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Hydrogeochemistry of Magra Valley (Italy) aquifers: geochemical background of an area investigated for seismic precursors

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Abstract

We present the results of a hydrogeochemical survey of 111 springs and wells from Magra Valley, a seismic area located in northern Tuscany, Italy. This survey was aimed at defining the geochemical background and the underground fluid circulation scheme of an area currently investigated for earthquake precursory phenomena, with the final goal of identifying a suitable location for installation of a continuous automatic monitoring station for the remote control of hydrogeochemical parameters. Six springs of the project were identified suitable for the purpose, and the Equi Na-Cl-type spring emerged as the best candidate for the installation of a monitoring station.

Keywords: hydrogeochemistry; underground fluid circulation scheme; Magra Valley, Tuscany, Italy.

1. Introduction

In the framework of a project funded by Seismic Service of Tuscany Region [1], some areas of highest seismic risk in Tuscany (Garfagnana, Lunigiana, Mugello, Tiber Valley and Mt. Amiata) were selected to identify possible hydrogeochemical precursors of earthquakes. The aim of this study was to find in the Lunigiana region (Magra Valley - northern Tuscany, Italy) a suitable site where install a continuous automatic monitoring station to identify possible hydrogeochemical anomalies related to seismic activity. The monitoring station is programmed to record continuous variations in temperature (T), pH, electrical conductivity (EC), redox potential (ORP), and dissolved gas contents (CO_2 and CH_4) of natural aqueous solutions. Additional motivation for study stems from the following: i) no detailed hydrogeochemical

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surveys of the Magra Valley area were available in the literature before the present contribution; ii) abnormal emanations of soil CO_2 have been reported in the eastern sector of Magra Valley and abnormal temperature increases were repeatedly measured in a well drilled in the same area (Cioni, personal communication, 2001).

2. Geological – structural setting

Lunigiana region belongs to the inner zone of the Northern Apennine, a fold-and-thrust belt consisting of structural units derived from both oceanic and continental domains [2]. The main evolutionary stages of this orogeny are represented by the following phases: i) subduction of oceanic crust (Cretaceous-Eocene); ii) pre- and sin-collisional continental underthrusting (Oligocene-Miocene); iii) late-and post-collisional deformation. During this phase of deformation, the tectonic units outcropping in the examined areas have been affected by low-angle and high-angle normal faults. The present semi-graben geometry of Magra intermountain basins is due to these extensional structures [3]. The geology of this basin is dominated by the presence of almost all the tectonic units (Ligurian, Subligurian and Tuscan Units) that make up the Northern Apennines.

3. Field work and laboratory analyses

A total of 111 water samples, uniformly distributed in whole valley, were collected during one field campaign between May and June 2002. All water samples were analyzed for major (Ca, Mg, Na, K, Cl, HCO_3, SO_4) and minor (NO_3, B, SiO_2, F) chemical constituents. T, pH, EC and total alkalinity were measured in the field. Total alkalinity was determined by acidimetric titration with HCl 0.1 N using methylorange as indicator. Water samples were collected and stored in HDPE plastic bottles. Aliquots for the determination of Ca, Mg, and SiO_2 were filtered through 0.45 μm membrane filters and acidified through addition of HCl 6.6 M. The chemical analyses were performed in the laboratories of IGG-CNR, Pisa as follows: Cl, SO_4, NO_3 by IC; Ca, Mg, Na, K, by AAS, SiO_2 and B by visible spectrophotometry, F by ISE. The percent charge-balance error of samples discussed in this study is typically below 5%.

4. Results and discussion

The chemistry of the waters sampled in the study area has been initially investigated on the basis of relative anion (Fig. 1a) and cation concentrations (Fig. 1b). Based on lithological, structural and hydrodynamic characteristics of the feeding aquifers and on the chemical composition of the waters, three different types of manifestations have been identified in the Magra Valley.

Type A: springs fed by superficial hydrogeological structures, consisting of arenaceous (A1), marly-limestones (A2), shales and siltstones interbedded with limestones and calcarenites (A3), ophiolitic rocks (A4), and wells draining loosely cemented detrital deposits (A5). Of largely variable areal extension, the aquifers feeding type A manifestations are characterized by reduced permeability at depth, due to the progressive filling of the fractures by precipitation of secondary minerals during silicates hydrolysis. In these aquifers, water circulation occurs along short and shallow circulation paths. The salinity is generally low (TDS from 29 to 644 mg/l), and outlet temperatures are close to mean air temperature at discharge elevation. The chemical composition, mainly Ca-HCO_3, is indicative of the early stages of interaction between meteoric waters and rocks and/or soils containing carbonate minerals [4]. In this group, also the waters circulating through the silico-clastic rocks of Macigno formation acquire a Ca-HCO_3 chemical facies, due to rapid equilibration with carbonate cement (up to 10% by vol.) and/or calcite veins present in the rock [5]. The more saline waters of group A2 are saturated or slightly oversaturated with respect to calcite and dolomite, reflecting the larger availability of these minerals in the rock.

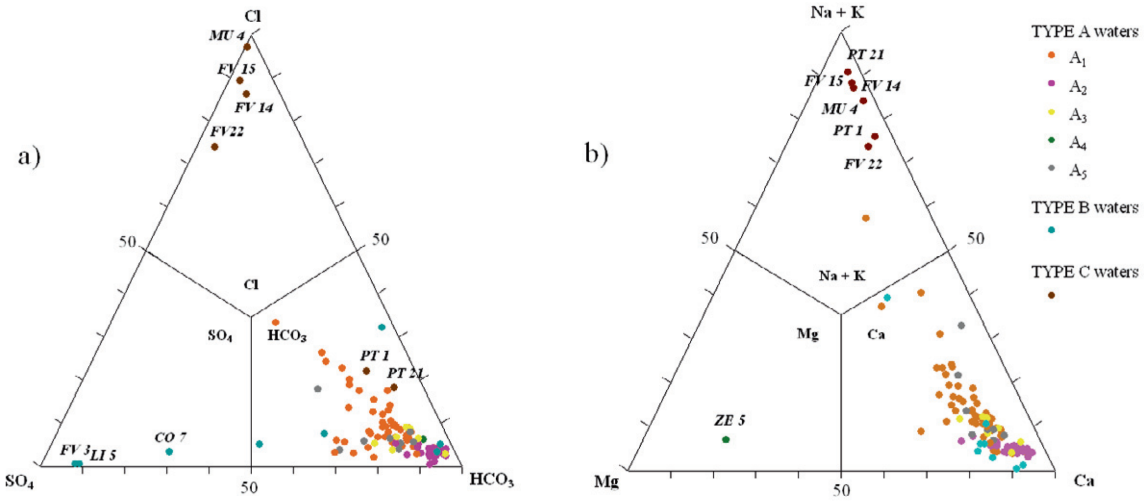

Fig. 1 Triangular plots of (a) HCO_3-SO_4-Cl and (b) Ca-Mg-(Na+K) for the water points of the Magra Valley.

Type B: springs fed by superficial hydrogeological structures, consisting of evaporite-carbonate rocks. These aquifers are characterized by high permeability values, due to fracturing and karst. Water temperature (from 9.0 to 12.3°C) is close to the mean annual air temperature. The chemical composition ranges from Ca-HCO_3, to Ca-HCO_3-SO_4, and Ca-SO_4. The salinity of Ca-SO_4 waters, between 542 mg/l to 2187 mg/l, strictly correlates with Ca and SO_4 total contents acquired during the progressive leaching of shallow evaporites of "Sassalbo Mesozoic Nucleous". Waters of type B are supposed to be related to relatively short and shallow circulation paths.

Type C: Springs fed by deep hydrogeological structures made up of evaporitic and carbonate rocks. In these aquifers, the morphology of the impermeable substratum allows the waters to circulate at relatively large depth and to emerge in the form of overflow and/or artesian thermo-mineral springs. The hydrochemical facies of these waters varies from Na-HCO_3 (2 springs) to Na-Cl-type (4 springs), and the outlet temperature range from 14.4 to 26.9°C.

Suitable sites for the installation of monitoring stations have been selected by coupling these structural, hydrological and geochemical information, with anomalies in P_{CO2} values. On these premises, type A and B manifestations have been discarded due to their short and shallow circulation paths, whereas type C springs have been further investigated as possible target for continuous monitoring of geochemical parameters. Type C springs issue in correspondence of major tectonic discontinuities, and their chemistry is expected to provide information on variations in physico-chemical parameters possibly occurring at depth, in association with deformation processes and/or the build -up and release of seismic energy.

The springs emerging in the eastern sector of Magra Valley have been discarded because of logistical reasons (e.g. LI9, LI5: areas of difficult accessibility, with no electricity supply), despite a promising anomaly in P_{CO2} (P_{CO2} values greater than statistical average of the area, P_{CO2} = 0.032 bar, have been measured).

The Equi Terme spring has been finally identified as the most suitable location for the purposes of the project. This manifestation is an overflow spring characterized by high flow rate (~20 l/s), Na-Cl chemical composition, P_{CO2} = 0.035 bar, T = 27°C and TDS of 5.7 g/l. The recharge area of this spring is located in the carbonate rocks outcropping in the northwestern sector of Apuan Alps. The rise of deep thermal water, after having deeply interacted with Triassic marine evaporites of the "Tuscan series", occurs along low and high-angle fault systems, located at the northern edge of Apuane Alps.

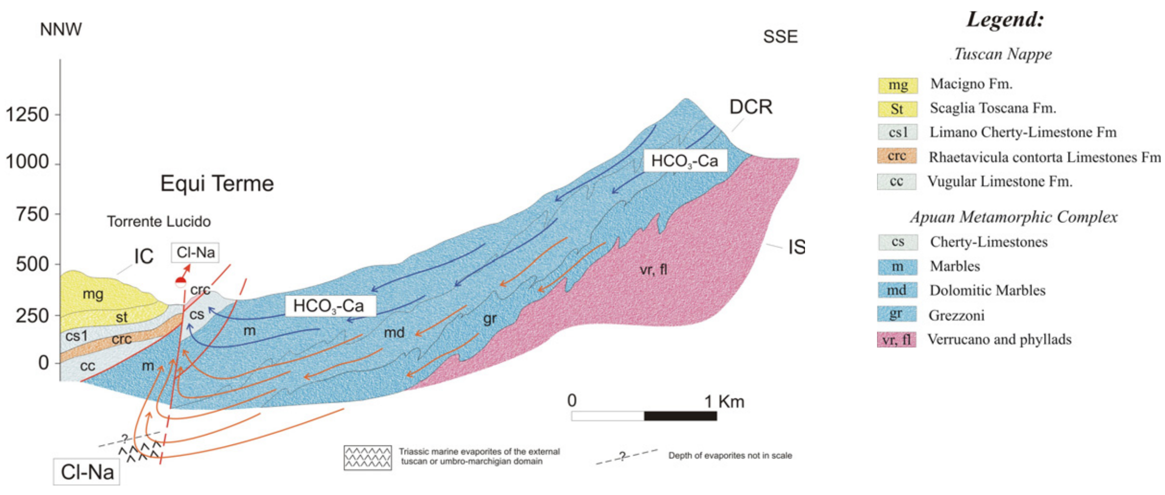

Fig. 2. Hydrogeological scheme of Equi Terme spring (FV22). *Legend*: IC: Impermeable Cover, DCR: Deep Carbonate Reservoir, IS: Impermeable Substratum.

5. Conclusions

Combined with geological and hydrogeological information, a detailed geochemical survey of 111 water points (springs and wells) has contributed to the definition of an integrated hydrogeochemical model of the Magra Valley, an area investigated for seismic precursors in Northern Tuscany, Central Italy. Based on mineralogical compositions of rocks, chemical composition of waters, and underground water circulation paths, three main types of hydrogeological structures have been identified in the area. Among the six springs issuing along major tectonic discontinuities, and fed by deep circulating waters, the Equi spring has been recognized as the most suitable location for installing a continuous automatic monitoring station for the remote control of hydrogeochemical parameters. This spring is currently being remotely controlled for geochemical seismic precursors.

Acknowledgements

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