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the Santa Ninfa karst system and possible
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Abstract

The Santa Ninfa karst system is an area strongly controlled by tectonics, whose intense fracturing gave rise to the formation of a large number of cavities that foster the drainage of water. The hydrogeochemical characters of groundwater circulating in this aquifer, together with its isotopic signature, were investigated in details. The chemistry of groundwater reflects the nature of the rocks hosting the aquifers, constituted by primary and diagenetic selenitic gypsum, salts, and gypsum-arenite, whose dissolution is responsible of the geochemical fingerprint of the quasi-totality of the samples. A single site (CAM) is characterised by a different chemical composition, indicating a mixing between Ca-sulphate, Ca-bicarbonate and a NaCl-rich water. From the chemical point of view, no evidence of interaction between shallow groundwater and deep fluids has been detected. Conversely, isotopic fluctuations highlight mixing processes between surficial (evaporated) runoff and groundwater.

Different mixing proportion among these endmembers can be reflected in variations of the chemical character of the sampled springs. Changes in mixing proportions can be the effect of differential permeability variations, in turn produced by local stress field changes during seismogenic processes. In this scenario the geochemical monitoring of the Santa Ninfa karst aquifer could be of relevant interest in the study of seismogenic processes in this area, with particular reference to the relationship between seismic and geochemical transients.

Keywords: hydrogeochemistry, gypsum karst system, neotectonics, groundwater

1. Introduction

Western Sicily is an area affected by seismicity, with several strong earthquakes that since historical times have caused relevant damages and fatalities (Guidoboni et al., 2002; Bottari et al., 2009); the most recent catastrophic earthquake (Mw=5.6) struck the Belice Valley in 1968, destroying 7 towns

and killing 330 people (De Panfilis and Marcelli, 1968; Marcelli and Pannocchia, 1971; Bottari, 1973; Anderson and Jackson, 1987; Rovida et al., 2011). A previous study carried out in the Belice earthquake area (Favara et al., 2001a) suggested a direct connection between local thermal springs (Acqua Pia and Terme Selinuntine) and the main tectonic features, with anomalies of temperature and concentration of dissolved ions (SO_4 , Cl, Na, Total Dissolved Solids) and gases (CO_2), in connection with the 1968 seismic sequence.

Other groundwater circulation systems in the area show evident relationships with tectonics; a very peculiar case is the aquifer of the Santa Ninfa gypsum karst system (Fig. 1), located within the area struck by the 1968 seismic sequence (the town of Santa Ninfa was completely destroyed). The Santa Ninfa karst system is strongly controlled by tectonics (Madonia et al., 2017), and the intense fracturing gave rise to the formation of a large number of cavities. The largest one, namely "La Grotta", is located at the end of a blind valley and it is a through-cave about 1350 m long and 30 m deep. It consists of at least three main levels of sub-horizontal galleries, the lowest of which is characterized by perennial flowing water, running along the water table (Madonia and Madonia, 2020).

In this study we integrated the results of the geochemical investigation published by Favara et al. (2001b) and Liotta et al. (2013) with unpublished data, with the aim of providing new insights on the hydrogeochemical characterisation of this aquifer. The hydrogeochemical system directly linked to the La Grotta hydrogeological tunnel, involving the mixing with surface runoff, is described in another paper from this volume (Madonia and Madonia, 2020). Here we report on the general chemical and isotopic character of groundwater, paying attention to the possible inferences on neotectonics.

2. Study area

The study area is located in western Sicily, along the southern part of the NNW-SSE trending San Vito Lo Capo-Sciacca (SVCS) band (Di Stefano et al., 2015). This band represents a crustal discontinuity, nearly orthogonal to the main thrust propagation of the Sicilian fold and thrust belt (SFTB), which separates two zones showing a different Permian to Tertiary evolution: thick carbonate platforms in the western sector, facing deep-water successions located in the eastern one. Upper Triassic reefs, huge megabreccia, and submarine volcanism suggest the existence of a long-lasting weakness zone, related to this discontinuity and located at the boundary between its western and eastern sectors. This discontinuity has been episodically reactivated with transpressional and/or transtensional mechanisms (Di Stefano et al., 2015). The historical and recent seismicity of the area identifies western Sicily as an active deformation zone; the strongest seismic activity was recorded

in 1968 (Belice seismic sequence, maximum $M_w=5.6$). A previously unknown Quaternary fault was identified at Monte Porcello (MPF; Michetti et al., 1995), showing geometry and kinematics consistent with a regional NNW-SSE trending, right-lateral strike-slip zone. The MPF, together with other adjacent faults, crosscuts upper Piacenzian to Gelasian calcarenites and clays, and accommodates the differential shortening of the large-ramp anticline (Gibellina anticline) formed by Tortonian to lower Pliocene sediments (Di Stefano et al., 2015).

The studied area of the Santa Ninfa gypsum karst system lies immediately NW of MPF, inside the Castelvetro Basin. Its sedimentary succession is composed of: i) upper Tortonian terrigenous and carbonate-clastic sediments (Terravecchia Fm); ii) lower Messinian evaporite deposits (Gessoso-Solfifera Series, including the Pasquasia Fm) composed of evaporitic limestones, primary and diagenetic selenitic gypsum, salts, gypsum-arenites, and greyish marly clay; iii) lower Pliocene globigerinid chalky-limestone (Trubi Fm); iv) middle-upper Pliocene marly arenaceous sands (Santa Margherita Belice Fm) (Basilone, 2012).

The surficial hydrography is mainly constituted by epigeic karst landforms (e.g. dolines and blind valleys) from which precipitations funnel into the underground feeding the aquifer.

Thermometric and pluviometric data recorded from 1951 to 1986 in 3 different local meteorological stations reveal an average annual temperature of 15.9 °C, which hottest month is August (average monthly temperature of 25.6 °C), whereas January is the coldest one (9.4 °C average monthly temperature). The average annual rainfalls account for 584 mm and are distributed in 73 days, with the wettest month in December (87 mm) and the driest in July (6 mm). Following the abovementioned seasonal distributions of air temperature and rainfall, the climate of the Santa Ninfa area can be classified as temperate-semiarid.

This area is characterised by well-developed karst phenomena, both at the surface and underground. Their formation is linked to the presence of both tectonic dislocations and impermeable levels that foster the drainage of water through preferential flow pathways (Madonia and Panzica La Manna, 1987). The hydrogeological setting of the studied area is characterised by an impermeable substrate constituted by clay of Terravecchia Fm, covered by Messinian gypsum that constitutes the main reservoir.

3. Analytical methods

This study is based on data acquired in different periods during the last 20 years. Six springs Rampinzeri, Risorgenza, Polla, Case Di Stefano, Capo D'Acqua and Case Monreale (hereafter referred as RAM, RIS, POL, CDS, CDA and CAM, respectively) were collected every three months, from April 1997 to May 1998. During the same period, isotopic composition of rainfall was measured

in samples collected in two rain-gauges, located at 430 m and 630 m a.s.l. (sites Case Biondo and Case Catalano, CAB and CAC, respectively). Other isotopic data of precipitation (SNI), related to the period 2004-06, are from the study of Liotta et al. (2013); additional chemical data from another spring (MEN) were collected in 2014. Location of sampling sites is shown in Fig. 1b.

Chemico-physical parameters (pH and electric conductivity) were measured directly in the field using Orion instruments. Water samples used for the determination of dissolved major and trace elements were first filtered using 0.45 μm Millipore MF filter and then collected in LD-PE (low-density polyethylene) bottles for major element analyses, acidifying to ca pH 2 the aliquot destined to cation determination with HCl. Untreated aliquots were stored for alkalinity determinations, made via titration with HCl (0.1 N). Major ions were determined by ionic chromatography using Dionex 2000i. Major elements data are presented in Table 1. All measured values were processed using the computer program PHREEQC, version 3.1.2, (Parkhurst & Appelo, 2013), in order to calculate ion activities and $P\text{CO}_2$ (partial pressure of CO_2) of the water samples, as well as saturation state with respect to relevant minerals.

The O and H isotopic compositions of groundwater and rain samples were determined using Analytical Precision AP 2003 and FinniganMAT Delta Plus IRMS devices, respectively. The isotopic ratios are expressed as the deviation per mil (δ ‰) from the international standard V-SMOW. The uncertainties are $\pm 0.1\%$ for $\delta^{18}\text{O}$ and $\pm 1\%$ for δD .

Contour maps were realised using the kriging algorithm implemented in the contouring options of Golden Software Surfer release 16; we adopted the blanking option for grid points outside the convex hull of data, for avoiding the generation of extrapolated information outside the area covered by measures.

4. Results

4.1 Chemico-physical parameters, concentration of major elements of groundwater

Chemico-physical parameters and the results of the chemical analyses are listed in Table 1. Values of pH, temperature and electrical conductivity range between 5.83 and 7.95, 12.4 and 24.6 $^{\circ}\text{C}$, 776 and 3430 $\mu\text{S cm}^{-1}$, respectively.

The data are also presented in the ternary diagrams of the main anions and cations (Fig. 2a-b). The quasi totality of samples falls close to the SO_4 -corner, whereas CAM samples show a more scattered distribution close to the HCO_3 -corner; in the ternary cations diagram data fall close to the Ca-corner. Total Dissolved Solids (TDS) show the lowest values in sample CAM ($< 500 \text{ mg L}^{-1}$), and range from 493 to 3217 mg L^{-1} in the first group, showing their maximum values in SUL.

The scatter plots reported in Fig. 3 correlate the molar abundance of Na vs Cl, SO₄ vs Ca and HCO₃ vs Ca/ SO₄. In the Na vs Cl diagram (Fig. 3a) samples fall close to the line representative of halite mainly due to dissolution processes of evaporite minerals, with some points showing Na or Cl excess probably related to ion-exchange reactions between water and clay minerals (Martin et al., 1996). The SO₄ vs Ca scatterplot (Fig. 3b) reveals that all samples belonging to the first group show both SO₄ and Ca concentrations above 30 meq L⁻¹ and a stoichiometric ratio close to that one of the gypsum. CAM samples are characterised by SO₄ and Ca concentrations below 10 meq L⁻¹ and variable Ca/SO₄ ratio. In the HCO₃ vs Ca/ SO₄ scatter plot (Fig. 3c) samples belonging to the first group fall along a line, parallel to the ordinate axis, whereas CAM samples deviate from this alignment and are more enriched in Ca concentration with respect to sulphate.

Saturation indexes of the main mineralogical phases are plotted in Fig. 4. Most of the samples are oversaturated in calcite, dolomite and gypsum, with the exception of MEN that is undersaturated in dolomite, and CAM in dolomite and gypsum.

4.2 Isotopic composition of precipitation and groundwater

The oxygen isotopic composition of rainwater, illustrated in Fig. 5a-b, shows a large variability, with a minimum of -9.54‰ (SNI, December 2005) and a maximum of -2.5‰ (SNI, August 2005); δD spans from -60 to -11 ‰ recorded in the same site and months.

The isotopic composition of groundwater (Fig. 5a-b) shows a lower range of variability, with δ¹⁸O from -6.7 to -5.9‰ and δD from -40 to -30‰.

5. Discussion

5.1 Chemico-physical character of groundwater

The observed geochemical differences between CAM and all other samples can be explained by the distinctive nature of the rocks hosting the aquifers. These are mainly constituted by primary and diagenetic selenitic gypsum, salts, and gypsum-arenite (Gessoso Solfifera Series), whose dissolution is responsible of the geochemical fingerprint of the quasi-totality of the samples. The site CAM is characterised by a different chemical character, indicating a mixing between Ca-sulphate, Ca-bicarbonate and a NaCl-rich water. CAM is located in the Terravecchia Fm, composed of terrigenous and carbonate-clastic sediments, that is sited stratigraphically below the Gessosa Solfifera Fm, from which it receives groundwater enriched in both sulphate and NaCl. During the hydrologic cycle CAM shows fluctuations, with the gypsum component prevailing on the bicarbonate one and vice versa. Saturation indexes of the first group of groundwater reveal that all samples are saturated with respect to gypsum, and quite all of them are oversaturated in carbonate minerals (both calcite and dolomite). CAM samples are undersaturated with respect to both carbonates and gypsum.

5.2 Isotope hydrology and reconstruction of hydrogeological circuits

The isotopic composition of rainwater shows a large range of values, mainly due to the high seasonal variability that reflects the climatic features of the Mediterranean area (Fig. 5a). The best fitting line in the diagram δD vs $\delta^{18}O$ represents the local meteoric water line (LMWL), calculated in this study, described by the equation: $\delta D = 6.09 \delta^{18}O + 5.05$. As expected, the most negative values were recorded during the cold months and conversely the less negative during the warm dry-season. The calculated LMWL is comprised between the Global (Craig, 1961) and the Mediterranean (Gat and Carmi, 1970) Meteoric Water Lines.

The isotopic vertical gradient can be computed using data from CAC and CAB but excluding SNI, because this site operated in a different period: its value ($\delta^{18}O$) is $-0.12 \delta \text{‰}/100 \text{ m}$, lower than that found by Longinelli and Selmo (2003) for southern Italy ($-0.2 \delta \text{‰}/100 \text{ m}$) but equal to that found by Liotta et al. (2013) for western Sicily.

The time distribution of isotopic compositions of groundwater (Fig. 5b) presents, as expected, minor fluctuations with respect to rain, with a range of less than $1 \delta \text{‰}$ for $\delta^{18}O$. In particular, the most variable is RAM ($0.8 \delta \text{‰}$) while the most constant is CDS ($0.1 \delta \text{‰}$); all the others exhibit a range of $0.3\text{--}0.5 \delta \text{‰}$. The smoothed isotopic signal recorded in groundwater suggests that: i) no direct connections between sinkholes absorbing surface runoff and the main aquifer exist, and ii) the average residence time of groundwater is close to one hydrologic year. The relationships between the isotopic signal and the hydrogeologic circuit are well evidenced in Fig. 6, where the isotopic composition contour map of groundwater is reported. The most variable spring is RAM, which is located at the highest altitude (487 m a.s.l.); this spring is the emergence point of a perched aquifer characterised by a thin hydrogeologic circuit (about 180 m, considered that the maximum elevation is Mt Finestrelle, 660 m high). The second more variable site is CAM ($0.5 \delta \text{‰}$), which is also the second highest (421 m a.s.l.) with a maximum thickness of the hydrogeological circuit of 240 m; the water body feeding this spring probably is a perched aquifer as the previous one. All the other springs (CDA, CDS, RIS and POL) are related to the basal aquifer, but they show a different time variability. The most constant is CDS ($0.1 \delta \text{‰}$), located in the northern part of the area and intersected by a tectonic discontinuity, as the close CDA showing a low variability ($0.3 \delta \text{‰}$). The other two springs, RIS and POL, are located in the southern margin of the gypsum outcrop and exhibit a slightly higher variability ($0.4 \delta \text{‰}$); this is not surprising because these springs are a part of the karst hydrogeological system of La Grotta, where recurrent inputs of surface runoff interact with the basal flow (Madonia and Madonia, 2020). The contribution of evaporated surface runoff is further confirmed by the comparison between the average isotopic composition of groundwater and the mean yearly composition of rain, weighted for rainfall amount (Table 2). We can distinguish between two

different groups. The first one includes the sites whose isotopic composition is comprised between those of the two rain gauges: CDA, RAM, CDS, CAM and MEN. This behaviour is compatible with aquifers fed by local rain. The second group is composed of sites (RIS and POL) showing an isotopic composition more positive than that of the rain gauge located at the lowest altitude (CAB). This apparent discrepancy can be explained by the contribution of evaporated surface runoff, absorbed by the Biviere sinkhole and mixing with the basal aquifer flow.

Another clue of different hydrogeological circuits characterising the two groups of springs above discussed is given by the spatial distribution of partial pressure of dissolved CO₂ (PCO_2 , Fig. 7). The behaviour of the contour lines highlights an anomaly centred on RIS and POL that interrupts its flat spatial distribution. The origin of the dissolved CO₂ in these springs is organic, as suggested by its $\delta^{13}C$ value calculated from the composition of the total dissolved inorganic carbon in RIS and POL: -21 and -22 ‰, respectively (INGV, Sezione di Palermo – internal database). The higher dissolved CO₂ values measured in samples from La Grotta hydrogeological system are due to the higher residence time, and consequent higher chemical maturity, of groundwater representing the local basal flow that circulates in this cave. Surface runoff drained underground by absorbing caves and smaller karst cavities transports huge amounts of suspended organic particular matter, which is accumulated in the small size karst discontinuities and fractures where groundwater flow is very slow or static. The following degradation of organic matter produces CO₂ that is drained by karst conduits of larger size, like the La Grotta system. This interpretation is supported by the values of soil CO₂ flux measured in a transect crossing the surface projection of the main gallery of La Grotta, which are lower ($4 \text{ g m}^{-2} \text{ d}^{-1}$) over the gallery and higher ($162 \text{ g m}^{-2} \text{ d}^{-1}$) on both sides (Camarda et al., 2020).

6. Hydrogeochemical characters and possible inferences on neotectonics

Our results highlight the lack of mixing processes between shallow groundwater and deep fluids. The study of this aquifer does not provide results useful as proxies for neotectonics processes involving circulation of deep fluids. Conversely, mixing processes between surficial (evaporated) and groundwater occur, as evidenced by isotopic variations with time. Studies on seismogenic areas (i.e. Favara et al., 2007; Madonia et al., 2013) highlighted that the variation in the stress fields during neotectonic activity cause permeability variations. The dynamics of the local stress field during seismic phase seemingly induces differential permeability variations, closing fractures (i.e. reducing permeability) in sub-volume interested by compression and, conversely enhancing permeability where tension prevails (Favara et al., 2007). Stress-induced permeability changes can result in variations of geochemical parameters (Favara et al., 2007), especially in multicomponent aquifers, like the Santa Ninfa aquifer; these variations can result in different mixing proportion among the

different endmembers. Therefore, the monitoring of such a system could be of relevant interest for the earthquake forecasting, using geochemical parameters for detecting anomalies of the crustal stress dynamics.

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Table 2 Weighted mean $\delta^{18}\text{O}$ compositions of groundwater and meteoric water

Sample	Altitude (m asl)	Weighted mean $\delta^{18}\text{O}$
CDA	367	-6.47
RAM	487	-6.35
CDS	323	-6.35
CAM	421	-6.33
RIS	414	-6.18
POL	362	-6.10
CAB	430	-6.22
CAC	635	-6.30

Figure captions

Fig. 1. a) Geological map of Sicily; b) detailed geological map of the Santa Ninfa area (modified from Agostini and Cucchi, 1989) with locations of sampling sites (see main text for explanation of acronyms).

Fig. 2. Ternary diagram of main anions.

Fig. 3. Scatter plots of: a) Na vs Cl b) SO_4 vs Ca; c) HCO_3 vs Ca/ SO_4 .

Fig. 4. Saturation index diagram of the main mineralogical phases.

Fig. 5. a) Oxygen and deuterium composition of groundwater and meteoric water. Grey dashed lines represent the Global Meteoric Water Line (GMWL, Craig, 1961) and Mediterranean Meteoric Water Line (MMWL, Gat and Carmi, 1970). Black line represents the Local Meteoric Water Line (LMWL); b) temporal variation of oxygen isotopic composition of rain water and groundwater and their relationship.

Fig. 6. Spatial distribution of oxygen isotopic composition of groundwater.

Fig. 7. PCO_2 of groundwaters and location of the main structural-tectonic features of the area.

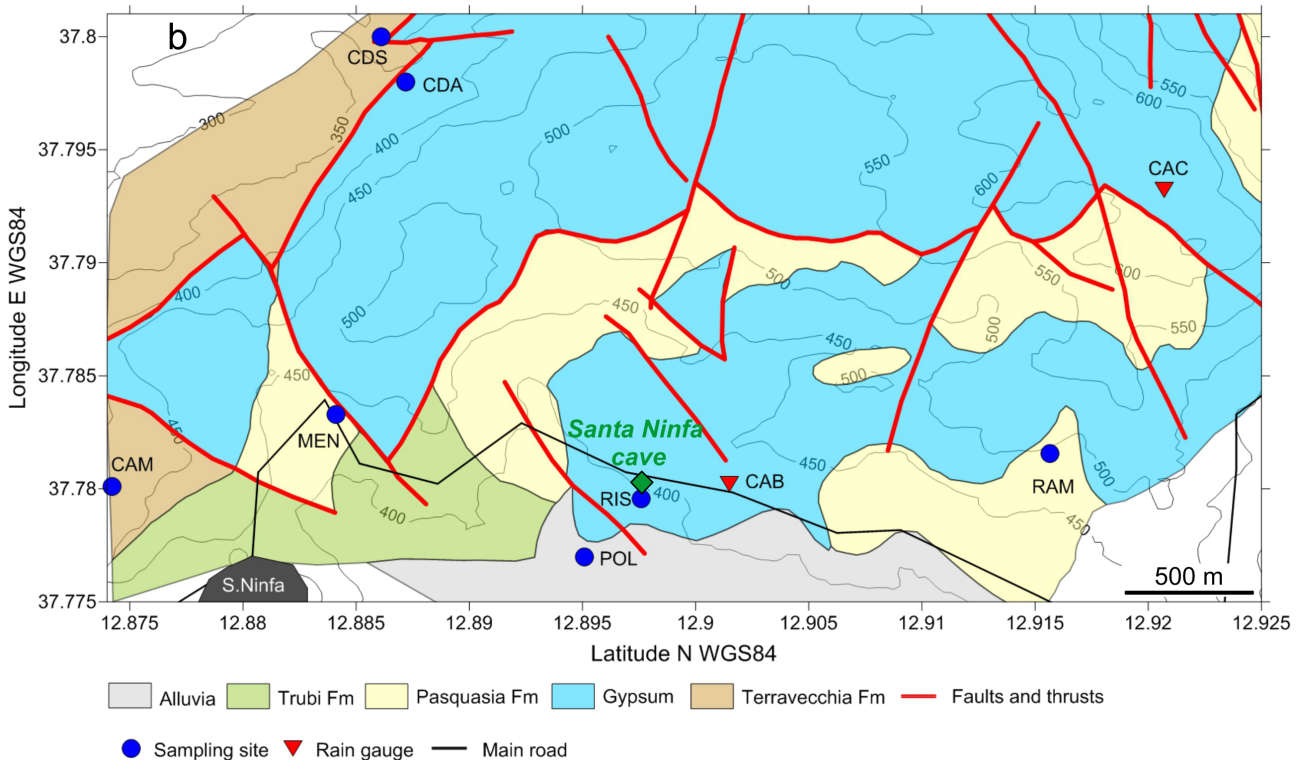
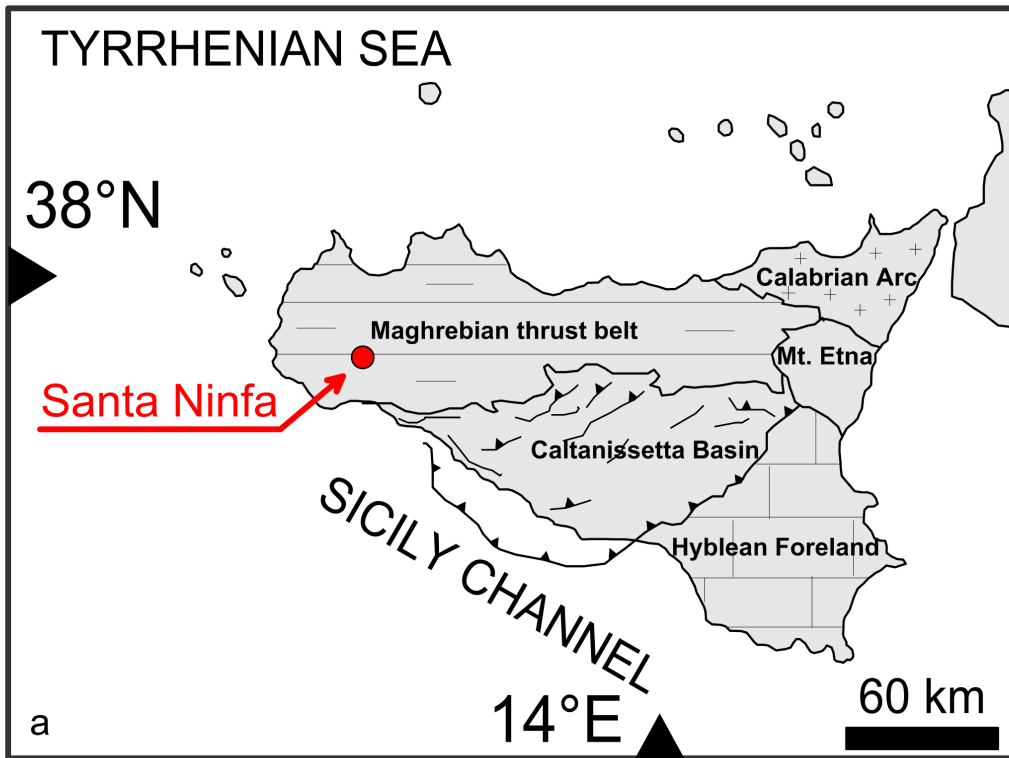


Fig. 1

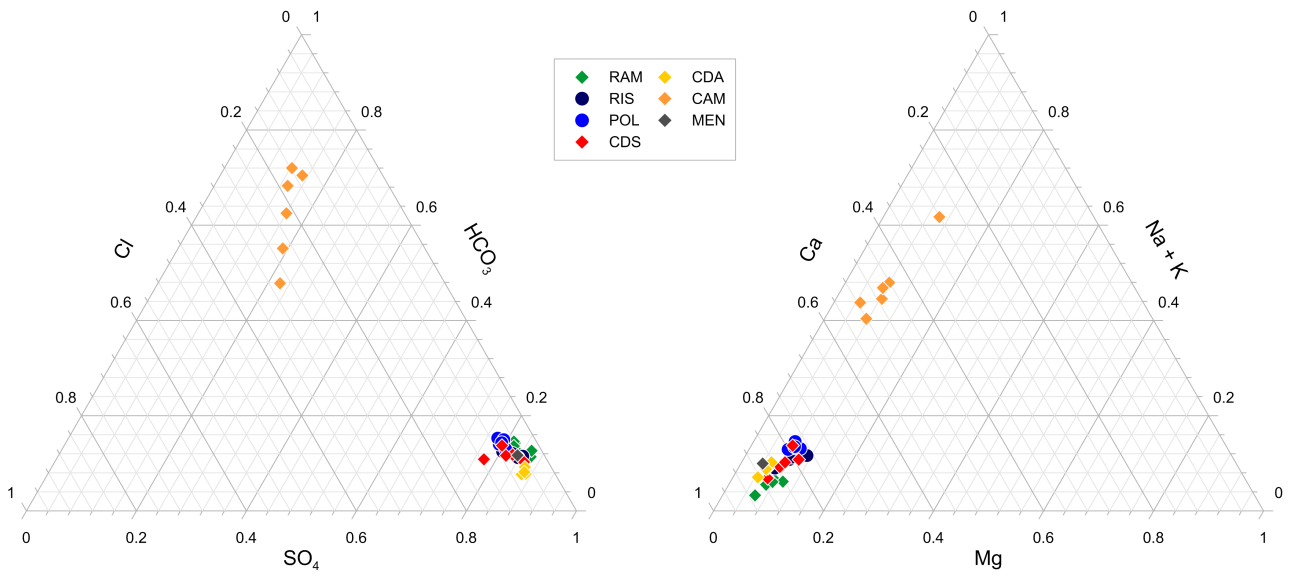


Fig. 2

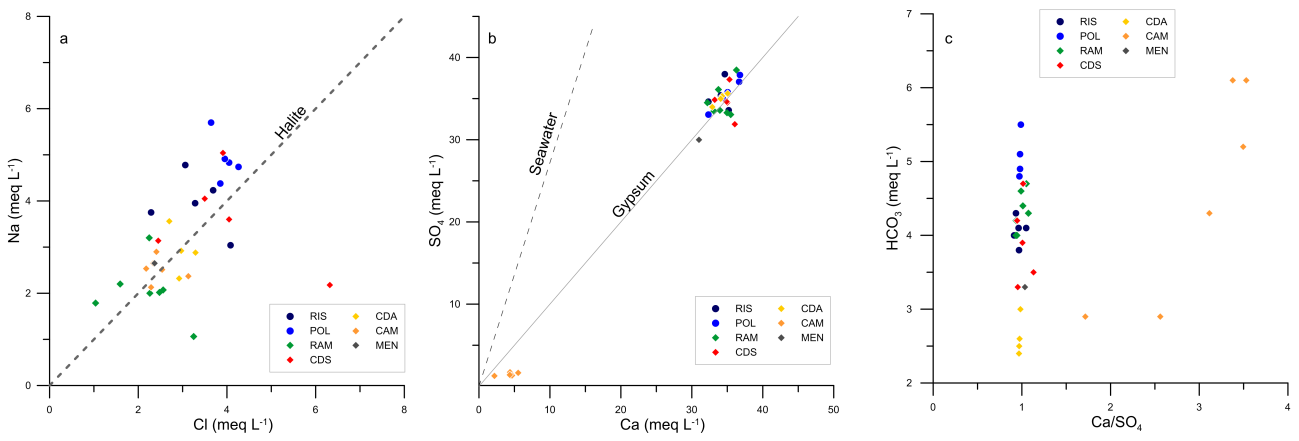


Fig. 3

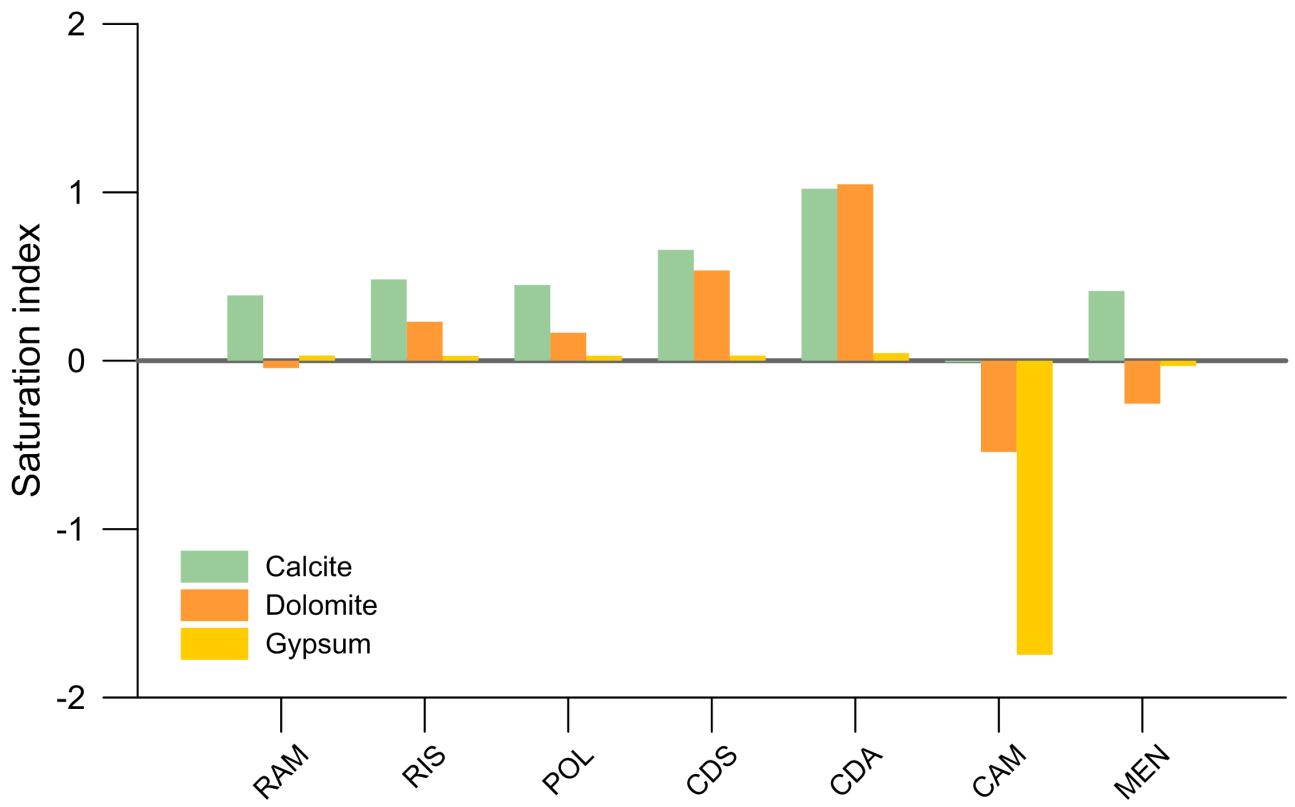


Fig. 4

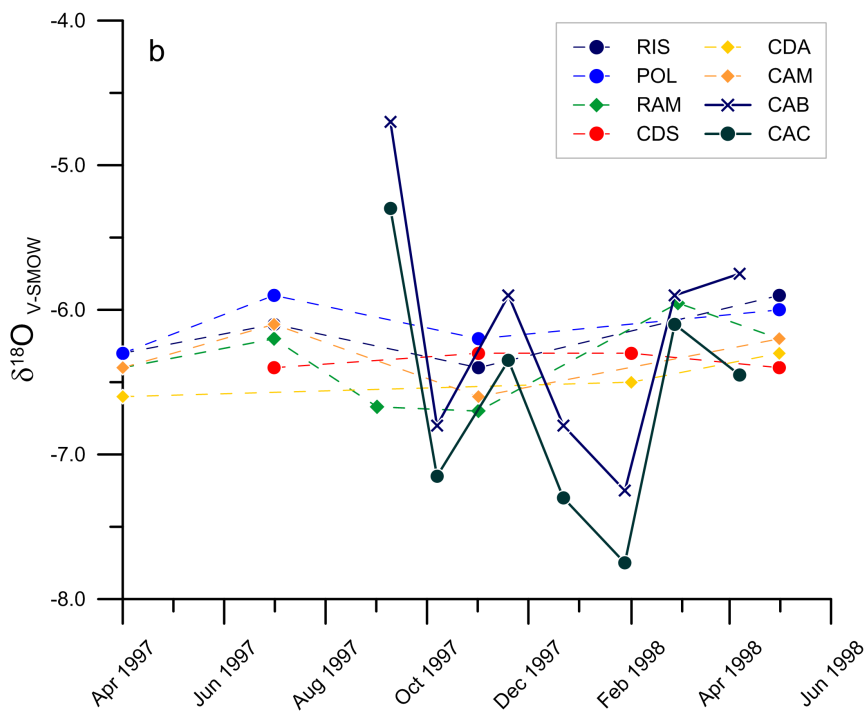
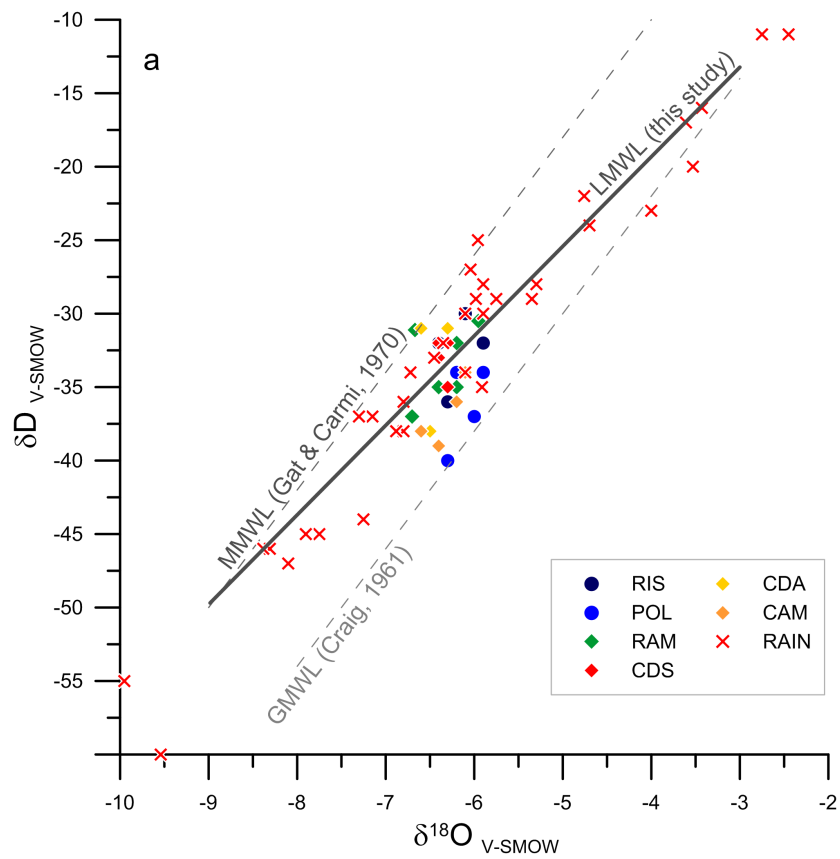


Fig. 5

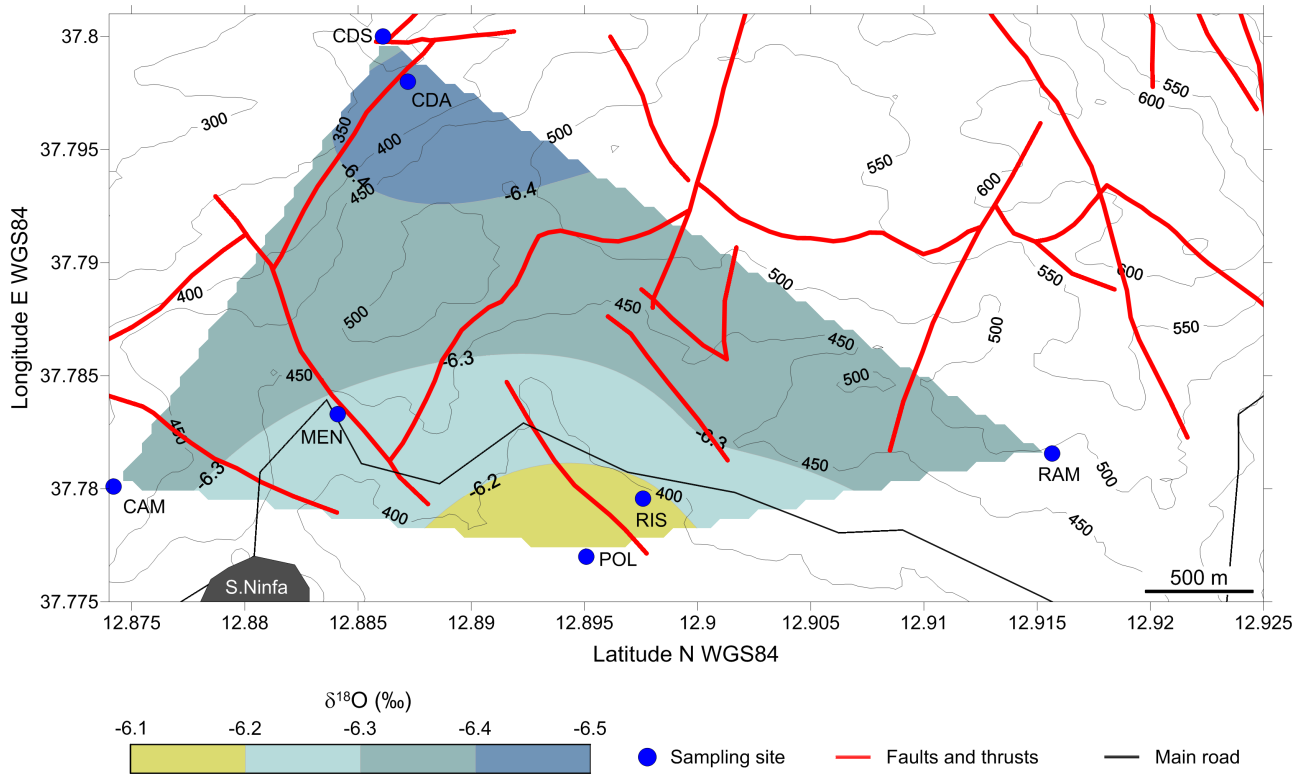


Fig. 6

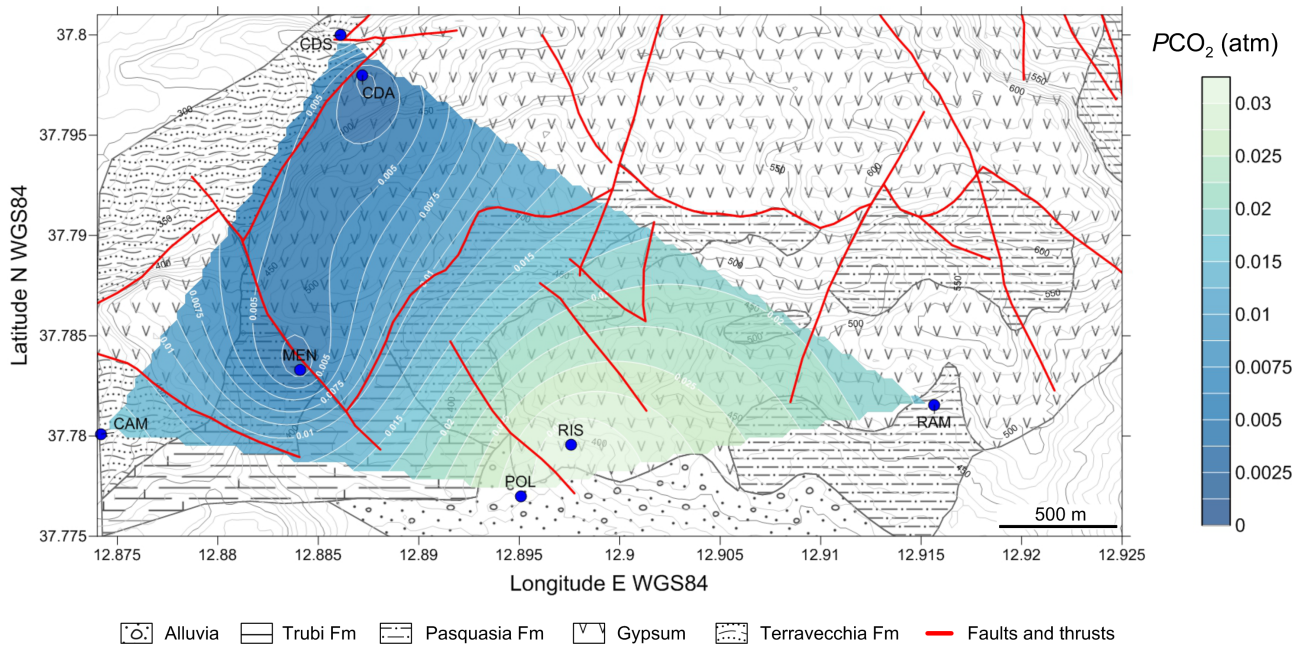


Fig. 7