*geologica***acta**

Sulfur and oxygen isotope compositions of Upper Triassic sulfates from northern Apennines (Italy): paleogeographic and hydrogeochemical implications

T. BOSCHETTI [1] [*]   **G. CORTECCI** [2]   **L. TOSCANI** [1]   **P. IACUMIN** [1]

[1] **Department of Earth Sciences, University of Parma**
Via G.P. Usberti 157/a, I-43100 Parma, Italy.   Boschetti E-mail: work@tizianoboschetti.com

[2] **Institute of Geosciences and Earth Resources, CNR Research Area**
Via Moruzzi 1, I-56124 Pisa, Italy

* Corresponding author. Fax: +39 0521 905305

┤ A B S T R A C T ├

Upper Triassic bedded evaporite sulfate of the Burano Formation outcropping at Cerreto Pass between Tuscany and Emilia-Romagna in the Northern Apennines were analyzed for sulfur and oxygen isotope compositions, yielding $\delta^{34}S$ and $\delta^{18}O$ values of 15.5±0.4‰ and 10.8±1.2‰, respectively (mean ±99% confidence intervals). Combining these values with those of other Burano Formation sulfate deposits along the Apennine chain, mean for $\delta^{34}S$ and $\delta^{18}O$ values are obtained (15.2±0.2‰ and 10.9±0.5‰, respectively). These isotopic signatures are interpreted as preserved primary features, despite the fact that the Burano Formation underwent anchizone to epizone metamorphism during the Apennine orogenesis. An overall $\delta^{18}O$ value of 10.9±1.5‰ (mean ± pooled standard deviation), obtained by combining consistent sets of data from Italy and Spain, closely approaches that of gypsum deposited from the Tethys ocean during the Late Triassic. In addition, reviewing the isotope data published on Late Triassic evaporite sulfates from the Mediterranean area and abroad, several $\delta^{34}S$ values appear to be lower than the inferred primary isotopic signature, and seemly decrease from East to West in the Mediterranean region, suggesting a similar trend for the Tethys ocean sulfate. Possibly, ^{34}S-depleted sulfate entered the ocean through oxidation of volcanic SO_2 emitted in the atmosphere and degassed from the seafloor during the development of Late Triassic rifting. On the other hand, positive shifts of $\delta^{34}S$ and $\delta^{18}O$ values also occur, defining a common trend that may be related to synsedimentary biological effects or post-depositional metasomatic-metamorphic effects, the latter affecting particularly the $\delta^{18}O$ signature. Therefore, the $\delta^{34}S$ and $\delta^{18}O$ signatures of evaporite sulfate may provide a like "slide-rule" diagram to distinguish between isotopic effects related to biological or abiological processes, thus contributing to the reconstruction of paleoenvironments and paleogeographic settings. Based on the $\delta^{34}S$-$\delta^{18}O$ "slide-rule", the isotopic composition of sulfate dissolved in spring and stream waters of northern Tuscany was interpreted in terms of origin of the sulfate and modifying processes in solution. It was concluded that sulfate in springs derives from Upper Triassic evaporite existing locally at depth (Burano Formation), whereas sulfate in streams is manifestly a mixture of Burano Formation sulfate with supergene sulfate from oxidation of sulfide in the rocks. In sulfurous springs, both sulfur and oxygen isotope fractionations with respect to the source sulfate signatures may be ascribed to bacterial effects. However, the oxygen isotope exchange of sulfate with water should have been a very minor process as supported by the near-surface temperature values estimated by sulfate-water oxygen isotope thermometry.

KEYWORDS │ Evaporite sulfate. Sulfur isotopes. Oxygen isotopes. Burano Formation. Late Triassic rifting.

INTRODUCTION

Evaporite deposits preserve much information about the Earth's past surface conditions. Such rocks are sensitive indicators of depositional environment (and climate), recorded by a variety of sedimentary structures and fabrics. Sulfate minerals are important to nearly-exclusive components of these deposits, and can help us to understand the geochemistry of ancient surface waters, including seawater.

Stable isotopes of sulfate can be used, in addition to mineralogy, chemical stratigraphy and geodynamic features, to unravel the geochemical history of the deposits. In fact, the dual isotope composition of sulfate minerals allow to trace the source of sulfur and oxygen and to possibly identify the chemical/biochemical (e.g., bacterial sulfate reduction) and physical (mixing of waters, volcanic events) processes that took place in the depositional basin. However, while sulfur isotope composition of sulfate minerals is generally preserved during burial, the oxygen isotopic composition can be modified by recrystallization and exchange with water. Oxygen isotope exchange kinetics between dissolved sulfate and water is generally very slow (Seal et al., 2000 and references therein) at temperatures lower than about 200°C. In addition to temperature, pH is another factor enhancing the exchange rate (Chiba and Sakai, 1985), and the isotopic effects are determined by the reaction time and the presence of catalysts. The latter may include sulfate-reducing bacteria, which can substantially enhance the oxygen isotope exchange rate between sulfate and water (Fritz et al., 1989; Grinenko and Ustinov, 1991), thus favouring the attainment of isotopic equilibrium even in low temperature environments.

Several sulfur-isotope age curves have been published for marine sulfate (e.g., Holser, 1977; Claypool et al., 1980; Strauss, 1997), structurally substituted sulfate in marine carbonate (SSS; Kampschulte and Strauss, 2004; Prokoph et al. 2008), and barite (Paytan et al., 2004) deposits. The sulfate-age record shows a sharp $\delta^{34}S$ increase towards the end of Lower Triassic (Claypool et al., 1980; see also Cortecci et al., 1981), related to a catastrophic chemical event in the oceans, by which stored in deeps high-$\delta^{34}S(SO_4^{2-})$ brine welled up and mixed with surface ocean (Holser, 1977). A corresponding large variation of sulfate $\delta^{18}O$ was not observed, this possibly depending on a concomitant sulfide and sulfate deposition and the isotopic effect of crystallization on sulfate that is about twice greater for $\delta^{18}O$ than for $\delta^{34}S$ (Claypool et al., 1980). Afterwards, the $\delta^{34}S$ signature decreased sharply, reaching values about 16‰ lower in the Middle Triassic, possibly followed by a gradual decrease to about 13‰ at the end of Triassic (Kampschulte and Strauss, 2004). Seemingly, the same trend occurred for the sulfate $\delta^{18}O$ signature (e.g. Claypool

et al., 1980). According to Holser et al. (1979) and Claypool et al. (1980), the isotopic composition of oceanic sulfate is basically controlled by a dynamic balance of the erosion input (oxidation of sulfide and dissolution of evaporite) and sedimentary output (deposition of sulfate and sulfide) fluxes in the ocean, and the isotopic fractionations involved in the cycle. Variations in these fluxes determined the sulfur and oxygen isotope age-curves over the geological time. Still, significant isotopic variations of evaporite sulfate most as high as about 3‰ were observed in different places within a given lithostratigraphic unit both vertically and horizontally (e.g., Claypool et al., 1980; Cortecci et al., 1981; Longinelli and Flora, 2007), possibly depending on a variety of depositional factors such as different degrees of restriction of the evaporitic basin to the open ocean (e.g., Fanlo and Ayora, 1998), bacterial sulfate reduction in local evaporating basins, or delayed oxidation of biogenic sulfide trapped in bottom waters. Post-depositional isotopic changes can also be caused especially by exchange of sulfate with water under metamorphic conditions that should affect the oxygen isotopes only. These isotopic effects should be nearly negligible, if metamorphism occurs in a practically closed system, where very low water to rock ratio is expected with anhydrous evaporite (anhydrite). The sulfur isotope composition is basically preserved during metamorphism, unless external fluids rich in sulfur are involved. Metamorphosed anhydrites from the Burano Formation of central-southern Italy (Cortecci et al., 1981) display rather consistent $\delta^{34}S$ values within 2.5‰ with a range of about 7.5‰ for the $\delta^{18}O$ values. Also, a $\delta^{34}S$ range of about 8‰ was observed for Keuper sulfate in northern-central Europe, with $\delta^{34}S$ values decreasing on average from Germany to Denmark (Nielsen, 1989). These two cases illustrate the problem of determining the isotopic composition of the parental oceanic sulfate by analyzing evaporite deposits, in the assumption that it should have been highly uniform as observed today for most samples, which display $\delta^{34}S$ and $\delta^{18}O$ values within only 0.5‰ (Longinelli, 1989).

The present study was undertaken to contribute to overcoming the general difficulty to assess the primary isotopic composition of oceanic sulfate and evaporites in the past, and more specifically during Late Triassic. This is of value for paleogeographic reconstruction, as well as for hydrogeochemistry when the isotopic composition is used to constrain the source of aqueous sulfate thus contributing to hydrogeological models. We were moved to the work by our interest in the Burano Formation of Italy, as it is frequently involved in the hydrologic systems through the peninsula. Therefore, the work was aimed to 1) delimit from new and past data sets the primary (synsedimentary) sulfur- and oxygen-isotope signatures of Burano Formation Late Triassic oceanic sulfate in the Apennines from Emilia

(Northern Italy) to Apulia (Southern Italy), 2) compare the Burano Formation isotopic values directly with those numerically reported in literature for other Upper Triassic evaporite, barite and structurally substituted sulfate occurrences in the Tethys area (Europe and abroad), rather than with the isotope-age curves for seawater sulfate which are presented as moving averages with uncertainties (Claypool et al., 1980; Strauss, 1997; Kampschulte and Strauss, 2004), 3) infer the syn- or post-depositional secondary processes modifying the primary isotopic signature of the sulfate, and 4) apply the sulfur- and oxygen-isotopic signatures to investigate the origin and evolution of aqueous sulfate in thermal-spring and stream waters of the Northern Apennines in Tuscany, where the Burano Formation occurs in the subsurface and in outcrops. With reference to points (1) and (4), original isotopic data on gypsum-anhydrite samples from some Burano Formation outcrops in Emilia and Tuscany were acquired, and treated together with published data on evaporites from other sectors of the Apennine chain.

GEOLOGICAL OUTLINE

Triassic sulfate evaporites in Italy are represented by Scythian, Anisian and Carnian to Rhaetian deposits. Lower and Middle Triassic deposits formed under a sub-tropical arid climate mostly in a few restricted basins of the western Alps and pre-Alps (Delfrati et al., 2002). Late Triassic deposits, corresponding to a paleoevolutionary phase of the Tethyan ocean domain characterized by climate changes from arid to humid to inter-tropical (Marcoux et al., 1993), are related basically to three events: the Keuper event (German facies; Carnian to Rhaetian; some outcrops in western Sardinia), the Carnian event in the eastern Alps and pre-Alps, and the Carnian-to-Rhaetian event in the Northern and Southern Apennines. Foraminiferal assemblages of carbonates in Burano Formation indicate age ranges from Carnian to Norian in Tuscany (Martini et al., 1989) and Norian to Rhaetian in Umbria (Ciarapica et al., 1987). The evaporite deposits in the Northern Apennines are represented by the Burano Formation and the Calcare Cavernoso Formation. Burano Formation is composed of meter-to-decameter alternations of gypsum-anhydrite and dolostones with minor halite, which were deposited mainly in a subaqueous environment (Lugli, 2001). Near to our study area in the Secchia River Valley a thickness of 2,200m was inferred for Burano Formation (Colombetti and Zerilli, 1987). In the Secchia River Valley, the Burano sequence is disrupted into thrust slides included tectonically into the younger allochthonous Ligurian units. Tectonization was strong, thus precluding a satisfactory reconstruction of the

stratigraphy of the formation (Lugli, 2001). The Calcare Cavernoso Formation is a rauhwacke at the base of the Tuscan Nappe; it should be the "autoclastic" derivative of the Burano Formation, through anhydrite hydration followed by dissolution of the resulting gypsum. The Calcare Cavernoso Formation is a carbonate-siliciclastic sequence deposited during the Mesozoic ingression of the Tethyan ocean into the rift system, cutting the Variscan orogen and its European foreland (Passeri, 1975). Locally, its thickness was found to be more than 700m (Costantini et al., 2002). The "plastic" Late Triassic lithotypes acted as glide horizons for the detachment of the sedimentary Tuscan Nappe from the Paleozoic basement during the formation of the Apennine chain (Boccaletti et al., 1987; Carmignani and Kligfield, 1990). The Burano Formation was delineated mainly by boreholes drilled in Emilia-Romagna, Tuscany, Umbria, Marche, Latium and Apulia (Figures 1 and 2; Martinis and Pieri, 1963). In Emilia (the Emilia-Romagna region's western portion), the Burano Formation (named Sassalbo Gypsum Unit) crops out along the Secchia River valley up to the divide (Western Emilia), and at Sassalbo (Northwestern Tuscany) in the upper Rosaro River valley. During the Apennine orogenesis, the Burano Formation and Calcare Cavernoso Formation in the Apuane Alps sector (Fig. 1) should have undergone anchizone to epizone metamorphism (e.g., Cerrina Feroni et al., 1983; Lugli, 2001).

A reconstruction of the Burano Formation history from sedimentation to the end of Northern Apennine orogenesis in the Secchia River Valley (Fig. 1) not far from the Apuane Alps metamorphic complex (greenschist facies) has been proposed (Lugli, 2001; Lugli et al., 2002): a) prevalent deposition of gypsum in Late Triassic basins; b) gypsum dehydration during burial to form anhydrite (Cretaceous?); c) syn-tectonic detachment of the anhydrite-bearing horizons and rock brecciation; d) hydrothermal deposition of minor sparry magnesite and partial metasomatic replacement of dolomite by magnesite. Homogenization temperatures of fluid inclusions in metasomatic magnesite and authigenic quartz in anhydrite beds range from 230°C to 315°C, corresponding to pressure-corrected maximum trapping values of 380°C to 400°C (Lugli, 2001; Lugli et al., 2002). The main source of these Mg-rich fluids was related to metamorphic reactions in the Apuane Alps complex (Lugli et al., 2002); e) sub-surface dissolution of halite to form residual caprock-like anhydrite mega-breccias; f) complete regypsification of anhydrite during exhumation at sub-surface conditions; and g) evaporite dissolution at surface exposure producing cellular dolomite breccias (Calcare Cavernoso Formation).

Some springs studied in the present work are located on the side of the Apuane Alps massif (open triangles MN, MS, Eq in Fig. 1). This massif underwent the Oligocene-Miocene greenschist facies metamorphism (380-465°C; Cortecci et al., 1989 and references therein) during the Apennine orogenesis, and is the site of stratiform and vein barite-iron oxide-pyrite ore deposits hosted within Middle to Late Triassic terrains. The vein ore should have been deposited by metamorphic fluids that remobilized the stratiform ore at estimated isotopic temperatures of 300-

400°C (Cortecci et al., 1989; see also Costagliola et al., 1997).

ANALYTICAL METHODS

Chemical analyses of water samples

In the field, temperature and pH were determined using an ORION 250A instrument equipped with a Ross glass electrode, and total aqueous sulfide as
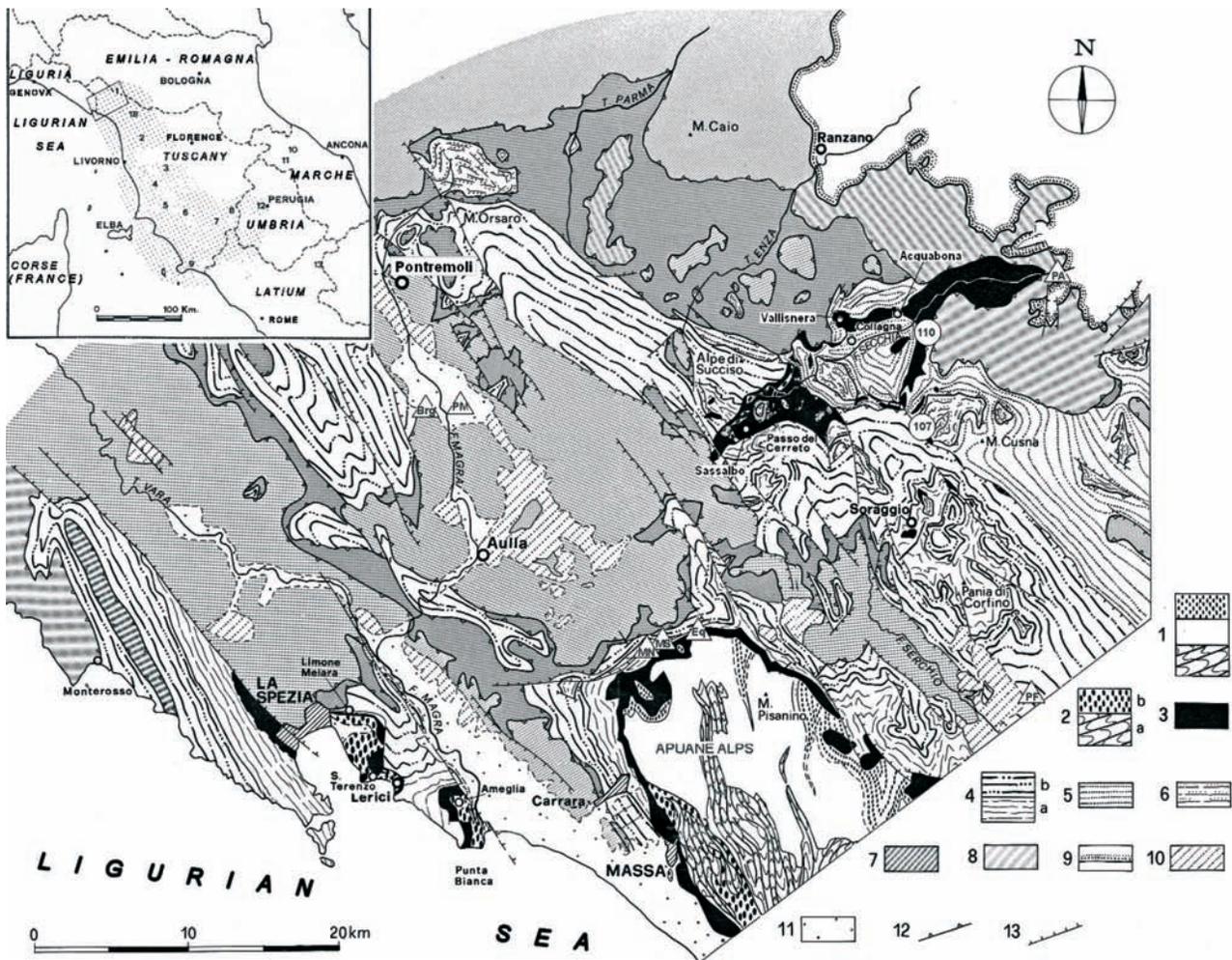

FIGURE 1 | Geological-structural map of the Northern Apennines sector of interest for the present work (modified from Leoni and Pertusati, 2002). 1) Autochthonous, a: Hercynian metamorphic basement, b: Mesozoic carbonatic cover, c: Sericitic Schists and Pseudo-Macigno (Upper Cretaceous-Oligocene); 2) Massa Unit, a: Hercynian metamorphic basement, b: Verrucano (Middle-Upper Triassic); 3) Anidriti di Burano/Calcare Cavernoso: evaporites, rauhwacke and tectonic breccias; 4) Tuscan Nappe, a: *Rhaetavicula contorta* limestone (Rhaetian), b: Macigno Fm. (Middle-Upper Oligocene); 5) Mt Modino and Mt Ventasso Units: turbiditic sandstones (Upper Oligocene-Lower Miocene) and Basal Complex (Lower Cretaceous-Upper Oligocene); 6) Cervarola Unit (Lower-Middle Miocene); 7) Canetolo Unit (Upper Cretaceous-Lower Miocene); 8) Internal and External Ligurian Units (Upper Jurassic-Paleocene); 9) Ranzano Epiligurian Unit (Middle-Upper Eocene-Lower Miocene); 10) intramountain basins (Pliocene-Pleistocene); 11) detritus and alluvia; 12) and 13) thrusts and faults. Locations of handled evaporite sulfate deposits, springs and river waters are shown: for evaporites, see locality names in Table 1; for springs, keys to symbols are in Table 3 and caption of Figure 4. In the inset, known occurrences and distribution of Upper Triassic evaporite sulfates from outcrops (1 to 9; 1: Passo del Cerreto between Emilia-Romagna and Tuscany) and drilled cores (10 to 12 in Northern Apennines: Fossombrone-1, Burano-1, Perugia-1 and 2 boreholes; and 13 in Central Apennines: Antrodoco-1 borehole).

$H_2S^0+HS^-+S^{2-}$ and aqueous silica as $SiO_2(aq)$ by means of a Merck SQ300 photometer with Merck Spectroquant kits and Eaton et al. (1995) methods. Water aliquots for laboratory analyses were filtered by Aquaprep® V 50mm syringe filters with Verspore® membrane (0.45μm) and then stored in the dark at 4°C. In the filtrate, SO_4^{2-} was determined by ionic chromatography (DX 100 DIONEX with auto-regenerated anionic suppression). Formaldehyde solution (3ml, 36.5%) and cadmium acetate solution (20ml, 20%, supplemented with acetic acid) were added in field to the water aliquots for sulfate isotope analysis (1.5liter) in order to stop
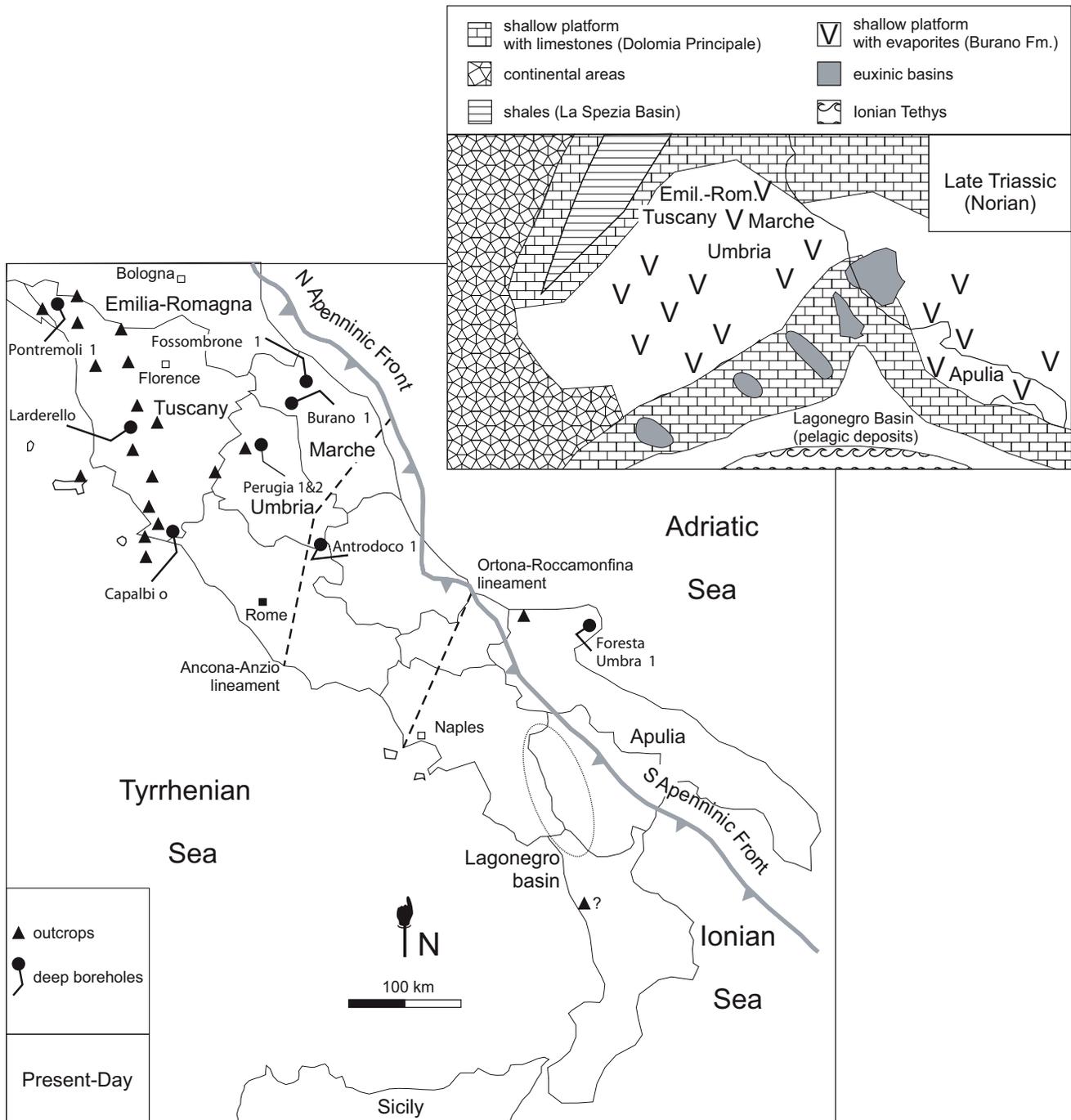

FIGURE 2 | **Occurrences and distribution of Upper Triassic sulfate evaporites as outcrops or drilled deposits in Italy. In the inset: paleogeographic map of the Apulia/Adria Plate during Late Triassic (modified after Ciarapica, 2007). See also Figure 3B for tectonic plate setting in the Western Tethys.**

bacterial activity and precipitate sulfides, respectively, then removing the latter as cadmium sulfide (CdS) by filtration in laboratory.

Isotopic analyses of gypsum-anhydrite, aqueous sulfate and water samples

Powered gypsum/anhydrite was milled in steel mortar and dissolved in Milli-Q ultrapure water. The solution was acidified with hydrochloric acid to pH≈2, heated at near boiling, and then added with $BaCl_2$ solution to precipitate the sulfate ions as $BaSO_4$. The same procedure was applied to precipitate sulfate as $BaSO_4$ from filtered, sulfide-free water samples. Before precipitation, organic matter in solution was removed before boiling by oxidation with $KMnO_4$ under acid conditions, then destroying the permanganate excess with KNO_2 solution. Cadmium sulfide was not kept for sulfur isotope analysis, due to the quite small, unusable amount recovered on the filter.

Aliquots of $BaSO_4$ were analyzed for S and O isotope composition by CF-IRMS (Continuous Flow-Ion Ratio Mass Spectrometry), following the procedures of Giesemann et al. (1994) and Boschetti and Iacumin (2005), respectively. A Eurovector 3028 HT elemental analyzer interfaced to a Micromass Isoprime mass spectrometer was used at the University of Nevada-Reno for sulfur isotopes, and a Thermo Finnigan TC/EA unit interfaced to a Delta Plus XP mass spectrometer was used at the University of Parma for oxygen isotopes. The obtained $\delta^{34}S$ and $\delta^{18}O$ values are given in ‰, relative to the Vienna Canyon Diablo Troilite (V-CDT) standard for S and V-SMOW standard for O. The precision of the methods (preparation and analysis) was within ±0.2‰ for S and ±0.4‰ for O. Standardization ($\delta^{34}S$ and $\delta^{18}O$) of the reference gases (SO_2 and CO) was made using NZ-1 (IAEA-S1; NIST RM 8554; -0.3‰ vs. V-CDT) and NZ-2 (IAEA-S-2; NIST RM 8555; 22.0‰ vs. V-CDT) for SO_2 (Coplen and Krouse, 1998), and NBS-127 (NIST RM 8557; $BaSO_4$ precipitated from seawater, with the recently assigned value of 8.6‰ vs. V-SMOW; Brand et al., 2009) as well as IAEA-CH-6 (sucrose, 36.4‰ vs. V-SMOW) for CO (see Boschetti and Iacumin, 2005).

The $\delta^{18}O$ of waters was determined by equilibration of CO_2 with water at 18°C using a Finnigan GLF 1086 automatic equilibration device on-line with a Delta Plus Finnigan mass spectrometer (University of Parma), and is reported in ‰ relative to the V-SMOW standard; the analytical precision was ±0.07‰. The procedure was calibrated against the international water standards recommended by the International Atomic Energy Agency (IAEA) (V-SMOW, GISP and SLAP) with assigned $\delta^{18}O$ values vs. V-SMOW of -24.8‰ for GISP, and -55.5‰ for SLAP (Brand et al., 2009).

Recently, Longinelli and Flora (2007) emphasized that the analytical procedures used to measure the $\delta^{18}O(SO_4)$ parameter led to rather large discrepancies between the obtained results. For instance, $\delta^{18}O$ values in the range of 8.1‰ to 11‰ were reported for modern seawater sulfate precipitated and reacted as $BaSO_4$ separate (see Longinelli and Flora, 2007 and reference therein). However, these analytical uncertainties refer to *off-line* preparation of CO_2 for mass spectrometry, which requires inductive heating of $BaSO_4$ with graphite plus glow-discharge conversion of produced CO fraction to CO_2 (e.g., Rees and Holt, 1991). Using this method, a first inter-comparison $\delta^{18}O$ value of 9.3±0.4‰ was assigned to the NBS-127 reference standard (seawater sulfate; IAEA; Gonfiantini et al., 1995). Nowadays, the certified $\delta^{18}O$ of the NBS 127 standard is 8.6‰ ±0.2‰ as obtained by the CF-IRMS *on-line* technique (NIST RM 8557; e.g., Böhlke et al., 2003). This value was confirmed by Boschetti and Iacumin (2005; 8.6±0.1‰) and Halas et al. (2007; 8.73±0.05‰), and should be accepted as representative of the oxygen isotope signature of sulfate ions in the present-day ocean. It should be noted that the $\delta^{18}O(SO_4)$ of 8.6‰ measured in H. Sakai's laboratory (Institute for Thermal Springs Research, Okayama University, Misasa, Japan) using the *off-line* technique was taken by Claypoool et al. (1980) as the normalizing value for their $\delta^{18}O$-age curve of marine sulfate. However, papers dealing with isotope geochemistry of marine sulfates often do not mention any analytical calibration or report measured values on seawater sulfate as long-ago recommended by Cortecci et al. (1981). The $\delta^{18}O$ values reported in the latter article were corrected by -0.9‰, as a $\delta^{18}O$ of 9.5‰ was measured for seawater sulfate. In conclusion, it is problematic to evaluate the reliability degree of published oxygen isotope data as often the application of the normalizing procedure is not documented, this precluding the possibility of making accurate comparisons of isotopic signatures at local and global scales.

STATISTICAL CALCULATIONS

Mean, standard deviation (SD), Student's t-test and Fisher's F-test values (for confidence intervals [C.I.] of 95% and 99%), were calculated using a Microsoft Excel 2003 spreadsheet. Pooled standard deviation (PSD) between two sample groups with SD_a and SD_b standard deviations and N_a and N_b sizes was calculated according to Motulsky (1995):

$$PSD = \sqrt{\frac{(N_a-1)*SD_a^2 + (N_b-1)*SD_b^2}{N_a + N_b-2}}$$

RESULTS AND DISCUSSION

Localizations of handled evaporite outcrops, springs and stream waters are shown in the geological-structural map of Fig. 1. Evaporite samples were collected from tectonic slides distributed in the Secchia River Valley within an interval of more than 10km. The strong tectonization and erosion phenomena did not allow to relate the samples to specific beds. The analytical results for studied evaporite sulfates are reported in Table 1. In Table 2, a compilation of the isotopic data is given for Late Triassic evaporites from the present work and from the literature. The analytical results for thermal springs are reported in Table 3.

Upper Triassic sulfate evaporites from Italy (Burano Formation)

Several Late Triassic (from 228±2 to 199.6±0.6Ma; Ogg, 2004) evaporite sulfate deposits in the world were investigated for their sulfur and oxygen isotope composition, e.g., in Israel and Canada (Claypool et al., 1980), Italian (Cortecci et al., 1981; Longinelli and Flora, 2007) and Austrian Alps (e.g., Schroll and Rantitsch, 2005), Italian Apennines (Cortecci et al., 1981, 2000; Bigazzi et al., 1996; Dinelli et al., 1999; Boschetti et al., 2005), Swiss Jura Mountains (Rick, 1990; Pearson et al., 1991), Northern and Northeastern Spain (Utrilla et al., 1992), and Lorraine Basin (Fanlo and Ayora, 1998). The compilation by Strauss (1997) of the δ^{34}S values available in 1992 for Phanerozoic evaporite sulfates was integrated by Kampschulte and Strauss (2004 and source references therein).

The Burano Formation sulfates analyzed in this study refer to the northern part of the Northern Apennines, and were sampled from Upper Triassic gypsum outcrops near the Passo del Cerreto (Sassalbo, Tuscany; Acquabona, Collagna and Vallisnera, Emilia-Romagna; Fig. 1). The δ^{34}S and δ^{18}O values of the samples of bedded gypsum-anhydrite (see Table 1) are quite consistent, with ranges of 15.1 to 16.0‰ (mean ±SD=15.5±0.4‰) and 9.1 to 12.6‰ (mean ±SD=10.8±1.0‰), respectively. These match with previous data from other minor Upper Triassic outcrops in Tuscany and Emilia-Romagna (δ^{34}S=14.6 to 16.7‰ and δ^{18}O=8.7 to 10.7‰; Dinelli et al., 1999; Boschetti et al., 2005), as well as with the δ^{18}O values of 11.0±1.4‰ obtained by Longinelli (1968) when analyzing Burano Formation anhydrite from deep drillings in Tuscany and normalized to the present-day accepted seawater δ^{18}O value of 8.6‰. All-inclusive mean (±SD) δ^{34}S and δ^{18}O

TABLE 1 | **Oxygen and sulfur isotope composition of Upper Triassic evaporite sulfates from the Burano Formation at the Passo del Cerreto (Secchia River Valley) between Emilia-Romagna and Tuscany. The mineralogical composition of samples is gypsum prevalent on anhydrite (± celestine). The statistical parameters do not include the vein sulfate**

Sample	δ^{18}O(SO$_4$) ‰ vs. V-SMOW	δ^{34}S(SO$_4$) ‰ vs. V-CDT
Acquabona1	10.3	15.1
Acquabona2	11.2	15.9
Collagna1	12.6	15.5
Sassalbo1	11.4	15.7
Sassalbo2	9.1	15.4
[†]Sassalbo3	12.9	17.0
Sassalbo4	10.7	16.0
Vallisnera1	10.4	15.1
Vallisnera2	11.0	15.1
Mean	10.8	15.5
SD	1.0	0.4
CI 95%	0.8	0.3
CI 99%	1.2	0.4

† vein sulfate.

values for Burano Formation sulfate in Tuscany and Emilia-Romagna are 15.4±0.6‰ for sulfur and 10.7±1.2‰ for oxygen (Table 2). A gypsum vein from the Sassalbo deposit (Table 1) is enriched in ^{34}S and ^{18}O by about 2‰, as expected from the isotope fractionations involved in the dissolution-crystallization cycle (e.g., Szaran et al., 1998).

Burano Formation anhydrites (metamorphosed) at different depths between 2,000 and 2,300m from borehole Burano-1 drilled in the Marche region, which borders Tuscany and Emilia in the southern-eastern sector of the Northern Apennines, show consistent δ^{34}S (15.2±0.2‰) and δ^{18}O (10.9±0.3‰) values (Cortecci et al., 1981; Fig. 2). In this sector, however, metamorphosed anhydrite samples from borehole Perugia-2 in the Umbria region are appreciably enriched in ^{34}S by about 2‰ and in ^{18}O by about 6‰, and may be considered as outliers. In fact, metamorphosed anhydrite in the more southern Apulia region in the Southern Apennines from borehole Foresta Umbra-1 (Cortecci et al., 1981) and outcrops (Pietre Nere locality; Bigazzi et al., 1996; Cortecci et al., 2000) has fairly normal δ^{34}S of 15.0±0.8‰ (N=18) and δ^{18}O of 12.7±0.6‰ (N=2). Finally, presumed Upper Triassic gypsum and anhydrite from layers in boreholes drilled in the Larderello-Travale geothermal area of Tuscany were found to have δ^{34}S=14.9±0.4‰ (N=5), with an outlier of +19.3‰ associated with skarn as a result of metamorphic and metasomatic processes (Milanese, 1993). Overall, mean (±SD) δ^{34}S and δ^{18}O of 15.2±0.7‰ (N=38) and 10.9±1.3‰ (N=26) values can be assigned to primary (i.e., unaffected

TABLE 2 | **Mean isotope values and statistical parameters of Upper Triassic evaporite sulfates from Italy and other countries in the world. Treated occurrences are those for which both sulfur and oxygen isotopic data are available**

Number as in Fig. 2	Upper Triassic Formations	Country	$\delta^{18}O(SO_4)$ ‰ vs. V-SMOW				$\delta^{34}S(SO_4)$ ‰ vs. V-CDT				References
			mean	SD	CI	N	mean	SD	CI	N	
1	†Burano (overall excluding Umbria)	Italy	10.9	1.3	0.5	26	15.2	0.7	0.2	38	this work; Bigazzi et al. 1996; Boschetti et al. 2005; Cortecci et al. 1981, 2000; Dinelli et al. 1999; †Longinelli 1968; Milanese 1993
not shown	Burano (Tuscany-Emilia Romagna, N Apennines)	Italy	10.7	1.2	0.6	22	15.4	0.6	0.3	18	this work; Boschetti et al. 2005; Dinelli Et Al. 1999; †Longinelli 1968; Milanese 1993
not shown	Burano (Marche, N Apennines)	Italy	10.9	0.3	-	2	15.2	0.2	-	2	Cortecci et al. 1981
1*	Burano (Umbria, N Apennines)	Italy	17.4	1.0	-	2	17.2	0.3	-	2	Cortecci et al. 1981
not shown	Burano (Apulia, S Apennines)	Italy	12.7	0.6	-	2	15.0	0.8	0.4	18	Bigazzi et al. 1996; Cortecci et al. 1981; Cortecci et al. 2000
2	Gypskeuper (Folded Jura)	Swiss	11.3	1.7	1.8	6	16.5	0.7	0.8	6	Rick 1990
2*	Gypskeuper (Tabular Jura)	Swiss	13.2	0.8	1.0	5	14.6	0.6	0.8	5	Pearson et al. 1991
3	Keuper	Spain	11.9	0.6	0.3	15	14.5	0.7	0.4	15	Alonso-Azcárate et al. 2006
3*	CRA	Spain	21.4	1.1	0.6	15	18.2	1.1	0.6	15	Alonso-Azcárate et al. 2006
4	†Charlie Lake	Canada	12.2	0.4	-	2	14.2	0.7	0.5	9	Claypool et al. 1980
5	†Keuper	Spain	11.1	1.7	0.8	21	13.4	1.5	0.7	21	Utrilla et al. 1992
6	Lorraine Basin	France	13.0	0.8	0.7	8	15.4	0.4	0.2	26	Fanlo and Ayora 1998
7	†Mohilla	Israel	12.7	1.8	2.2	5	16.6	0.8	0.6	9	Claypool et al. 1980
8	NE Alps	Italy	14.7	1.2	0.6	20	15.0	0.4	0.6	4	Longinelli and Flora 2007
9	†S Alps	Italy	14.1	1.5	1.9	5	16.8	0.4	0.6	5	Cortecci et al. 1981
10	†CW Alps	Italy/Swiss	16.7	1.3	2.0	4	16.2	0.5	0.8	4	Cortecci et al. 1981

* significative difference in comparison with other data from the same formation; SD: standard deviation, CI: confidence interval at 95%, N: number of samples.

† oxygen isotope values normalized to the present-day accepted value of 8.6‰ for seawater sulfate.

by bacterial reduction and metamorphic effects) Burano Formation sulfate of the Italian Apennines from Emilia to Tuscany to Marche to Apulia, with 95% confidence intervals of 0.2 and 0.5‰, respectively (Table 2). Based on the concomitant positive variation of sulfur and oxygen isotopes, the sulfate from Umbria may feel some effects due to microbial reduction in the depositional basin, and was not included in the Apennine mean calculation for primary sulfate.

Let us discuss in more detail the vein sulfate from Sassalbo. Its isotopic composition is $\delta^{34}S=17.0‰$ and $\delta^{18}O=12.9‰$ (Table 1). These values are consistent with the following 1) values measured in metamorphic-vein barite from the Apuane Alps ore showing $\delta^{34}S$ and $\delta^{18}O$ values in the ranges 14-20‰ and 13-14‰, respectively (Cortecci et al., 1989), suggesting that the vein gypsum is the hydrated product of a metamorphic anhydrite vein deposited during the Apennine orogenesis; 2) vein-gypsum precipitation

may have occurred from a Ca-sulfate solution similarly to present-day thermal springs in northern Tuscany (see later section on spring and stream waters).

Upper Triassic sulfate evaporites from Italy and abroad

In Fig. 3, the reported data refer only to deposits for which dual sulfur and oxygen isotopic data are available. Note especially the high $\delta^{34}S$ consistency of the Upper Triassic evaporite sulfates from Italian occurrences (like the Northern Apennines and Northeastern Alps) and the Carnian ones from the Austrian Eastern Alps, with a $\delta^{34}S$ mean of $15.8\pm0.4‰$ (Götzinger et al., 2001; quoted in Schroll and Rantitsch, 2005), which in turn is nearly equal to the mean $\delta^{34}S$ of $14.6\pm1.1‰$ shown by barites from the Bleiberg deposit (Eastern Alps, Carinthia, Austria) and presumed to be Carnian and marine (Schroll et al., 1983; Schroll and Rantitsch, 2005).

TABLE 3 | **Isotopic compositions of dissolved sulfate and water of the springs sampled in northern Tuscany, and relevant hydrochemical data**

Spring (code) [†]temperature & chemical classification	Sampling date	Catchment	T °C	pH	TDS mg/L	SiO$_2$(aq) mg/L	H$_2$S mg/L	SO$_4^{2-}$ mg/L	δ^{18}O(SO$_4^{2-}$) ‰ vs. SMOW	δ^{34}S(SO$_4^{2-}$) ‰ vs. CDT	δ^{18}O(H$_2$O) ‰ vs. SMOW
Bergondola (Brg)	12-Oct-2006	Magra	14.2	7.24	16283	9.3	-	372	10.8	19.6	-7.50
14.2-15.3°C (orthothermal), Na-Cl	05-Jul-2007	Magra	15.3	7.50	16885	8.5	0.6	338	-	19.6	-7.48
Ponte Magra (PM)	2005	Magra	-	-	15500	-	-	84	-	-	-
16.8°C (orthothermal), Na-Cl	05-Jul-2007	Magra	16.8	7.84	14294	6.4	1.2	95	12.2	23.1	-7.82
Equi Terme (Eq)	31-Aug-2004	Lucido	25.0	6.82	5121	12.6	1.1	890	11.6	16.4	-7.56
23.8-25.0°C (thermal), Na-Cl	14-Apr-2005	Lucido	23.8	7.10	3369	9.8	0.6	554	11.4	15.7	-7.49
Monzone Nera (MN)	31-Aug-2004	Lucido	16.4	7.60	3135	5.0	0.5	229	11.5	15.9	-7.10
14.3-16.4°C (orthothermal), Na-Cl	14-Apr-2005	Lucido	14.3	7.66	2692	4.7	0.7	131	10.8	15.8	-7.16
Monzone Salata (MS)	31-Aug-2004	Lucido	17.1	7.42	10064	9.3	0.6	688	12.0	16.6	-7.20
15.5-17.1°C (orthothermal), Na-Cl	14-Apr-2005	Lucido	15.5	7.33	6336	7.4	0.7	551	10.9	16.5	-7.04
Pieve Fosciana (PF)	31-Aug-2004[†]	Serchio	32.3	6.44	5983	23.0	0.5	1905	12.4	15.8	-7.82
	14-Apr-2005[†]	Serchio	33.4	6.66	6098	23.4	0.8	1751	12.4	16.0	-7.87
32.3-36.3°C (thermal), Na-Cl	14-Apr-2005*	Serchio	36.3	6.63	6365	25.1	-	2075	12.3	16.3	-7.84

[†]thermal: T > Ta + 4°C, orthothermal: Ta < T < Ta + 4°C; where T and Ta are spring and mean annual air temperature of the area, respectively (Schoeller, 1962).

† well 1; * well 2.

Our mean δ^{34}S and δ^{18}O values for Late Triassic evaporites from the Northern Apennines are compared in Fig. 3 with those of coeval occurrences in the Italian Alps and abroad. The data seem to show a triangular distribution. The lowest δ^{18}O values presumably better approach the oxygen isotopic signature of primary Upper Triassic sulfate minerals, whose δ^{34}S in coeval basins may have been variable at nearly constant δ^{18}O, depending on a) bacterial reduction that may have significantly altered the sulfur isotope composition of the residual aqueous sulfate and only slightly altered the oxygen isotope composition, as found for fast cell-specific sulfate reduction rates (high sSRR; Brunner et al., 2005); b) oxidation of pre-Late Triassic biogenic sulfide minerals (Longinelli and Flora, 2007) providing sulfate similar for δ^{18}O (see Van Stempvoort and Krouse, 1994) but distinct for δ^{34}S with respect to seawater sulfate; and possibly c) conspicuous undersea SO$_2$ degassing during the active Late Triassic oceanic rifting (e.g., Tanner et al., 2004). On the other hand, the ^{34}S and ^{18}O enrichments towards the apex of the triangle can be related to syndepositional effects (mainly for sulfur isotopes via bacterial reduction at slow to intermediate sSRR values; Brunner et al., 2005) or to postdepositional effects (mainly for oxygen isotopes via exchange with aqueous fluids at metamorphic temperatures). The highest enrichments are shown by secondary gypsum from the lacustrine sequence in the Cameros Basin of Spain (Alonso-Azcárate et al., 2006; point 3* in Fig. 3). This sequence is Late Jurassic, but sulfate in the evaporating lake was basically provided by dissolution of older Late Triassic (Keuper) marine evaporite (point 3 in Fig. 3). According to Alonso-Azcárate et al. (2006), the δ^{34}S signature of CRA sulfate is influenced by the effects of bacterial reduction before crystallization, whereas the δ^{18}O signature should be related to metamorphic effects due to water-mediated exchange with host dolomite before exhumation to the surface. In our opinion, however, an alternative explanation may be provided by the synsedimentary bacterial reduction of sulfate in the lake under slow cell-sSRR, in agreement with the steep slope of the δ^{34}S-δ^{18}O line connecting points 3 and 3* in Fig. 3 (Brunner et al., 2005). It is possible that a large number of sulfate-reducing bacteria was at work in the lake sediments due to the presumably high abundance of organic matter, thus resulting in a high bulk sulfate reduction rate. These two alternatives (metamorphic or microbial effects) can also be considered for the other isotopically heavier evaporite sulfates, including the outlier anhydrite samples (point 1* in Fig. 3) from Umbria. On the other hand, the different isotopic composition of Keuper sulfates in Swiss (Table 2) from an outcrop (point 2 in Fig. 3; Folded Jura; Rick, 1990) and a borehole (2* in Fig. 3 and Table 2; Tabular Jura; Pearson et al., 1991) might be interpreted in terms of a contribution to the borehole of ^{34}S-depleted sulfate from oxidation of sulfide minerals during the exhumation and hydration of the anhydrite after the metamorphic peak. This result agrees with the finding of pyrite with δ^{34}S of -33‰ in the underlying Muschelkalk bituminous dolomitic mudstone (Pearson et al., 1991) and the observation that the hydration of the anhydrite from the borehole was pervasive and complete (Dronkert, 1987). The higher δ^{18}O sulfate signature in the borehole does not conflict with the above interpretation based on the δ^{34}S signature, if a stepwise oxidation mechanism for pyrite is accepted with the formation of intermediate sulfite ion (van Stempvoort and Krouse, 1994). Moreover, it should be noted that in another borehole drilled in the Tabular Jura, sulfate in deep waters interacting with the Keuper deposit showed δ^{34}S values of 15.5 to 16.6‰ and δ^{18}O values of 10.6 to 11.4‰ (Pearson et al., 1991), in keeping with the values found by Rick (1990) for outcropping Keuper deposits.

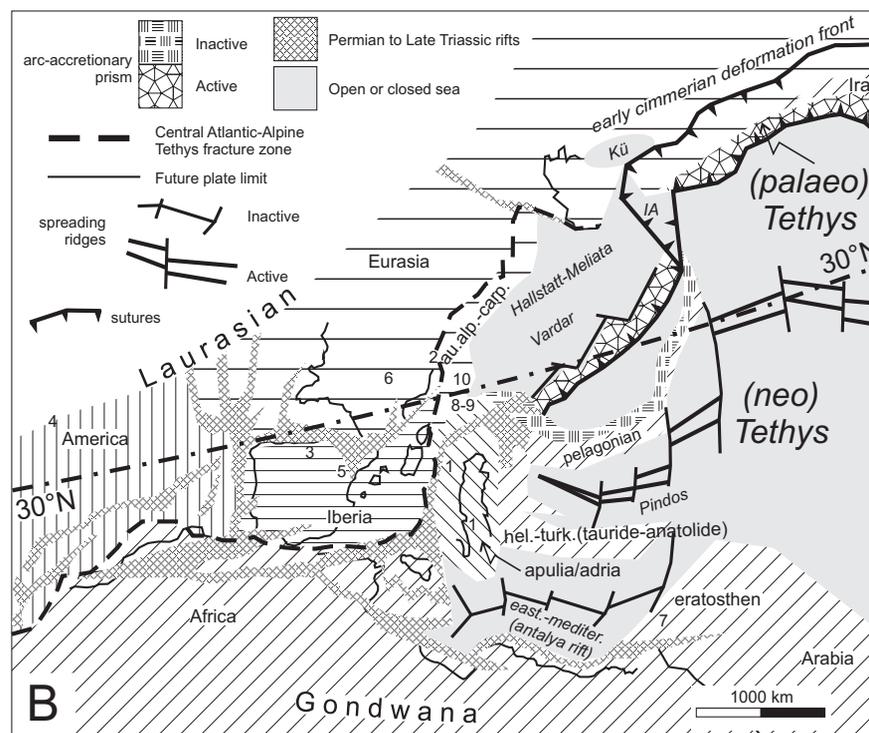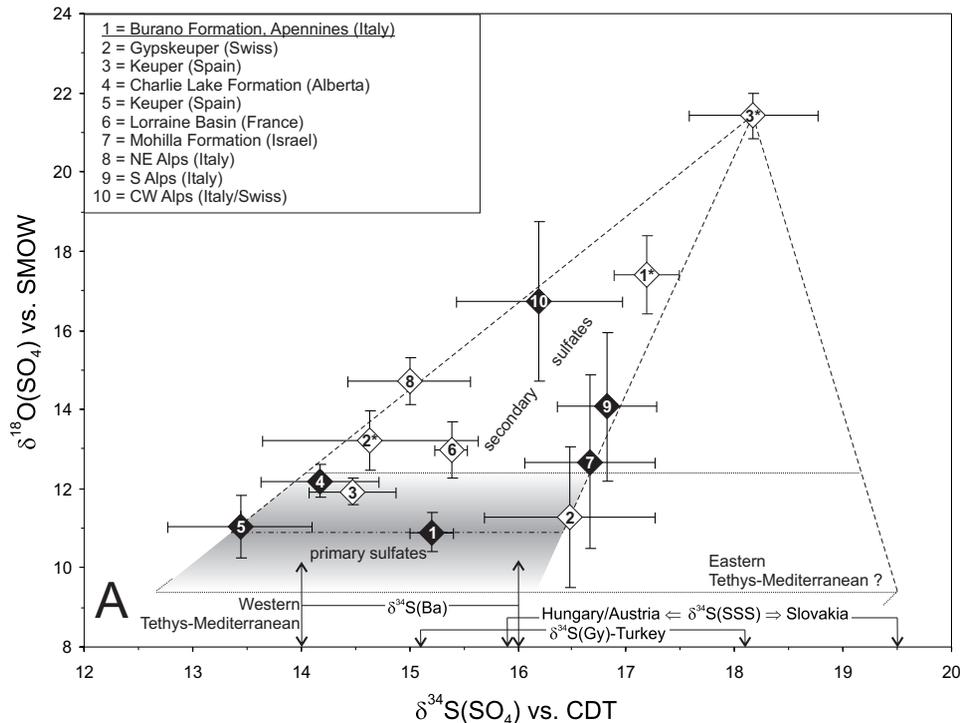FIGURE 3 | **A)** $\delta^{18}O(SO_4)$ vs. $\delta^{34}S(SO_4)$ of Upper Triassic evaporite sulfates. Grey area delimits the "primary sulfate" values and the pooled standard deviation for the oxygen isotope data (see text for details). Diamonds and bars denote mean values and their 95% confidence intervals (C.I.), respectively. Filled symbols: the $\delta^{18}O$ values were normalized to +8.6‰ (see text); open symbols refer to uncorrected $\delta^{18}O$ values. 1: this work, Longinelli (1968) and Cortecci et al. (1981) (1* = outlier mean values from Cortecci et al., 1981, with standard deviations); 2: Rick et al. (1990); 3: Alonso-Azcárate et al. (2006; 3* = CRA unit, Keuper evaporite sulfate reworked to form Late Jurassic deposits); 4: Claypool et al. (1980); 5: Utrilla et al. (1992); 6: Fanlo and Ayora (1998); 7: Claypool et al. (1980); 8: Longinelli and Flora (2007); 9:, 10: Cortecci et al. (1981). These identification numbers correspond to those reported in Table 2. The $\delta^{34}S$ ranges of other Upper Triassic materials are also reported for comparison: SSS: structurally substituted sulfate in microfossils and rock carbonate (Kampschulte and Strauss, 2004); Gy: gypsum samples from Turkey (Gündoğǎn et al., 2008); Ba: Carnian marine barite from Eastern Alps in Austria (Schroll and Rantitsch, 2005). **B)** Late Triassic paleogeography of Western Tethys (modified after Stampfli and Marchant, 1997 and Stampfli and Borel, 2002). Numbers localize approximately the evaporite sulfate deposits reported in Table 2 and Figure 2A. Kü: Küre basin and IA: Izmir-Ankara basin (Turkey).

It would seem from the above discussion that the δ^{34}S and δ^{18}O values and their relation for metamorphosed sulfates do not help to distinguish the isotopic effects due to metamorphism from those related to bacterial reduction. Anyway, these processes should enrich the sulfate in ^{34}S and/or ^{18}O, and then the best approximate S- and O-isotopic signatures of the possibly unaffected parental sulfate should be the lowest ones within a set of data. In this sense, the diagram of Fig. 3 may be used as a slide-rule to evaluate the primary or secondary (altered) isotopic signature of Upper Triassic sulfates.

Seawater sulfate isotopes and tectonic rifting during Late Triassic

Student's t-test for means and Fisher's F-test for variances confirmed that the δ^{18}O values of the Burano Formation sulfates from this work and the -0.7‰ corrected values of the Keuper sulfates from Spain (Utrilla et al., 1992) are statistically consistent, thus allowing the calculation of an overall mean (±PSD) δ^{18}O value of 10.9±1.5‰ (grey field in Fig. 3). This δ^{18}O signature should closely approach the oxygen isotope composition of gypsum deposited from the Tethyan ocean. The lower δ^{34}S values of the ranges observed for Spain and Canada, presumably primary sulfates (Fig. 3), cannot be explained as isotopic effects due to different degrees of restriction of the basins to the open ocean, as these effects tend to increase rather than decrease the isotopic composition of the evaporite relative to seawater sulfate (e.g., Fanlo and Ayora, 1998). Instead, the entry of ^{34}S-depleted sulfate in the evaporating basins from oxidation of biogenic sulfide is a more reliable candidate. However, the supply of ^{34}S-depleted sulfate from oxidation of volcanogenic S-bearing volatiles entering the ocean during the rifting in the western Tethys cannot be excluded. This sulfur may have entered directly the ocean from seafloor degassing or may have entered the atmosphere first and then was removed as sulfate in meteoric precipitation. The amount of S (as SO_2) introduced in the atmosphere by the Central Atlantic Magmatic Province in end-Triassic times was estimated to have been of $2.3*10^{12}$ metric tons (McHone, 2003). To this volcanogenic sulfur a δ^{34}S value close to 0‰ may be assigned, as observed for OIB and MORB fluids (e.g. Taylor, 1986), thus providing substantial amounts of ^{34}S-depleted sulfate to the ocean through oxidation processes. The disproportionation of volcanic SO_2 with seawater should produce a sulfate with a similar δ^{34}S value both at low and high temperature, provided that SO_2 in the supplied gas is largely prevailing with respect to H_2S (Kusakabe and Komoda, 1992).

We conclude this subsection with some selected gypsum (after anhydrite) samples from western Turkey deposits (δ^{34}S values of 15.1 to 18.1‰, N=4), hosted in the Lycian Nappes (Fig. 3) and interpreted to be Late Triassic (Gündoğan et al., 2008). The history of these sulfates may have been complex as was also the geodynamic history of the Cimmerian Plate, thus resulting in the observed range of isotopic values. During the Late Triassic, the Neotethys was forming along the margin of the Tauride-Anatolide continental fragment, which was itself rifted from Gondwana, followed by the collisional event along the Eurasian margin that determined the diachronous closure of the Paleotethys in the area from Iran to Turkey and the opening of the Küre marginal basin (Robertson et al., 2004; Fig. 3B). Some authors have suggested that the Lycian Nappes come from the Izmir-Ankara basin (Eurasian-derived), others that they come from the Tauride-Anatolide (Gondwana-derived) or both. In any case, the progressive evolution of the Lycian Nappe complex from continental rifting to passive margin to ocean basin during the Triassic to the Late Cretaceous was followed by metamorphism related to regional compression up to the Late Miocene. It is possible that the ^{34}S-enriched isotopic composition of the evaporite deposits was influenced by the latter tectonic event.

The structurally substituted sulfate age-curve

Recently, an original sulfur isotope age-curve for Phanerozoic marine sulfate was presented by Kampschulte and Strauss (2004), based on the analysis of the structurally substituted sulfate (SSS; δ^{34}S$_{SSS}$ values) in biogenic calcites (microfossils) and rock carbonates. This was followed by a compilation and time-series analysis of the δ^{34}S database of sulfate in marine carbonate (i.e., SSS) through Earth history by Prokoph et al. (2008). According to the authors, the δ^{34}S$_{SSS}$ record should replace the previous datasets on marine evaporite sulfates. This recommendation apparently matches results obtained by Nishimura and Kajiwara (2000) in a study on the sulfur-isotope fractionation of SSS in modern marine mollusk shells, as the isotope fractionation of SSS with respect to seawater was found to be in general smaller than that of gypsum obtained from fractional crystallization of seawater (Raab and Spiro, 1991). Support for the reliability of the seawater δ^{34}S$_{SSS}$ record can be found in the δ^{18}O analyses of sulfate associated with modern marine shells (Cortecci and Longinelli, 1971), but not in the δ^{18}O analyses of fossil shells due to post-depositional alteration (Cortecci and Longinelli, 1973). The same conclusions were basically reached by Newton et al. (2004) for ancient carbonate-associated sulfate (CAS, i.e., SSS), i.e., the δ^{34}S signature of this material is thought to correspond closely to that of seawater sulfate, whereas the δ^{18}O signature may be less reliable. Specifically, for the Late Triassic (Fig. 3), mean δ^{34}S$_{SSS}$ values of 18.5 to 19.7‰ obtained for Carnian microfossils from the Western Carpathians in Slovakia (Kampschulte and Strauss, 2004) are about 4‰ higher than those of coeval marine evaporites (15.8±0.4‰) and barites (15±1‰) in the Eastern Alps of

Austria (Schroll and Rantitsch, 2005). Lower mean $\delta^{34}S_{SSS}$ values down to about 16‰ were obtained for Norian to Rhaetian samples from Austria and Hungary (Kampschulte and Strauss, 2004). On the other hand, the $\delta^{34}S$ signature of Upper Triassic evaporites was found to be 2 to 4‰ lower with respect to that of microfossils from the same stratigraphic unit, with mean values of 14.9‰ and 17.8‰, respectively (Kampschulte and Strauss, 2004). Are vital effects the cause of this discrepancy?

DISSOLVED SULFATE IN SPRING AND STREAM WATERS

The $\delta^{34}S$ and $\delta^{18}O$ values from this study (Table 3) and from the literature (Boschetti et al., 2005; Cortecci et al., 2008) for sulfate dissolved in orthothermal to thermal springs and in stream waters of the Northern Apennines (Tuscany-Emilia sector) are compared in Fig. 4 with the slide-rule diagram of Fig. 3, that is with the isotopic signature (± PSD for oxygen) of the primary Late Triassic sulfate (grey field) and the mean isotopic signature for Tuscany-Emilia Burano Formation sulfate (± 95% and 99% confidence intervals). Since dissolution of evaporite sulfate basically does not involve isotopic fractionation of sulfur and oxygen isotopes (e.g., Claypool et al., 1980), the main source of aqueous sulfates within the grey field should be Burano Formation evaporite sulfate. Stream water samples are from the Serchio River catchment in northern Tuscany, and include the main river and its tributaries (Cortecci et al., 2008). The catchment hosts Upper Triassic gypsum outcrops and thermal springs. The sulfate $\delta^{34}S$ and $\delta^{18}O$ values of the stream samples show a statistically sound relationship (r=0.97; N=17), with ranges from -8.9 to 13.6‰ for sulfur and -2.3 to 11.4‰ for oxygen. The highest values are shown in Fig. 4 and denote a substantial contribution of Upper Triassic sulfate from dissolution of outcropping evaporites or mixing with thermal springs that leach evaporite beds at depth. The other major source of sulfate should be supergene sulfate from oxidation of sedimentary sulfide (pyrite) disseminated in the drained rocks. Upper Triassic evaporite should be the nearly exclusive source of sulfate in the PA cold spring sample from the Secchia River catchment on the Emilia side of the Northern Apennines, as well as an important source of sulfate in cold springs 107 and 110 issuing in the same catchment (Fig. 1; Boschetti et al., 2005). The Na-Cl salinization of spring PA (6 to 8g/L as total dissolved solids (TDS); Forti et al., 1988 and our unpublished data) was attributed to dissolution of Upper Triassic halite at depth. Salt deposits of this age are also the source of sulfate (and sodium and chloride) in the thermal springs of northern Tuscany for both Na-Cl (Pieve Fosciana, Gallicano, Equi, Monzone Nera, Monzone Salata, Bergondola and Ponte Magra samples; 14°C to 36°C) and Ca-SO$_4$ (M and Bagni di Lucca samples; 31°C to 53°C) waters (see Fig. 4), whose

TDS ranges between 3 and 25g/L (Boschetti et al. 2005 and our unpublished data). The Bagni di Lucca, Monsummano, Bergondola and Ponte Magra springs fall outside the isotopic field of evaporite sulfate in the Tuscany-Emilia sector of the Apennines (Burano Formation), as well as the band including other Upper Triassic sulfates from Italy and elsewhere. However, it is worth noting that the isotopic composition of the sulfate dissolved in these spring waters is distributed within a fanwise space (Fig. 4) with the apex at the Burano Formation mean value obtained in this study and with a spreading towards higher δ-values delimited by trend lines describing the isotopic effects expected for sulfate undergoing bacterial reduction at low (higher slope trend) and high (lower slope trend) cell-specific rates (Brunner et al., 2005; see also Turchyn et al., 2010). The fanwise space also includes other experimentally determined isotopic effects during bacterial reduction that yielded linear $\delta^{18}O$-$\delta^{34}S$ relationships with $\Delta^{18}O/\Delta^{34}S$ slopes ranging from 0.25 to 0.4 (cf. Seal et al., 2000). In keeping with the absence of H$_2$S in the Bagni di Lucca springs (Boschetti et al., 2005), it may be argued that the aqueous sulfate does not suffer bacterial reduction during its travel to the surface, but simply records the isotopic composition of the parental sulfate. This sulfate can be searched locally in the Burano Formation-Calcare Cavernoso Formation occurring at a depth of about 2,500m, ("Brecce di Casoli"; Fazzuoli et al., 1998), and its enrichments in ^{34}S and ^{18}O may feel the isotopic effects of syn-sedimentary reducing bacteria (see also Boschetti et al., 2005).

Sulfate-water oxygen isotope geothermometry

The sulfate-water oxygen isotope fractionation factor can be used as geothermometer of thermal water reservoirs. Very recently, Zeebe (2010) showed theoretically by quantum-chemistry computation that the isotopic behaviour of the SO$_4^{2-}$-H$_2$O pair as a function of temperature is substantially different than those of the HSO$_4^-$-H$_2$O (Lloyd, 1968; Mizutani and Rafter, 1969; Zeebe, 2010) and anhydrite -H$_2$O (Lloyd, 1968; Chiba et al., 1981; Zheng, 1999) pairs. Therefore, a speciation analysis of the aqueous sulfate cannot be omitted when applying the oxygen isotope sulfate-water geothermometry. Unfortunately, oxygen isotope fractionation between CaSO$_4^0$ and water is unknown. However, because the aqueous ion pair CaSO$_4^0$ is the predominant sulfate species in water supersaturated with respect to anhydrite, we may suppose that oxygen isotope fractionation-temperature equation of the CaSO$_4^0$-H$_2$O pair will be approximated by the anhydrite- H$_2$O equation.

In Fig. 5, the available oxygen isotope fractionations between sulfate species and water are graphically reported as a function of temperature limitedly to the interval 0 to 150°C. Bisulfate-water fractionations were merged,

obtaining a quite good relationship with temperature ($R^2=0.994$). The same was done successfully for the anhydrite-water systems ($R^2=0.989$), discarding the Lloyd's (1968) anhydrite-water fractionations following the censure by Chiba et al. (1981). The bisulfate-water curve is shown just for sake of completeness, as the pH values of studied spring waters are near neutral, and then HSO_4^- is totally negligible compared to SO_4^{2-} and $CaSO_4^0$ species.

The sulfate-water isotopic fractionations in springs of Table 3 (all Na-Cl type) and other two (Ca-SO_4^{2-} type) from Bagni di Lucca (Doccione spring) and Monsummano (Parlanti and Giusti springs) vary between 17.4 to 20.4‰, defining the dashed area in Fig. 5. Therefore, isotopic temperatures of about 30 to 110°C can be drawn, depending on sulfate SO_4^{2-} and $CaSO_4^0$ proportions. As an exercise, the

molality percentage of the dissolved sulfate species in the Bergondola sulfurous spring was calculated (EQ3/6 code; Wolery and Jarek, 2003) from a complete chemical analysis to be 84% SO_4^{2-} and 16% $CaSO_4^0$ assuming a temperature of 81°C as inferred from a nearby borehole (Pontremoli-1 well log; Reutter et al., 1983) in correspondence of a halite-anhydrite deposit set at about 3km (Bernini and Papani, 2002), and in keeping with the Na-Cl character of the water and its high TDS value (table 3). The sulfate-water oxygen isotope fractionation in the spring is 18.3‰, and yields a considerably lower temperature estimate of 50°C or 59°C combining the molality percentage and the relative fractionation equation of the dissolved sulfate species, respectively. Instead a comparable isotopic temperature of 92°C is obtained applying the HSO_4^- - H_2O thermometer (Table 4), but this conflicts with the calculated speciation of dissolved sulfates. Similar results are obtained for the
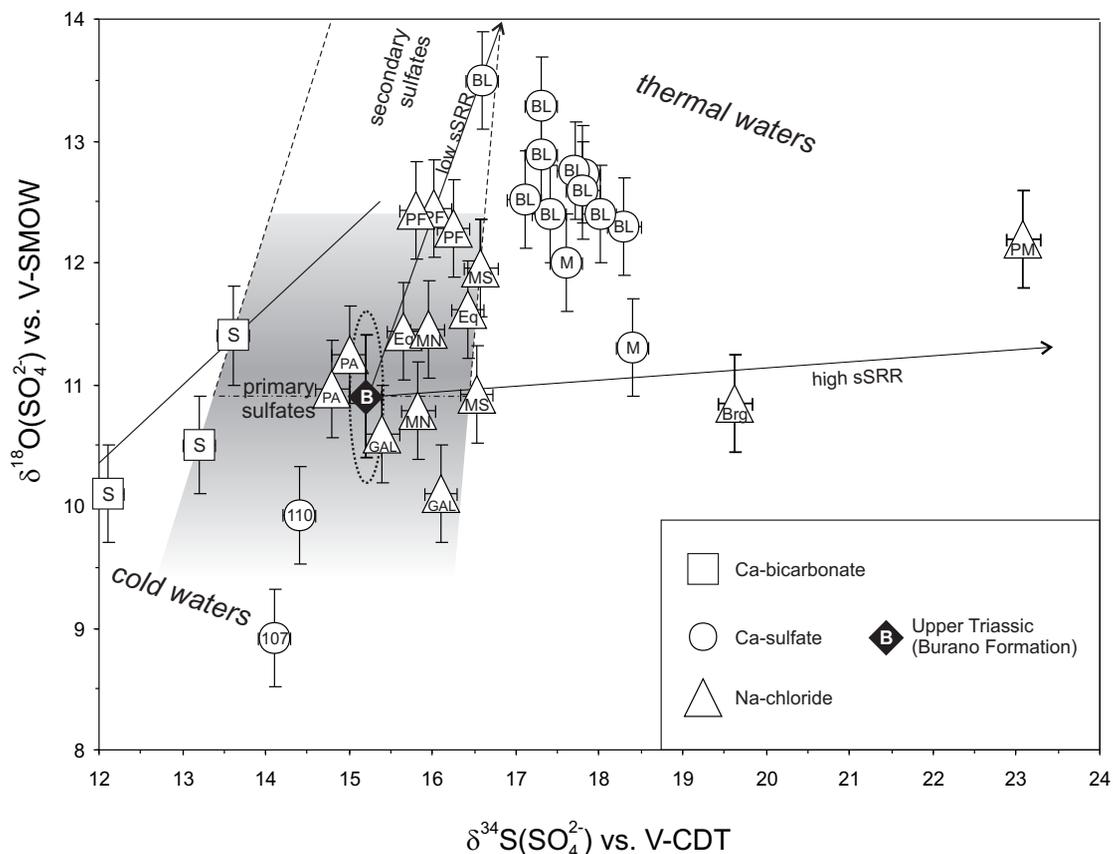

FIGURE 4 | $\delta^{18}O(SO_4^{2-})$ vs. $\delta^{34}S(SO_4^{2-})$ plot for cold to thermal springs and stream waters in the Northern Apennines (Southern Emilia and Northern Tuscany). Grey area delimits the Upper Triassic "primary evaporite sulfate" values and the pooled standard deviation for the oxygen isotope composition values (see text for details). Dotted ellipse delimits the C.I. at 99% of the mean δ-values (filled diamond) of Upper Triassic sulfate evaporites in Emilia and Tuscany. Open symbols with analytical error bars refer to springs in southern Emilia and northern Tuscany, and stream waters in northern Tuscany (see Figure 1). S: streams (main stem and tributaries) from the Serchio River catchment, northern Tuscany (Cortecci et al., 2008); PA, 107 and 110: cold springs in the Secchia River catchment, southern Emilia (Boschetti et al., 2005); PF: Pieve Fosciana thermal springs in the Serchio River catchment (this work); GAL and BL (not shown in Figure 1): Gallicano and Bagni di Lucca thermal springs in the Serchio River catchment (Boschetti et al., 2005); Eq, MN, MS: Equi, Monzone Nera, Monzone Salata orthothermal springs in the Lucido River catchment (this work); Brg and PM = Bergondola and Ponte Magra orthothermal springs in the Magra River catchment (this work). sSRR: microbial cell-specific sulfate reduction rate (see Brunner et al., 2005).
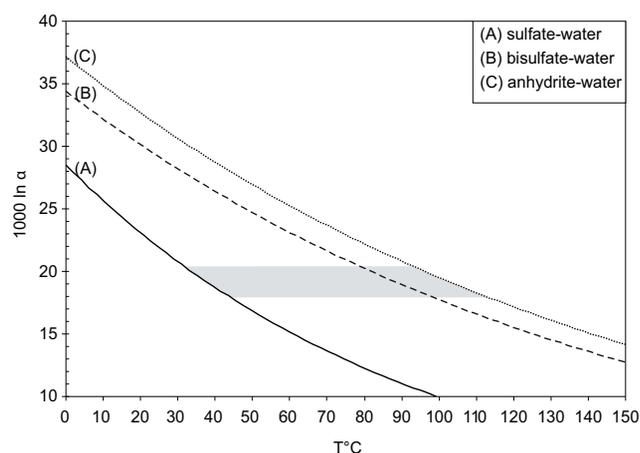
FIGURE 5 | **Oxygen isotope fractionations as a function of temperature for different sulfate-water systems. Curves: A) is from Zeebe (2010), B) is a combination of Zeebe (2010), Mizutani and Rafter (1969) and Lloyd (1968), and C) is a combination of Chiba et al. (1981) and Zheng (1999). Coefficients of determination (R^2) are 0.994 for B) and 0.989 for C).The grey area accounts for the sulfate-water oxygen isotope fractionations in the investigated springs (see Table 4).**

mean chemical composition of the Doccione spring (Bagni di Lucca) speciated at the depth conditions (73°C at about 3.3km; see Boschetti et al., 2005): 79% SO_4^{2-} and 21% $CaSO_4$, with an isotopic temperature of 37°C by SO_4^{2-}-H_2O equation or 49°C by sulfate species combination, both lower than 73°C at depth and 53°C at the outlet. Therefore, it may be concluded that the sulfate-water system in the Bergondola and Doccione springs is not in isotopic equilibrium, as well as also in the other springs shown in Table 4. This interpretation agrees with the sluggishness of sulfate to exchange oxygen with water at low temperature, in keeping with the remarkable uniformity of the $\delta^{18}O$ (SO_4^{2-}) values in the studied springs. The lack of equilibrium also occurs in the sulfurous springs in which the sulfate-water oxygen isotope exchange may have been enhanced by sulfate-reducing bacteria, especially those with a slow cell-specific reduction rate (Turchyn et al., 2010; see also Fig. 4).

The application of quartz (Fournier, 1977; Verma, 2001) and chalcedony (Fournier, 1977; Arnòrsson, 1983) geothermometers yield discordant estimations, which in

TABLE 4 | **Oxygen isotope and silica geothermometric estimates for the springs sampled in northern Tuscany. When samples have N>1, standard deviation on replicates is reported**

Spring (code)	Isotopic (sulfate-water)			Chemical (**SiO$_2$)			
	SO_4^{2-}-H_2O	HSO_4^--H_2O	anhydrite-H_2O	Quartz		Chalchedony	
N=number of samples (reference)	(A)	(B)	(C)	Fournier (1977)	Verma (2001)	Fournier (1977)	Arnòrsson (1983)
†temperature & chemical classification	*0-150°C	70-350°C	0-1200°C	0-250°C	0-374°C	0-250°C	25-180°C
Ponte Magra (PM)							
N=1 (this work)	40	79	93	27	15	(n)	(fd)
16.8°C (orthothermal), Na-Cl							
Bergondola (Brg)							
N=2 (this work)	50	92	106	38 ± 2	26 ± 2	(fd)	(fd)
14.2-15.3°C (orthothermal), Na-Cl							
Pieve Fosciana (PF)							
N=3 (this work)	38 ± 1	78 ± 1	92 ± 1	72 ± 2	62 ± 2	40 ± 2	44 ± 2
32.3-36.3°C (thermal), Na-Cl							
Bagni di Lucca (BdL; Doccione spring)							
N=2 for isotope; 4 for chemical (Boschetti et al. 2005)	37 ± 1	78 ± 1	90 ± 1	106 ± 7	101 ± 7	76 ± 7	77 ± 7
53.3°C (thermal), Ca-SO$_4$							
Monsummano (M)							
N=2 (Boschetti et al. 2005)	53 ± 3	96 ± 3	111 ± 3	70 ± 2	62 ± 2	40 ± 2	44 ± 2
30.6-31.5°C (thermal), Ca-SO$_4$							
Equi Terme (Eq)							
N=2 (this work)	45 ± 1	87 ± 2	101 ± 1	45 ± 6	34 ± 6	17 ± 6	12 ± 6
23.8-25.0°C (thermal), Na-Cl							
Monzone Salata (MS)							
N=2 (this work)	48 ± 4	90 ± 5	105 ± 5	35 ± 1	24 ± 5	(fd)	(fd)
15.5-17.1°C (orthothermal), Na-Cl							
Monzone Nera (MN)							
N=2 (this work)	50 ± 1	93 ± 2	107 ± 2	40 ± 2	44 ± 2	(n)	(n)
14.3-16.4°C (orthothermal), Na-Cl							

†thermal: T > Ta + 4°C, orthothermal: Ta < T < Ta + 4°C; where T and Ta are spring and mean annual air temperature of the area, respectively (Schoeller, 1962).

(A) Zeebe (2010); (B) combination of Lloyd (1968), Mizutani and Rafter (1969) and Zeebe (2010), i.e. 1000lnα = 2.99x10^{6}T^{-2} - 4.15 (r^2 = 0.989); (C) combination of Chiba et al. (1981)

and Zheng (1999), i.e. 1000lnα = 3.31x10^{6}T^{-2} – 4.69 (r^2 = 0.994). α = oxygen isotope fractionation factor. *Calibration range.

**When reservoir temperature is presumed to be less than 180°C, both quartz and chalcedony silica geothermometers should be calculated and compared (Fournier 1991).

(n): negative value; (fd) a few °C.

turn are contradictory with the isotopic ones or unrealistic for springs with lower temperature (orthothermal springs in Table 4). In this latter case, as was verified elsewhere for low enthalpy systems (<150°C; e.g. Adam and Dowgiałło, 2009), we have to do with chemical and isotopic disequilibrium situation for which the application and comparison of respective geothermometers is not suitable.

CONCLUSIONS

Upper Triassic bedded evaporite sulfate of the Burano Formation cropping out at Cerreto Pass between Tuscany and Emilia-Romagna in the Northern Apennines gave sulfur and oxygen isotope composition mean values, at 99% confidence level, of 15.5±0.4‰ and 10.8±1.2‰, respectively. Combining the values for these sulfates with those of other Burano Formation occurrences along the Apennine chain, $\delta^{34}S$ and $\delta^{18}O$ values of 15.2±0.2‰ and of 10.9±0.5‰ are respectively obtained (mean ±99% confidence intervals). These isotope values are interpreted as preserved primary features, despite the fact that Burano Formation underwent metamorphism during the Apennine orogenesis. Isotopic effects possibly related to metamorphism or synsedimentary bio-reduction are suggested in a few cases (e.g., Umbria and some Tuscany borehole samples) by statistically significant higher isotopic signatures.

The average $\delta^{18}O$ value of 10.9±1.5‰ (mean ± PSD), obtained by combining consistent sets of data on evaporite deposits from Italy and Spain, can be considered to closely approach that of gypsum deposited from unaffected ocean sulfate. This isotopic signature may characterize the Upper Triassic evaporite sulfate deposited in the large domain of the Western Tethys ocean between Laurasian and Gondwana. Also, it can be used as a reference value to distinguish evaporite sulfate altered by syn- or post-depositional processes.

A possible interpretation of the observed negative bias in the $\delta^{34}S$ range of the Upper Triassic evaporite sulfate throughout the world is that sulfate in the Tethys ocean have been altered at times by the entry of [34]S-depleted volcanic sulfur during rifting episodes. This sulfur may have entered directly the ocean from seafloor or may have entered the atmosphere first and then was removed as sulfate in meteoric precipitation. A $\delta^{34}S$ value lower than about 13.5‰ for oceanic Late Triassic sulfate may be considered to be largely affected by volcanogenic sulfate, compared to a value of 13.5 to 15.5‰ that should sign the normal sulfate. Evidently, sulfur and oxygen isotope data on selected evaporite sulfate deposits must be acquired to try to mark geological effects on the marine sulfate isotopic composition related to the switch between Eastern Paleo-

Tethys and Neo-Tethys during the Late Triassic. These deposits should be situated in the Cimmerian Plate, at present represented by Turkey, Iran, Afghanistan, Tibet, Indo-China and Malaysia.

Adding the isotope composition of dissolved sulfates in spring and stream waters of northern Tuscany to the $\delta^{34}S$-$\delta^{18}O$ "slide-rule" diagram for solid sulfate has allowed us to: i) recognize deviations from the primary sulfur and oxygen isotope compositions expected for local Burano Formation sulfate evaporite, due to synsedimentary effects on the evaporite (e.g. sulfate in thermal, not sulfurous Bagni di Lucca springs) or nowadays bacterial reduction of sulfate in solution (e.g. in orthothermal, sulfurous Bergondola and Ponte Magra springs); ii) highlight that in sulfurous springs both sulfur and oxygen isotope fractionations from the source sulfate should be ascribed to bacterial effects; however, the oxygen isotope exchange of sulfate with water appears to have been a very minor process as supported by the near-surface temperature values estimated by sulfate-water oxygen isotope thermometry, iii) identify mixing phenomena involving Upper Triassic and supergene sulfate in stream water, and iv) cross-check the primary Upper Triassic sulfate isotopic signature and the mean oxygen and sulfur isotope compositions of gypsum-anhydrite from the local Burano Formation.

REFERENCES

Adam, P., Dowgiałło, J., 2009. Application of selected geothermometers to exploration of low-enthalpy thermal water: the Sudetic Geothermal Region in Poland. Environmental Geology, 58, 1629-1638.

Alonso-Azcárate, J., Bottrell, S.H., Mas, J.R., 2006. Synsedimentary versus metamorphic control of S, O and Sr isotopic compositions in gypsum evaporites from the Cameros Basin. Spain, Chemical Geology, 234, 46-57.

Arnòrsson, S., 1983. Chemical equilibria in Icelandic geothermal systems, implications for chemical geothermal investigations. Geothermics, 12, 119-128.

Bernini, M., Papani, G., 2002. La distensione della fossa tettonica della Lunigiana nord-occidentale (con Carta Geologica alla scala 1:50000). Bollettino della Societa Geologica Italiana, 121, 313-341.

Bigazzi, G., Laurenzi, M.A., Principe, C., Brocchini, D., 1996. New geochronological data on igneous rocks and evaporites of the Pietre Nere Point (Gargano Peninsula, southern Italy). Bollettino della Societa Geologica Italiana, 115, 439-448.

Boccaletti, M., Decandia, F.A., Gasperi, G., Gelmini, R., Lassarotto, A., Zanzucchi, G., 1987. Note illustrative della Carta Strutturale dell'Appennino Settentrionale. Siena (Italy), Consiglio Nazionale delle Ricerche, Progetto Finalizzato Geodinamica, Sottoprogetto 5, Modello Strutturale – Gruppo Appennino Settentrionale, Tipografia Senese, 429-1982, 203pp.

Böhlke, J.K., Mroczkowski, S.J., Coplen, T.B., 2003. Oxygen isotopes in nitrate: new reference materials for $^{18}O:^{17}O:^{16}O$ measurements and observations on nitrate-water equilibration. Rapid Communication in Mass Spectrometry, 17, 1835-1846.

Boschetti, T., Venturelli, G., Toscani, L., Barbieri, M., Mucchino, C., 2005. The Bagni di Lucca thermal waters (Tuscany, Italy): an example of Ca-SO_4 waters with high Na/Cl and low Ca/SO_4 ratios. Journal of Hydrology, 307, 270-293.

Boschetti, T., Iacumin, P., 2005. Continuous-flow ^{18}O measurements: new approach to standardization, high-temperature thermodynamic and sulfate analysis. Rapid Communication in Mass Spectrometry, 19, 3007-3014.

Brand, W.A., Coplen, T.B., Aerts-Bijma, A.T., Böhlke, J.K., Gehre, M., Geilmann, H., Gröning, M., Jansen, H.G., Meijer, H.A.J., Mroczkowski, S.J., Qi, H., Soergel, K., Stuart-Williams, H., Weise, S.M., Werner, R.A., 2009. Comprehensive inter-laboratory calibration of reference materials for $\delta^{18}O$ versus VSMOW using various on-line high-temperature conversion techniques. Rapid Communication in Mass Spectrometry, 23, 999-1019.

Brunner, B., Bernasconi, S.M., Kleikemper, J., Schroth, M.H., 2005. A model for oxygen and sulfur isotope fractionation in sulfate during bacterial sulfate reduction processes. Geochimica et Cosmochimica Acta, 69, 4773-4785.

Carmignani, L., Kligfield, R., 1990. The transistion from compression to extention in mountain belts: evidence from Northern Apennines Core Complex. Tectonics, 9, 1275-1303.

Cerrina Feroni, A., Plesi, G., Fanelli, G., Leoni, L., Martinelli, P., 1983. Contributo alla conoscenza dei processi di grado molto basso (anchimetamorfismo) a carico della Falda Toscana nell'area del ricoprimento apuano. Bollettino della Società Geologica Italiana, 102, 269-280.

Chiba, H., Kusakabe, M., Hirano, S.I, Matsuo, S., Somiya, A., 1981. Oxygen isotope fractionation factors between anhydrite and water from 100 to 550°C. Earth and Planetary Science Letters, 53, 55-62.

Chiba, H., Sakai, H., 1985. Oxygen isotope exchange rate between dissolved sulfate and water at hydrothermal temperatures. Geochimica et Cosmochimica Acta, 49, 993-1000.

Ciarapica, G., Cirilli, S., Passeri, L., Trincianti, E., Zaninetti, L., 1987. Anidriti di Burano et Formation du Monte Cetona (nouvelle formation), biostratigraphie de deux series-types du Trias superieur dans l'Apennin septentrional. Revue de Paléobiologie, 6, 341-409.

Ciarapica, G., 2007. Regional and global changes around the Triassic–Jurassic boundary reflected in the late Norian–Hettangian history of the Apennine basins. Palaeogeography, Palaeoclimatology, Palaeoecology, 244, 34-51.

Claypool, G.E., Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. Chemical Geology, 28, 199-260.

Colombetti, A., Zerilli, A., 1987. Prime valutazioni dello spessore dei gessi triassici mediante sondaggi elettrici verticali nella Valle del F. Secchia (Villa Minozzo-R.E.). Memorie della Società Geologica Italiana, 39, 83-90.

Coplen, T.B., Krouse, H.R., 1998. Sulphur isotope data consistency improved. Nature, 398, 32.

Cortecci, G., Longinelli, A., 1971. $^{18}O/^{16}O$ ratios in sulfate from living marine organisms. Earth and Planetary Science Letters, 11, 273-276.

Cortecci, G., Longinelli, A., 1973. $^{18}O/^{16}O$ ratios in sulfate from fossil shells. Earth and Planetary Science Letters, 19, 410-412.

Cortecci, G., Reyes, E., Berti, G., Casati, P., 1981. Sulfur and oxygen isotopes in Italian marine sulfates of Permian and Triassic ages. Chemical Geology, 34, 65-79.

Cortecci, G., Lattanzi, P., Tanelli, G., 1989. Sulfur, oxygen and carbon isotope geochemistry of barite-iron oxide-pyrite deposits from the Apuane Alps (northern Tuscany, Italy). Chemical Geology, 76, 249-257.

Cortecci, G., Dinelli, E., Civitavecchia, V., 2000. Isotopic and geochemical features of rocks from Punta delle Pietre Nere, Gargano peninsula, southern Italy. Periodico di Mineralogia, 69, 205-216.

Cortecci, G., Dinelli, E, Boschetti, T., Arbizzani, P., Pompilio, L., Mussi, M., 2008. The Serchio River catchment, northern Tuscany: Geochemistry of stream waters and sediments, and isotopic composition of dissolved sulfate. Applied Geochemistry, 23, 1513-1543.

Costagliola, P., Barbieri, M., Benvenuti, M., Lattanzi, P., Castorina, F., 1997. Sr-isotope composition of barite veins at Pollone deposit, Apuane Alps, Tuscany (Italy). Chemie der Erde, 57, 231-242.

Costantini, A., Lazzarotto, A., Liotta, D., Mazzanti, R., Mazzei, R., Salvatorini, G., 2002. Note illustrative della Carta geologica d'Italia, alla scala 1:50.000, Firenze, Massa Marittima. Siena (Italy), Servizio Geologico d'Italia, Università degli Studi di Siena, Foglio 306, 174pp.

Delfrati, L., Falorni, P., Groppelli, G., Petti, F.M., 2002. Carta Geologica d'Italia - 1:50.000 - Catalogo delle Formazioni. Fascicolo III - Unità Validate. Agenzia per la Protezione dell'Ambiente e per i Servizi Tecnici (APAT), Quaderni del Servizio Geologico d'Italia, 7(3), 208pp.

Dinelli, E., Testa, G., Cortecci, G., Barbieri, M., 1999. Stratigraphic and petrographic constraints to trace element and isotope geochemistry of Messinian sulfates of Tuscany. Memorie della Società Geologica Italiana, 54, 61-74.

Dronkert, H., 1987. Diagenesis of Triassic evaporites in northern Switzerland. Eclogae Geologicae Helvetiae, 80, 397-413.

Eaton, A.D., Clesceri, L.S., Greenberg, A.E., 1995. Standard Methods for the Examination of Water and Wastewater. Washington DC. (USA), 19th Edition, American Public Health Association-American Water Works Association-Water Environment Federation (APHA-AWWA-WEF), 1325pp.

Fanlo, I., Ayora, C., 1998. The evolution of the Lorraine evaporite basin: implications for the chemical and isotope composition of the Triassic ocean. Chemical Geology, 146, 135-154.

Fazzuoli, M., Sani, F., Ferrini, G., Garzonio, C.A., Sguazzoni, G., Becarelli, S., Burchietti, G., Mannori, G., 1998. Geologia del nucleo mesozoico della Val di Lima (Province di Pistoia e Lucca, Appennino Settentrionale). Nota illustrativa della carta geologica (scala 1:25.000). Bollettino Società Geologia Italiana, 117, 479-535.

Forti, P., Francavilla, F., Prata, E., Rabbi, E., 1988. Idrochimica ed idrogeologia della formazione evaporitica Triassica dell'alta val Secchia con particolare riguardo alle fonti di Poiano. In: Forti, P. (ed.). L'area carsica dell'alta val Secchia - Studio interdisciplinare dei caratteri ambientali. Regione Emilia-Romagna e Provincia di Reggio Emilia, 82-111.

Fournier, R.O., 1977. Chemical geothermometers and mixing models for geothermal systems. Geothermics, 5, 41-50.

Fournier, R.O., 1991. Water geothermometers applied to geothermal energy. In: D'Amore, F. (ed.). Application of Geochemistry in Geothermal Reservoir Development. Rome (Italy), United Nations Institute for Training and Research/United Nations Development Programme (UNITAR/UNDP) Publications, 37-69.

Fritz, P., Basharmal, G.M., Drimmie, R.J., Ibsen, J., Qureshi, R.M. 1989. Oxygen isotope exchange between sulfate and water during bacterial reduction of sulfate. Chemical Geology, Isotope Geoscience Section, 79, 99-105.

Giesemann, A., Jager H.J., Norman, A.L., Krouse, H.P., Brand, W.A. 1994. On-line sulfur-isotope determination using an elemental analyzer coupled to a mass spectrometer. Analytical Chemistry, 66, 2816-2819.

Gonfiantini, R., Stichler, W., Rozanski, K., 1995. Standards and intercomparison materials distributed by the International Atomic Energy Agency for stable isotope measurements. Viena (Austria), Reference and Intercomparison Materials for Stable Isotopes of Light Elements, International Atomic Energy Agency - Technical Document (IAEA-TECDOC), 825, 13-29.

Götzinger, M.A., Lein, R., Pak, E., 2001. Geologie, Mineralogie und Schwefelisotopie ostalpiner "Keuper-Gipse": Vorbericht und Diskussion. Mitteilungen der Österreichische Mineralogische Gesellschaft, 146, 95-96.

Grinenko, V.A., Ustinov, V.I., 1991. Dynamics of sulfur and oxygen isotope fractionation during bacterial reduction. Geochemistry International, 28, 21-30.

Gündoğan, İ., Helvaci, C., Sözbilir, H., 2008. Gypsiferous carbonates at Honaz Dağı (Denizli): First documentation of Triassic gypsum in western Turkey and its tectonic significance. Journal of Asian Earth Sciences, 32, 49-65.

Halas, S., Szaran, J., Czarnacki, M., Tanweer, A., 2007. Refinements in $BaSO_4$ to CO_2 preparation and $\delta^{18}O$ calibration of the sulfate reference materials NBS-127, IAEA SO-5 and IAEA SO-6. Geostandards and Geoanalytical Research, 31, 61-68.

Holser, W.T., 1977. Catastrophic chemical events in the history of the ocean. Nature, 267, 403-408.

Holser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1979. Isotope geochemistry of oxygen in the sedimentary sulfate cycle. Chemical Geology, 25, 1-17.

Kampschulte, A., Strauss, H., 2004. The sulphur isotopic evolution of Phanerozoic seawater based on the analysis of structural substituted sulphate in carbonates. Chemical Geology, 204, 255-286.

Kusakabe, M., Komoda, Y., 1992. Sulfur isotopic effects in the disproportionation reaction of sulfur dioxide at hydrothermal temperatures. Report of Geological Survey of Japan, 279, 93-96.

Lloyd, R.M., 1968. Oxygen isotope behaviour in the sulfate-water system. Journal of Geophysical Research, 73, 6099-7110.

Leoni, L, Pertusati, P.C., 2002. Il metamorfismo dei depositi clastici triassici di Lerici – S. Terenzio, del Passo del Cerreto, di Collagna (Val di Secchia) e di Soraggio (Appennino Settentrionale). Atti della Società Toscana di Scienze Naturali, Memorie, Serie A, 108, 113-124.

Longinelli, A., 1968. Oxygen isotopic composition of sulfate ions in water from thermal springs. Earth and Planetary Science Letters, 4, 206-210.

Longinelli, A., 1989. Oxygen-18 and sulphur-34 in dissolved oceanic sulphate and phosphate. In: Fritz, P., Fontes, J.Ch. (eds.). Handbook of Environmental Isotope Geochemistry, The Marine Environment. Amsterdam, Elsevier, 3, 219-255.

Longinelli, A., Flora, O., 2007. Isotopic composition of gypsum samples of Permian and Triassic age from the north-eastern Italian Alps: Palaeoenvironmental implications. Chemical Geology, 245, 275-284.

Lugli, S., 2001. Timing of post-depositional events in the Burano Formation of the Secchia valley (Upper Triassic, Northern Apennines), clues from gypsum-anhydrite transitions and carbonate metasomatism. Sedimentary Geology, 140, 107-122.

Lugli, S., Morteani, G., Blamart, D., 2002. Petrographic, REE, fluid inclusion and stable isotope study of magnesite from the Upper Triassic Burano Evaporites (Secchia Valley, northern Apennines): contributions from sedimentary, hydrothermal and metasomatic sources. Mineralium Deposita, 37, 480-494.

Marcoux, J., Baud, A., Ricou, L.E., Gaetani, M., Krystyn, L., Bellion, Y., Guiraud, R., Besse, J., Gallet, Y., Jaillard, E., Moreau, C., Theveniaut, H., 1993. Late Norian (215-212 Ma). In: Dercourt, J., Ricou, L.E., Vrielynck, B. (eds.). Atlas Tethys Palaeoenvironmetal Maps. Gauthier-Villars (Paris), Explanatory Notes, 35-53.

Martini, R., Gandin, A., Zaninetti, L., 1989. Sedimentology, stratigraphy and micropaleontology of the Triassic evaporitic sequence in the subsurface of Boccheggiano and in some outcrops of southern Tuscany (Italy). Rivista Italiana di Paleontologia e Stratigrafia, 95, 3-28.

Martinis, B., Pieri, M., 1963. Alcune notizie sulla formazione evaporitica del Triassico nell'Italia centrale e meridionale. Memorie della Società Geologica Italiana, 4, 649-678.

McHone, J.G., 2003. Volatile Emissions From Central Atlantic Magmatic Province Basalts: Mass Assumptions and Environmental Consequences. In: Hames, W., Mchone, J.G., Renne, P.R., Ruppel, C. (eds.). The Central Atlantic Magmatic Province. Insights from Fragments of Pangea. American Geophysical Union (AGU), Geophysical Monograph series, 136, 241-254.

Milanese, F., 1993. Metamorfismo ed assetto strutturale del basamento nella porzione sud-orientale dell'area geotermica toscana. Master Degree Thesis. Pisa (Italy), University of Pisa, 292pp.

Mizutani, Y., Rafter, T.A., 1969. Oxygen isotopic composition of sulphates: Part 3. Oxygen isotopic fractionation in the bisulphate ion water system. New Zealand Journal of Science, 12, 54-59.

Motulsky, H.M.D., 1995. Intuitive Biostatistics. New York, Oxford University Press, 386pp.

Newton, R.J., Pevitt, E.L., Wignall, P.B., Bottrell, S.H., 2004. Large shifts in the isotopic composition of seawater sulphate across the Permo-Triassic boundary in northern Italy. Earth and Planetary Science Letters, 218, 331-345.

Nielsen, H., 1989. Local and global aspects of the sulphur isotope age curve of oceanic sulphate. In: Brimblecombe, P., Lein, A.Yu. (eds.). Evolution of the Global Biogeochemical Sulphur Cycle, SCOPE 39. New York, John Wiley & Sons Ltd., 57-64.

Nishimura, Y., Kajiwara, Y., 2000. Sulfur isotope fractionation of carbonate structurally substitutes sulfate in modern marine mollusk shells. University of Tsukuba, Annual Report of the Institute of Geoscience, 26, 37-40.

Ogg, J.G., 2004. The Triassic Period. In: Gradstein, F.M., Ogg, J.G., Smith, A.G. (eds.). A Geologic Time Scale. Cambridge, Cambridge University Press, 271-306.

Passeri, L., 1975. L'ambiente deposizionale della formazione evaporitica nel quadro della paleogeografia del Norico Tosco-Umbro-Marchigiano. Bollettino della Società Geologica Italiana, 94, 231-268.

Paytan, A., Kastner, M., Campell, D., Thiemens, M.H., 2004. Seawater sulfur isotope fluctuations in the Cretaceous. Science, 304, 1663-1665.

Pearson, F.J., Balderer, W., Loosli, H.H., Lehaman, B.E., Matter, A., Peters, Tj., Schmassmann, H., Gautschi, A., 1991. Applied Isotope Hydrogeology-A case study in Northern Switzerland. Studies in Environmental Science 43. Amsterdam, Elsevier, 439pp.

Prokoph, A., Shields, G.A., Veizer, J., 2008. Compilation and time-series analysis of a marine carbonate $\delta^{18}O$, $\delta^{13}C$, $^{87}Sr/^{86}Sr$ and $\delta^{34}S$ database through Earth history. Earth Science Review, 87, 113-133.

Raab, M., Spiro, B., 1991. Sulfur isotopic variations during seawater evaporation with fractional crystallization. Chemical Geology, Isotope Geoscience Section, 86, 323-333.

Rees, C.E., Holt, B.D., 1991. The isotopic analysis of sulfur and oxygen. In: Krouse, H.R., Grinenko, V.A. (eds.). Stable Isotopes - Natural and Anthropogenic Sulphur in the Environment, SCOPE 43. New York, John Wiley & Sons Ltd., 43-64.

Reutter, K.J., Teichmüller, M., Teichmüller, R., Zanzucchi, G., 1983. The Coalification Pattern in the Northern Apennines and its Palaeogeothermic and Tectonic Significance. International Journal of Earth Sciences, 72, 861-893.

Rick, B., 1990. Sulphur and oxygen isotopic composition of Swiss Gipskeuper (Upper Triassic). Chemical Geology, Isotope Geoscience Section, 80, 243-250.

Robertson, A.H.F., Ustaömer, T., Pickett, E.A., Collins, A.S., Andrew, T., Dixon, J.E., 2004. Testing models of Late Palaeozoic–Early Mesozoic orogeny in Western Turkey: support for an evolving open-Tethys model. Journal of the Geological Society, 161, 501-511.

Seal, R.R.II, Alpers, C.N., Rye, R.O., 2000. Stable isotope systematics of sulfate minerals. In: Alpers, C.N., Jambor, J.L., Nordstrom, D.K. (eds.). Sulfate Minerals - Crystallography, Geochemistry, and Environmental Significance. Reviews in Mineralogy and Geochemistry, 40, 541-602.

Schoeller, H., 1962. Les eaux souterraines. Hydrologie dynamique et chimique, Recherche, Exploitation et Évaluation des Ressources. Paris, Masson et Cie, 642pp.

Schroll, E., Shulz, O., Pak, E., 1983. Sulphur isotope distribution in the Pb-Zn-deposit Bleiberg (Carinthia, Austria). Mineralium Deposita, 18, 17-25.

Schroll, E., Rantitsch, G., 2005. Sulfur isotope patterns in the Bleiberg deposit (Eastern Alps) and their implications for genetically affiliated. Mineralogy and Petrology, 84, 1-18.

Stampfli, G.M., Borel, G.D., 2002. A plate tectonic model for the Paleozoic and Mesozoic constrained by dynamic plate boundaries and restored synthetic oceanic isochrons. Earth and Planetary Science Letters, 196, 17-33.

Stampfli, G.M., Marchant, R.H., 1997. Geodynamic evolution of the Tethyan margins of the western Alps. In: Pfiffner, O.A, Lehner, P., Heitzmann P., Müller, St., Steck A. (eds.). Deep Structure of the Swiss Alps – Results from NRP20. Birkhaüser Verlag, Basel, 123-138.

Strauss, H., 1997. The isotopic composition of sedimentary sulfur through time. Palaeogeography, Palaeoclimatology, Palaeoecology, 132, 97-118.

Szaran, J., Niezgoda, H., Halas, S., 1998. New determination of oxygen and sulphur isotope fractionation between gypsum and dissolved sulphate. Materials and Geoenvironment (RMZ), 45, 180-182.

Tanner, L.H., Lucas, S.G., Chapman, M.G., 2004. Assessing the record and causes of Late Triassic extinctions. Earth-Science Reviews, 65, 103-139.

Taylor, B.E., 1986. Magmatic volatiles: isotopic variation of C, H, and S. In: Valley, J.W., Taylor, H.P., O'Neil, J.R. (eds.). Stable Isotopes in High Temperature Geological Processes.

Washington D.C., Mineralogical Society of America, Reviews in Mineralogy, 16, 185-225.

Turchyn, A.V., Brüchert, V., Lyons, T.W., Engel, G.S., Balci, N., Schrag, D.P., Brunner, B., 2010. Kinetic oxygen isotope effects during dissimilatory sulfate reduction: a combined theoretical and experimental approach. Geochimica et Cosmochimica Acta, 74, 2011-2024. doi: 10.1016/j.gca.2010.01.004

Utrilla, R., Pierre, C., Ortí, F., Pueyo, J.J., 1992. Oxygen and sulphur isotope compositions as indicators of the origin of Mesozoic and Cenozoic evaporites from Spain. Chemical Geology, Isotope Geoscience Section, 102, 229-244.

Van Stempvoort, D.R., Krouse, H.R., 1994. Controls of $\delta^{18}O$ in sulfate. In: Alpers, C.N., Blowes, D.W. (eds.). Environmental geochemistry of Sulfide Oxidation. Washington D.C, American Chemical Society, Symposium Series, 550, 446-480.

Verma, S.P., 2001. Silica solubility geothermometers for hydrothermal systems. In: Cidu, R. (ed.). Proceedings of the 10th International Symposium on Water–Rock Interaction. Lisse, Villasimius, Italy, June 10-15, A.A. Balkema, 1, 349-352.

Wolery, T.W., Jarek, R.L., 2003. EQ3/6, version 8.0 – Software User's Manual. Civilian Radioactive Waste Management System, Management & Operating Contractor. Albuquerque (New Mexico), Sandia National Laboratories, 376pp.

Zeebe, R.E., 2010. A new value for the stable oxygen isotope fractionation between dissolved sulfate ion and water. Geochimica et Cosmochimica Acta, 74, 818-828.

Zheng, Y.F., 1999. Oxygen isotope fractionation in carbonate and sulfate minerals. Geochemical Journal, 33, 109-126.