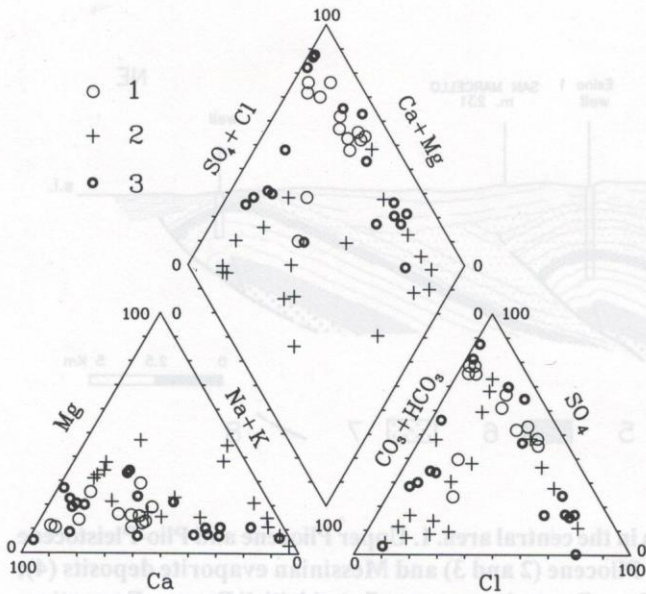
The waters with the lowest salinity are present in the central-eastern part of the External Marche Basin, especially to the south of the Cingoli-Mt Conero line. Many springs emerge from the eluvio-colluvial and alluvial deposits. Therefore, their waters are in contact with the groundwater present in these deposits and characterised by low salinity. Besides, in this case, the Plio-Pleistocene sequence, generally constituting a monocline towards the west, covers the pre-orogenic Pliocene succession characterised by the presence of thrusts. In front of the thrusts, after the Pliocene compressive phenomenon, the salt waters accumulated. The Plio-Pleistocene sequence is characterised by the presence of the Apennine and Antiapennine faults (probably at contact with the buried structures), which permit the movement of salt waters through the action of the gas. The salt waters of these zones are very diluted by the supply of vadose waters in the Pliocene arenaceous successions through the fault zones.

## THE SULPHUREOUS SPRINGS

The sulphureous springs generally emerge from the Messinian deposits but they sometimes also emerge from the Meso-Cenozoic sequence of the limestone ridges and from the Plio-Pleistocene deposits (Fig. 1).

The origin of sulphureous springs is always connected with the presence of the Messinian deposits and their chemical composition depends on the amount of minerals leaching from the evaporite levels. On the basis of hydrochemical analysis of the sulphureous springs, it is possible to differentiate three main facies (Fig. 7): Ca-sulphate, Na-Cl-sulphate, and Cl-Na-sulphate, depending on the lithotypes present in the emergence areas. Consequently, it is possible to identify the following three types of sulphureous spring: those emerging from the Messinian deposits, those emerging from the Plio-Pleistocene deposits, and those emerging from the Meso-Cenozoic limestone ridges (Nanni and Vivalda, 1999b).

A majority of sulphureous springs, with a typical Ca-sulphate facies, emerge from the Messinian lithotypes of the Gessoso-Solfifera Formation. Their chemistry (indicating the enrichment in bicarbonates, magnesium, and silica) is dependent on the amount of minerals leaching from the Gessoso-Solfifera Formation. The recharge of the gypsiferous aquifers is mainly from the rain and vadose waters in the pre- and post-evaporite arenaceous bodies, which are always in contact with gypsum. On the basis of isotopic data on tritium, it is inferred that the water circulation is superficial and not dispersive. It takes place in short circuits and is connected with the hydrological cycle. The enrichment in Cl and Na of the springs emerging from the Messinian succession (especially, from the post-evaporites)



**Fig. 7: Piper diagram of the sulphureous springs. 1. Springs emerging from the Messinian deposits; 2. Springs emerging from the Plio-Pleistocene deposits; 3. Springs emerging from the limestone ridges**

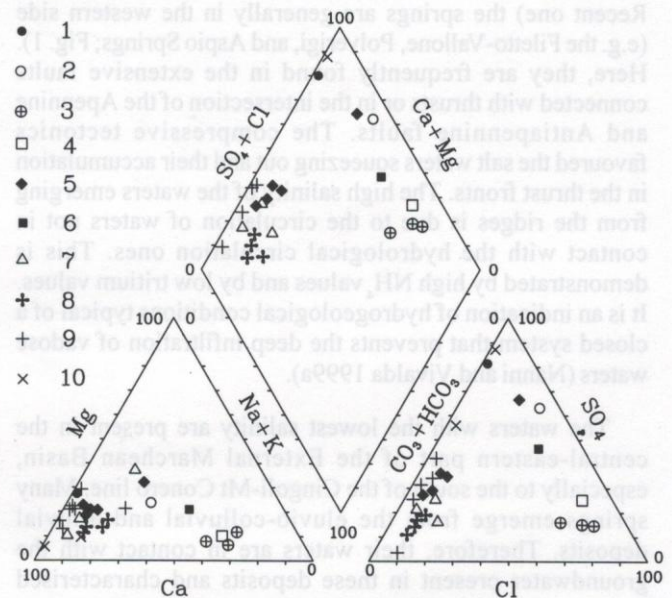
is related to the mixing with the salt waters present in these deposits (Nanni and Vivalda 1999a).

The sulphureous waters emerging from the Plio-Pleistocene deposits have a Na-Cl-sulphate facies. The springs are located in fractured zones and through these, the deep waters (circulating in the Messinian deposits and enriched in sulphates) are lifted by gas and mixed with the Pliocene salt waters (Nanni and Vivalda 1998). These springs may produce peculiar superficial forms as in the Offida zone (Fig. 1).

The sulphureous waters in the new wells and in the aquifers of the alluvial plains are connected with the Pliocene ridges, which are the substratum of the alluvial plains. In the alluvial plains of the Esino River (Moie Ridge) and Misa River (Senigallia Ridge), the substratum of alluvial deposits may be constituted of the Messinian deposits. Therefore, the supply of sulphates is probably due to the leaching of the Messinian gypsum from the unconfined aquifer waters or from the supply of the Messinian waters circulating in the evaporite levels. In the medium-lower part of the Musone and Potenza River alluvial plains, the presence of waters enriched in sulphates is connected with the coastal ridges that were buried by the Plio-Pleistocene sequence. In this case too, there is lifting of the Messinian waters along the fractured zones and mixing with those of the plains.

The chemistry of the waters emerging from the Marche limestone ridges (Fig. 8) changes from a typical Ca-sulphate facies in the inner part of the Umbrian-Marchean Ridge to a facies characterised by the enrichment in Cl and Na in the Marche and External Ridges.

The emergence of Ca-sulphate waters from the limestone in the western side of the Umbrian-Marchean Ridge is related to the lifting of waters that leached the Anidriti di Burano Formation or those coming from its upper contact. An example is the San Nicolò Spring in the M. Catria - M. Nerone Structure (Fig. 1 and 8). Proceeding to the western side of the Umbrian-Marchean Ridge, where there is the Gorgo a Cerbara Spring, and to the minor ridges in the Acqualagna-Visso Depression, where there are the Bellisio Solfare and Frasassi Springs, enrichment in Cl and Na is noticed (Fig. 1 and 8). It may be related to the supply of Messinian waters to the limestone in fronts of the thrusts. Unlike the western structures of the Umbrian-Marchean Ridge, the eastern ones are probably thrust over the deposits of the Acqualagna-Visso Depression, where the Messinian sequence crops out. Therefore, the Messinian and Pliocene deposits in the thrusts front can also be found at the base of the limestone ridges. Their presence further proves the enrichment in Cl and Na of the Ca-bicarbonate springs



**Fig. 8: Piper diagram of the sulphureous springs emerging from the limestone ridges. 1. S. Nicolò Spring; 2. Gorgo a Cerbara Spring; 3. Frasassi Springs; 4. Bellisio solfare Spring; 5. Castel Trosino Springs; 6. Acquasanta Spring; 7. Springs emerging from the basal aquifer of the Umbrian-Marchean Ridge in the Marche area; 8. Springs emerging from the Marche Ridge; 9. Springs emerging from the Umbrian-Marchean Ridge in the Umbrian area; 10. Springs emerging from the Maiella limestone ridge**

(Fig. 1) recharged by the base aquifer of the Marche Ridge (e.g. the Gorgovivo Spring) and of the external ridges (e.g. the Crevalcore Springs).

The situation of the sulphureous thermal springs of Acquasanta (Fig. 1 and 8) is more complex. The waters, enriched with Cl and Na and with a higher temperature, lead us to suppose a recharge connected with a deep circulation. Such enrichments, considering the structural setting of the Acquasanta Ridge (AA.VV. 1991; Mattei 1987; Vezzani and Ghisetti 1997; Calamita et al. 1998), can be connected with the mixing between the Messinian waters transferred through joints and the waters circulating in limestones. On the other hand, the high temperature and Cl and Na enriched sulphureous waters emerging from the limestone deposits are also found in the Umbria region, in the Nerina Valley (i.e., the Triponzo Spring). By the litho-structural characteristics of this zone, the chemical composition of the Triponzo waters can be attributed to the presence of halite deposits in the Triassic Anidriti, already found through hydrocarbon drilling in Tuscany and Umbria (Passeri 1994). A similar hypothesis might prove the chemical composition and the temperature of the Acquasanta waters too.

Finally, the chemistry of the Ca-sulphate waters of the Casteltrosino Springs (Fig. 1), in the Montagna dei Fiori, is different from that of the mineralised waters emerging from the minor and the external ridges, because it is not characterised by the enrichment in Cl and Na. From the geophysical data, the mineralisation of the Casteltrosino Springs (Fig. 8) may be due to lifting of the deep waters in contact with the Anidriti di Burano and transferred through the fault zones.

## CONCLUSIONS

The mineralised springs are salt springs with a Na-chloride facies, and sulphureous springs with a Ca-sulphate facies and enriched in Cl and Na.

The salt springs generally emerge from the Plio-Pleistocene sequence and from the alluvial plain deposits where small mud volcanoes often form in the emergence area. In the Marche area, unlike other Adriatic areas, the salt springs rarely emerge from the post-evaporite Messinian deposits.

The sulphureous springs principally emerge from the Gessoso-Solfifera Formation, from the bituminous gypsiferous marls, marly clays of the Colombacci Formation, limestones of the Meso-Cenozoic sequence and, rarely, from the Plio-Pleistocene deposits. The hydrochemical facies of the sulphureous springs is Ca-sulphate, Na-Cl-sulphate, and Cl-Na-sulphate.

The origin of salt springs is connected with the structural setting of the emergence area. They emerge where there are Pliocene ridges, and the clays and marly clays are intensely fractured. The emergence areas are often located at the

intersection between the Apennine and Antiapennine faults. The role of tectonics is also important for the origin of the sulphureous springs emerging from the limestone ridges and from the Plio-Pleistocene deposits.

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CONCLUSIONS

The mineralised springs are salt springs with a Na-chloride facies, and sulphurous springs with a Ca-sulphate facies and enriched in Cl and Na.

The salt springs generally emerge from the Pliocene sequence and from the alluvial plain deposits where small mud volcanoes often form in the emergent area. In the Marche area, unlike other Adriatic areas, the salt springs rarely emerge from the post-evaporite Messinian deposits.

The sulphurous springs principally emerge from the Gessoso-Solifera Formation, from the bituminous gypsiferous marls, marly clays of the Colombari Formation, limestones of the Meso-Cenozoic sequence and rarely from the Plio-Pleistocene deposits. The hydrochemical facies of the sulphurous springs is Ca-sulphate, Na-Cl-sulphate, and Cl-Na-sulphate.

The origin of salt springs is connected with the structural setting of the emergent area. They emerge where there are Pliocene ridges, and the clays and marly clays are intensely fractured. The emergent areas are often located at the

The situation of the sulphurous thermal springs of Acquasanta (Fig. 1 and 8) is more complex. The waters, enriched with Cl and Na and with a higher temperature, lead us to suppose a recharge connected with a deep circulation. Such enrichment, considering the structural setting of the Acquasanta Ridge (AA.VV. 1991; Mantel 1987; Vezzani and Ghisetti 1997; Calamita et al. 1998), can be connected with the mixing between the Messinian waters transferred through joints and the waters circulating in limestones. On the other hand, the high temperature and Cl and Na enriched sulphurous waters emerging from the limestone deposits are also found in the Umbria region, in the Nerina Valley (i.e., the Triponto Spring). By the litho-structural characteristics of this zone, the chemical composition of the Triponto waters can be attributed to the presence of halite deposits in the Triassic Anidriti already found through hydrocarbon drilling in Tuscany and Umbria (Passerl 1994). A similar hypothesis might prove the chemical composition and the temperature of the Acquasanta waters too.

Finally, the chemistry of the Ca-sulphate waters of the Castellino Springs (Fig. 1), in the Montagna dei Fiori, is different from that of the mineralised waters emerging from the minor and the external ridges, because it is not characterised by the enrichment in Cl and Na. From the geological data, the mineralisation of the Castellino Springs (Fig. 8) may be due to lifting of the deep waters in contact with the Anidriti di Brano and transferred through the fault zones.

The mineralised springs (e.g. the Cervalcore springs)