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# Isotopic composition of gypsum samples of Permian and Triassic age from the north-eastern Italian Alps: Palaeoenvironmental implications

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## Abstract

Over the last fifty years, only relatively few measurements have been carried out on the oxygen isotopic composition of evaporite sediments, probably because of the technical problems related to these measurements, among other reasons. To make a further contribution to our knowledge of $\delta^{18}$O values of seawater sulphate through time, we report here the results obtained from forty gypsum samples of Permian and Triassic age coming from the north-eastern section of Italian Alps. The $\delta^{18}$O values of the samples of Permian age range from 15.4 to 17.9‰ (VSMOW) with a mean value of 16.7‰, while the samples of Triassic age range from 11.7 to 16.3 with a mean value of 14.7‰ . The $\delta^{34}$S values measured on four samples for each group to provide indirect confirmation of the age of the samples yield homogeneous results, with mean values of 11.8‰ vs. VCDT (Permian) and 15.0‰ (Triassic). Both these values agree with the sulphur isotope age curve. The isotopic signatures of our samples seem to be well preserved and the reported values are in reasonable agreement with previous results. The interpretation of our data fits well in the framework of the global sulphur cycle and the reported values can be reasonably considered to represent the isotopic composition of oceanic sulphate during the related geologic periods.

*Keywords:* Oxygen isotopes; Sulphur isotopes; Permian gypsum; Triassic gypsum; North-eastern Italian Alps

## 1. Introduction

Over the last five decades, a number of papers have been published dealing with the sulphur isotopic composition of sea-water and fresh-water dissolved sulphate, sedimentary sulphate, sulphide of magmatic and metamorphic origin, etc. Yet considerably fewer papers have been published dealing with the oxygen isotopic composition of dissolved or solid sulphate. Consequently, while reliable curves were published showing the variations through time of the sulphur isotopic composition of the sulphate minerals of evaporites (e.g. Holser, 1977; Claypool et al., 1980, and, more recently, based on measurements of non-evaporite materials, Strauss, 1997; Kampschulte and Strauss, 2004) a precise and statistically significant

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distribution of the $\delta^{18}O(SO_4^{2-})$ values through geologic time has not yet been defined. Claypool et al. (1980) gathered all the available $\delta^{18}O(SO_4^{2-})$ values obtained from sedimentary sulphates and tried to use them to evaluate a best estimate age curve as they did for sulphur. Data from their study and those previously published were grouped by geological ages rejecting highly divergent values and introducing some corrections to try to obtain more homogeneous results.

Unfortunately, also because of technical problems related to the measurement of $\delta^{18}O(SO_4^{2-})$ which led to relatively large discrepancies between the results obtained by different authors, the data reported in the literature for this variable are limited. The $\delta^{18}O(SO_4^{2-})$ values measured for sea-water sulphate by various laboratories are rather different from one another. Longinelli and Craig (1967) reported an almost constant oxygen isotopic composition of marine-dissolved sulphate of about 9.5‰ vs. SMOW and Lloyd (1967) a value of 9.7‰ for a set of several samples from different areas. Preliminary $\delta^{18}O(SO_4^{2-})$ results obtained by Rafter were close to 11‰; after improving the preparation technique, Rafter and Mizutani (1967a,b) reported a mean value of 9.9‰. After these sets of data Rösler et al. (1968) obtained two values (9.5 and 9.1‰) from samples from the northern Atlantic and Cortecci (1975) reported an average value of 9.5 ± 0.2‰ for some South Pacific deep water samples. In contrast with these data, Sakai and Krouse (1971) and Sakai (1972) obtained values of 8.6‰. Holser et al. (1979) and Zak et al. (1980) reported average oxygen isotopic compositions of oceanic sulphate of 8.6 and 8.7‰ respectively. At UCLA Claypool et al. (1980) obtained even lower values (8.1‰); Solomon et al. (1971) reported oxygen isotope values of 10.4‰, while Pilot and Harzer (1970) accepted an oxygen isotope value of 9.7‰. Longinelli et al. (1975) and Longinelli (1989) reported $\delta^{18}O(SO_4^{2-})$ values as low as 8.6 and 8.8‰ for some samples from Atlantic and Pacific GEOSECS vertical profiles, mainly in subsurface waters but also at various depths. Such a wide range of values cannot easily be explained, particularly considering that interlaboratory calibrations carried out at that time on non-marine samples between Longinelli's laboratory in Pisa and Sakai's laboratory in Misasa yielded no significant systematic differences, as reported by Sakai and Krouse (1971). This variability in modern seawater sulphate may indicate real variability rather than the effect of problems with the different preparation techniques (see the discussion on this point in Bottrell and Newton, 2006).

Sulphate isotope values have mainly been derived from evaporite measurements that are considered to record ocean water dissolved sulphate values with only minor fractionation. However, the evaporite-derived data sets are not continuous and poorly time constrained. As an alternative to the discontinuous evaporite-based isotope age curve, new analytical methods on different sedimentary materials were first suggested by Cecile et al. (1983) measuring the sulphur and oxygen isotope values in barites of Palaeozoic age from western Canada. Although these results have some limitations, Goodfellow and Jonasson (1984) showed the usefulness of sulphur isotope data derived from sedimentary barites and, recently, Turchyn and Schrag (2004) showed that isotopic values from marine barites may be used for studying palaeo-oxygen isotope values. A further important alternative to the evaporite study for sulphate isotope measurements was suggested by Burdett et al. (1989) analysing the sulphate contained in the structural lattice of biogenic carbonates (carbonate-associated sulphate, CAS) and showing that these values provide a reliable record of the marine sulphate isotopic composition through time. More recently Newton et al. (2004) and Kampschulte and Strauss (2004) showed that CAS measurements in inorganic carbonates also provide a reliable record of $\delta^{18}O$ in ancient marine sulphate. This is very important in view of the possibility of obtaining continuous records through time of both sulphur and oxygen isotope values of oceanic sulphate and to reconstruct detailed changes in global sulphur cycling. As pointed out by Kampschulte and Strauss (2004) some offset does exist between the isotopic values obtained from CAS of biogenic carbonates and those obtained from coeval evaporites. These offsets are difficult to explain but, in a general way, they could be related to differences in the input terms relevant to their environments of formation. However, it is rather difficult to separate these effects because all the isotopic values related e.g. to the addition to seawater of sulphate determined by the oxidation of pyrite should equally affect the CAS record and that of evaporites derived directly from marine dissolved sulphate. Localised input of terrestrial weathering products could be considered in the case of specific depositional environments (e.g. modern coastal sabkhas) but are difficult to consider in the case of most marine evaporites.

The sulphate anion can be removed from seawater by the precipitation of evaporites (gypsum and anhydrite) and by bacterial reduction (BSR) that generally takes place at the water-sediment interface or within a depth of a few centimetres (Kaplan et al., 1963), where sulphate-reducing bacteria produce isotopically light sulphide and heavily enriched sulphate. In the presence of iron, the light sulphide reacts to form pyrite, a common constituent of organic carbon-rich marine sediments.

Geologic environmental evolutions may expose sulphide minerals to oxidation (either direct or bacterially mediated) producing sulphates with light $\delta^{34}$S values and variable $\delta^{18}$O values according to different oxidation processes (Balci et al., 2007, and references therein).

The two principal components of the sulphur cycle are therefore the oxidized components (dissolved oceanic sulphate and evaporite sulphate) and the reduced component (sedimentary iron sulphides). It follows that the variations through time of the $\delta^{34}$S values of evaporites and hence of seawater sulphate are related in principle to variations of the sulphur redox cycle which, in turn, results from an interaction of geological, geochemical and biological processes. A marked evolution of seawater sulphate (and evaporitic sulphate) towards more positive $\delta^{34}$S values may be related to the enhanced burial of isotopically light pyrite, while a decrease of the $\delta^{34}$S values may be related to the enhanced inflow of sulphate produced by sulphide oxidation. The processes related to the variations of the sulphur isotopic composition through time have been reviewed by Strauss (1997), while Berner (2005) reports the results of a theoretical isotope mass balance model relating the combined effect of the carbon and sulphur cycles from middle Permian to middle Triassic. This is a period of special interest because of the large changes of the isotopic composition of sulphate and because of the mass extinction at the Permian–Triassic boundary. An exhaustive review of the global sulphur cycling has recently been published (Bottrell and Newton, 2006). An important conclusion is that "marine sulphate-oxygen isotopes respond in more complex ways, to a wider variety of factors than those of the sulphate–sulphur, and their variation through time is therefore more difficult to interpret".

The main purpose of this work is to add a further set of oxygen isotope values of evaporite sulphate to the known results in order to improve our knowledge of its variations through time, to check their reliability by comparison with previous data, and to check their interpretation in the framework of the global sulphur cycle.

## 2. Materials and methods

Twenty gypsum samples of Permian age and twenty gypsum samples of Triassic age were collected from the Alpi Tolmezzine (a section of the north-eastern Alps, near the border between Italy and Austria, Fig. 1) at different elevations ranging from a few hundred metres above sea level to about 1700 m. This Alpine section includes the uppermost level of the flysch of Carboniferous age (Hochwipfel Formation) overlain by the Damon Formation (mainly spilitic submarine lava flows, pillow lavas, sandstones and siltstones) overlain by the basal transgressive conglomerate of the Val Gardena sandstone of Permian age. Above the Val Gardena sandstone, the Bellerophon Formation of Upper Permian age includes gypsum horizons, dolomite breccias, limestones and dolomitic limestones (Martinis, 1971). These Permian evaporites, as well as the Triassic ones, outcrop in a very discontinuous way along the deep valleys with main east–west direction such as the lay-out

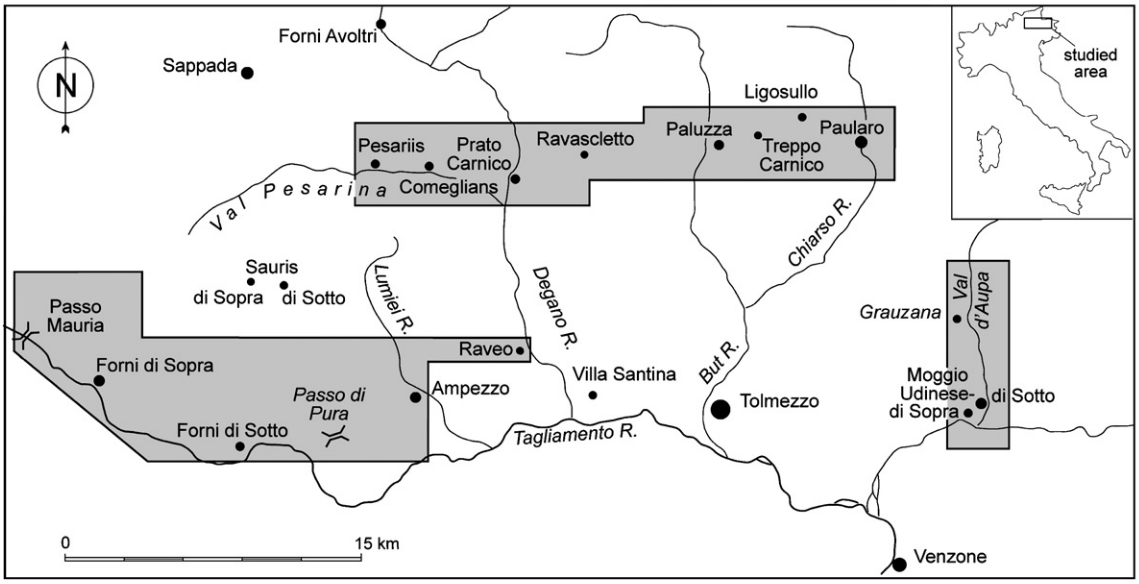

Fig. 1. Studied section of the Italian north-eastern Alps and sampled areas.

of Val Pesarina–Ravascletto–Paluzza–Paularo to the north and the upper Tagliamento river Valley to the south (Fig. 1). It is important to point out that the Permian evaporites are generally purer than the Triassic ones and that the purity of both evaporites increases from the base to the top. Frequent calcite and clay impurities have been found by means of powder X-ray diffractometry (XRD), while only very low and occasional traces of chloride were found by chemical analysis. Anhydrite is frequently found by X-ray diffractometry: Carulli and Colussi (1974) concluded that the gypsum of this Alpine section is the product of hydration processes of primary anhydrite as suggested also by the frequent folding and bending of these formations.

Because of the presence of impurities in several gypsum samples the sample treatment was carried out as follows: after accurate cleaning of the sample surface, about two grams of gypsum were crushed in a steel mortar, finely ground in an agate mortar, and dissolved in 1 L of double distilled water. The solution was filtered to eliminate insoluble impurities and 40 ml were passed through a column packed with cation exchange resin, hydrogen form, diluted to 200 ml with double distilled water and acidified to pH 2 by means of 1 M HCl solution. After heating the solution to boiling, 20 ml of 0.25 M $BaCl_2$ solution were added, the $BaSO_4$ precipitate was digested for at least 3 hours, filtered and washed with double distilled water until chloride free, and dried overnight in a partial-vacuum oven at 120 °C.

The $BaSO_4$ sample was reacted according to the procedure established long ago by Longinelli and Craig (1967). A mixture of $BaSO_4$ and pure powdered graphite was heated *in vacuo* at 1100 °C; the evolved CO was converted to $CO_2$ by a high voltage glow discharge and added to the evolved $CO_2$, condensed in a liquid nitrogen cooled trap. The final sample was measured in a Finnigan Delta S mass spectrometer: the mean standard deviation of the oxygen isotope measurements was about ±0.10/0.15‰ (1σ).

Some $\delta^{34}S(SO_4^{2-})$ measurements were carried out in order to have further confirmation of the geologic age of the studied samples collected long ago. The method used was that described by Robinson and Kusakabe (1975). Pure $Cu_2O$ was prepared by heating reagent grade CuO at about 900 °C in the furnace tube of a vacuum line. The gypsum samples were converted to $Ag_2S$ using the technique proposed by Thode et al. (1961). The $BaSO_4$ precipitated from the solution of gypsum was reduced by means of a boiling solution of HI, HCl, and $H_3PO_2$ and the $H_2S$ formed was carried by a flow of ultrapure nitrogen through a cadmium acetate solution. The precipitated CdS was filtered, washed and reacted with a 0.2 N $AgNO_3$ solution with the precipitation of $Ag_2S$. An amount of 5 to 10 mg of $Ag_2S$ was mixed with a large excess of $Cu_2O$ and finely ground in an agate mortar, introduced in a pre-heated ceramic boat and reacted in a furnace, after accurate degassing, at about 850 °C. Traces of $CO_2$ produced with $SO_2$ were separated by the use of a *n*-pentane-liquid nitrogen trap according to Oana and Ishikawa (1966). The $SO_2$ samples were measured in a Finnigan Delta E mass spectrometer versus a laboratory $SO_2$ standard calibrated versus a repeatedly measured internal $Ag_2S$ sub-standard from Mediterranean seawater sulphate, calibrated long ago versus CDT. A further calibration was made versus the IAEA-S-1 (NZ1) calibration material. The standard deviation of our measurements was of about ±0.15‰ (1σ). The raw isotopic results were corrected according to the procedure suggested by Coleman (1980) since these measurements were carried out before the publication of the most recent procedures (Coleman, 2004).

## 3. Results and discussion

### 3.1. Sulphur isotope results

The isotopic results obtained are reported in Table 1 (gypsum of Permian age) and in Table 2 (gypsum of Triassic age). The few measurements of the sulphur isotopic composition can be compared with the age curve

Table 1
Gypsum samples of Permian age

| Sample No. | Location | $\delta^{18}O$ $(SO_4^{2-})$ | $\delta^{34}S$ $(SO_4^{2-})$ |
|---|---|---|---|
| G1 | Paularo, Rufosco Stream | 16.3 | |
| G4 | Paularo, Minischitte Stream | 17.9 | |
| G9 | Paularo, Minischitte Stream | 17.0 | |
| G12 | Ligosullo, Lius Fork | 16.8 | |
| G15 | Ligosullo, Lius Fork | 16.5 | |
| G17 | Ligosullo, Pontaiba Stream | 16.7 | |
| G23 | Cercivento, Gladegna Valley | 15.8 | 11.9 |
| G25 | Cercivento, Gladegna Valley | 16.3 | |
| G27 | Comeglians, Entrampo Quarry | 16.7 | |
| G30 | Comeglians, Entrampo Quarry | 16.2 | |
| G31 | Comeglians, Entrampo Quarry | 17.7 | |
| G33 | Comeglians, Entrampo Quarry | 16.6 | 12.0 |
| G67 | S.of Comeglians, near Cella | 16.9 | 12.1 |
| G70 | Prato Carnico, Pesarina Stream | 17.7 | |
| G72 | Prato Carnico, Pesarina Stream | 17.2 | |
| G78 | Prato Carnico, Pesarina Stream | 16.8 | |
| G80 | SE of Pesariis, Pesarina Stream | 17.2 | |
| G83 | Sauris, Casera Razzo Road | 16.7 | |
| G86 | Sauris, betw.di Sotto and di Sopra | 15.4 | 11.4 |
| G88 | Sauris, road near the graveyard | 15.8 | |

The oxygen isotope values are reported versus VSMOW.
The sulphur isotope values are reported versus VCDT.

Table 2
Gypsum samples of Triassic age

| Sample No. | Location | $\delta^{18}O$ ($SO_4^{2-}$) | $\delta^{34}S$ ($SO_4^{2-}$) |
|---|---|---|---|
| G51 | Ampezzo, road to Oltris | 14.9 | |
| G53 | Ampezzo, road to Oltris | 15.9 | |
| G54 | Ampezzo, road to Oltris | 14.9 | |
| G56 | Ampezzo, road to Oltris | 16.3 | |
| G57 | Ampezzo, Lumiei stream | 11.7 | |
| G63 | Raveo, Chiarzo stream | 14.9 | 14.7 |
| G92 | W of Passo Pura | 15.0 | |
| G101 | Passo della Mauria,Stabia stream | 12.4 | |
| G104 | Passo della Mauria,Stabia stream | 12.6 | |
| G109 | SE Passo Mauria,road 52 bis | 15.7 | 15.0 |
| G110 | SE Passo Mauria,road 52 bis | 13.9 | |
| G112 | SE Passo Mauria, Stabia stream | 15.1 | |
| G116 | SE Passo Mauria, Stabia stream | 15.3 | 15.5 |
| G118 | SE Passo Mauria, Stabia stream | 15.6 | |
| G122 | NW of Forni di Sopra, Fossiana str. | 14.0 | |
| G127 | Forni di Sopra, Varmost road | 15.0 | 14.8 |
| G131 | W of Forni di Sotto, Chiaradia stream | 15.4 | |
| G137 | Forni di Sotto, near Vico | 15.1 | |
| G151 | Grauzaria, Val d´Aupa | 16.2 | |
| G152 | Grauzaria, Val d´Aupa | 14.4 | |

The oxygen isotope values are reported versus VSMOW.
The sulphur isotope values are reported versus VCDT.

of sulphur isotope values reported by Claypool et al. (1980) but, more conveniently, with the sulphur isotope values reported by Strauss (1997) in his review paper or, even better, with the age curve of sulphur isotopes reported by Kampschulte and Strauss (2004) based on the measurement of structural substituted sulphate (SSS) in carbonates. This curve shows a marked overall decrease in $\delta^{34}S$ from extremely positive values (up to about 50‰ in the Cambrian) to about 12‰ in the uppermost Carboniferous, low sulphur isotope values persisting for most of the Permian, defining the minimum for the Phanerozoic $\delta^{34}S$ values at about 10‰ during Upper Permian. A decline in $\delta^{34}S$ values is interpreted as the result of a decrease in the fractional burial of isotopically light sedimentary pyrite. According to Kampschulte and Strauss (2004) mass balance calculations show the Phanerozoic decrease of $\delta^{34}S$ corresponding to a decrease in fractional burial of pyrite from 0.6 to 0.2, in reasonable agreement with the modelling data by Lasaga (1989) on the decrease of pyrite burial from early Cambrian to late Permian. A rapid increase in the $\delta^{34}S$ values is recorded only at the very end of the Permian (e.g. Newton et al., 2004; Kampschulte and Strauss, 2004), and is related to a period of marked deep-water anoxia. The four $\delta^{34}S$ values in Table 1 (11.4 to 12.1‰) are in good agreement with the values reported previously for samples of Permian age. For example, Claypool et al. (1980) report an overall range of values from about 11 to about 13‰, and Cortecci et al. (1981) report values from 9.3 to 13.8‰ for Upper Permian samples from Southern Alps, an area not far from our sampling area. Peryt et al. (1998) reported $\delta^{34}S$ values from 10.3 to 11.6‰, obtained from anhydrite and polyhalite samples of Upper Permian age (Zechstein) from northern Poland. Strauss (1997) reports an overall $\delta^{34}S$ range from about 8 to about 14‰ for the whole Permian and only Newton et al. (2004) obtained a very wide range of values from a Late Permian minimum of 11.5‰ to a maximum of 26.9‰ immediately above the mass extinction level.

The four $\delta^{34}S$ obtained from Triassic samples (Table 2, 14.7 to 15.5‰) are in good agreement with the results obtained from evaporites of Upper Triassic (Carnian/Keuper) age by several authors (e.g. Cortecci et al., 1981 (15.8 to 17.4‰); Rick, 1990 (15.4 to 17.4‰); Alonso-Azcárate et al., 2006 (13 to 15.8‰). These relatively low values result from a marked evolution from very heavy

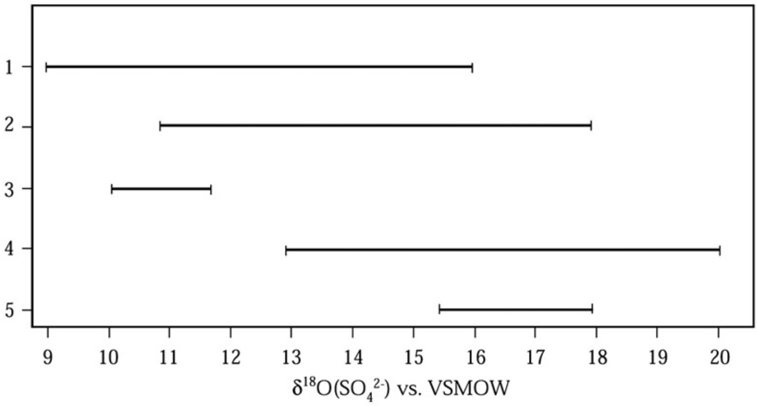

Fig. 2. Ranges of the oxygen isotopic composition of evaporites of Permian age according to: 1)Claypool et al. (1980); 2) Cortecci et al. (1981); 3) Peryt et al. (1998); 4) Newton et al. (2004); 5) this paper.

$\delta^{34}$S values in the Lower/Middle Triassic, up to 25/28‰ (Newton et al., 2004; Kampschulte and Strauss, 2004) to considerably lower values in the Upper Triassic. This evolution can be related to a sequence of events beginning with "superanoxia" conditions of oceanic waters during the uppermost Permian and Lower Triassic (Griensbachian and Dienerian) favouring bacterial sulphate reduction (BSR) in the water column and enhanced burial of sedimentary pyrite. The subsequent decline in $\delta^{34}$S during Middle and Upper Triassic could be related either to a marked decrease in the fractional burial of pyrite or to changes in the environmental conditions determining the oxidation of the previously buried $^{34}$S-depleted pyrite and the inflow of this $^{34}$S-depleted sulphate into the oceans. However, Kampschulte and Strauss (2004) point out the existence of a consistent offset in the Middle and Upper Triassic between the sulphur isotopic values obtained from SSS of biogenic carbonates and those obtained from evaporites that are consistently lower by about 3‰. This offset cannot yet be reconciled.

### 3.2. Oxygen isotope results

We can now compare our $\delta^{18}$O values from Permian and Triassic samples with the data reported in previous papers. Fig. 2 reports the range of $\delta^{18}$O values obtained by various authors from samples of Permian age. It can be seen that our results, even though not particularly $^{18}$O-enriched, are in the upper range of values. If we now compare our data with the oxygen isotope age curve for sulphate (Claypool et al., 1980) our results could only fall within the lowermost Permian section of the curve, in the shaded area which is the qualitative estimate of its uncertainty towards $^{18}$O-enriched values. Apart from the results in Newton et al. (2004), only few data reported by Cortecci et al. (1981) show similar values (Fig. 2). However, the latter results refer to the Upper Permian. Taking into account that these samples come from areas near our sampling sites, we could tentatively refer our samples to the Upper Permian and to that narrow time interval (Newton et al., 2004) marking the beginning of the evolution towards heavily $^{18}$O-enriched (as well as $^{34}$S-enriched) isotopic values related to a substantial increase of deep-water anoxia conditions. According to the interpretation of the processes that affected the oxygen isotope values of seawater sulphate and of evaporites during that period, one should conclude that two different processes affecting the global balance between oxidation and reduction of sulphur may be responsible for the increasing oxygen

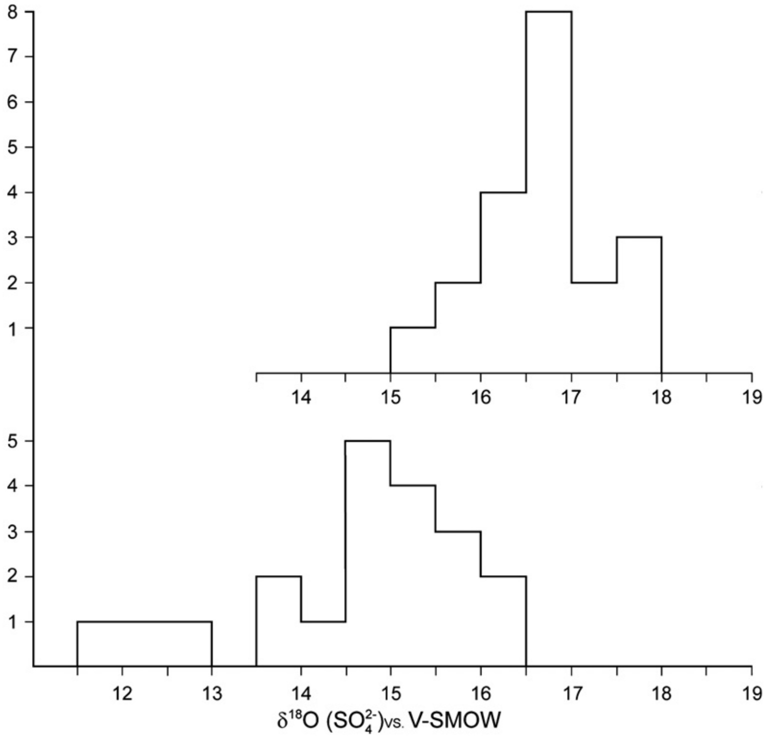

Fig. 3. Frequency distribution of the oxygen isotope values for class intervals of 0.5‰: Permian samples in the upper histogram, Triassic samples in the lower histogram.

isotope values of this period, both essentially related to BSR activity. In fact, the bacterial reduction of sulphate may cause a kinetic enrichment of the residual sulphate (generally considered lower for oxygen than for sulphur) but also provokes a secondary effect, since increased BSR may promote enhanced isotope exchange between intermediate sulphur compounds and water (Newton et al., 2004). On this subject Brunner et al. (2005) suggested a model of BSR that postulates a predominance of oxygen isotope exchange between cell-internal sulphur compounds and environmental water. If so, a kinetic oxygen isotope fractionation would be of minor or no importance and, however, the reported constant 1:4 ratio for oxygen and sulphur during sulphate reduction would be unreliable.

The relatively narrow range of our $\delta^{18}$O values from Permian samples (Fig. 3) and their fairly regular distribution suggest rather homogeneous environmental conditions during the deposition of these evaporites despite the fairly large area of sample collection, well over 20 km, mainly along E-W alignments (Fig. 1). This rather regular distribution also suggests a good preservation of the pristine values. If, according to geological considerations (Carulli and Colussi, 1974), the gypsum of this Alpine section derives from hydration processes of primary anhydrite, our Permian samples seem to have undergone a simple hydration process with no perceptible secondary effects.

The oxygen isotope values obtained from Triassic samples are reported in Table 2 and, graphically, in Fig. 4 for a direct comparison with the results reported in previous papers. The mean value of our samples (14.7‰) is not far from the mean values of other sets of data with the exception of the results reported by Newton et al. (2004) that refer to a particular time interval (Permo-Triassic boundary and adjacent geologic formations) during which relatively fast and large changes of the sulphate isotopic values took place. Our mean value is lower than the mean value obtained from Permian samples (16.7‰) and the results are less homogeneous than the Permian results showing a more irregular distribution with a marked “tail” towards lighter values (Fig. 3). This could be the effect of a minor, partial diagenetic alteration of the pristine isotopic values, possibly related to the intense tectonic activity of Upper Triassic age in this area (Braga et al., 1971; Martinis, 1971; Carulli, 1971), mainly resulting from compressive strength, with large overthrusts, probably favoured by the marked plasticity of the evaporitic formations often acting as a tectonic lubricant. The availability of water during this tectonic activity may have determined minor isotope changes in some of the evaporite samples. A marked $\delta^{18}$O shift up to about 6‰ towards more negative values with no parallel anomalies in sulphur isotopes was reported by Richardson and Hansen (1991) in the case of some Devonian and Mississippian evaporites from southeastern Iowa, USA. These anomalies were related to relatively gentle exchange processes of one or more oxygen atoms leaving the rest of the group intact and taking place after deposition, at a relatively high temperature. However, Alonso-Azcárate et al. (2006) reach a completely different conclusion in their study of Upper Jurassic evaporites that underwent metamorphic processes. In that case the enriched $\delta^{18}$O (close to 22‰) was considered to be the result of re-equibration of oxygen isotopes with aqueous fluids and/

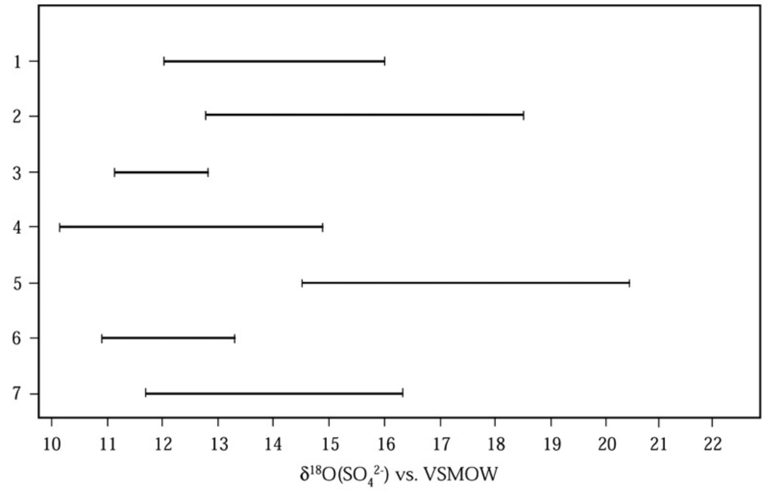

Fig. 4. Ranges of the oxygen isotopic composition of evaporites of Triassic age according to: 1)Claypool et al. (1980); 2) Cortecci et al. (1981); 3) Rick (1990); 4) Utrilla et al. (1992), apart from a couple of outliers; 5) Newton et al. (2004); 6)Alonso-Azcárate et al. (2006); 7) this paper.

or sedimentary carbonates during the low grade metamorphism of the basinal sequence. In the case of our samples, carbonate formations are rather common in the sedimentary sequence. Because of the uncertainty in the definition of the possible influence of low grade metamorphism on evaporites we do not try to explain the "tail" effect in our Triassic samples, an effect that may also be related to minor differences in the environmental conditions in different basins.

The comparison of our results with the data reported in previous papers (Fig. 4) shows that the sets of data obtained from U. Triassic samples, as well as the overall range of values reported for the whole Triassic by Claypool et al. (1980), are not far from one another. Different areas of origin of the samples, e.g. southern Italian Alps (Cortecci et al., 1981), Swiss Jura Mountains (Rick, 1990), northern and north-eastern Spain (Utrilla et al., 1992; Alonso-Azcárate et al., 2006), and slightly different geological ages do not play an important role in substantially shifting the oxygen isotope values of the measured U. Triassic evaporites. The major difference refers to the data reported by Newton et al. (2004), obtained from SSS in limestone samples of lowermost Triassic age (Griensbachian and Dienerian) right above the Permian–Triassic boundary. This set of values is reported in Fig. 4, despite the large age difference with our samples, to visually quantify the effect on the $\delta^{18}$O of seawater sulphate of relatively fast changes in the environmental conditions. However, even excluding the results in Newton et al. (2004), the overall range of values reported in Fig. 4 suggests a comparable variety of environmental conditions in the evaporite deposition. One of the important points concerning our $\delta^{18}$O values as well as almost all the other values obtained from U. Triassic samples is the evolution from the $^{18}$O-enriched values of Lower and Middle Triassic (up to about 20‰ according to Newton et al., 2004) to the considerably lower values of Carnian whose mean $\delta^{18}$O value is not far from 14‰. This evolution is similar to that of the $\delta^{34}$S values during the same time interval.

As the changes in the oxygen isotopic composition of marine sulphate are related to more complex processes than those affecting sulphur isotopes, a fairly large variability of the $\delta^{18}$O values can be expected, related not only to the changes in the BSR that largely affect the sulphur isotope values, but also to different oxidation processes of the buried sulphide. These different processes have been exhaustively discussed in the review paper by Bottrell and Newton (2006) and, in the case of a decrease in $\delta^{18}$O values, can mainly be related to the availability of molecular oxygen, of water molecules, and of $Fe^{3+}$cations during the oxidation processes of buried sulphides. Under anaerobic conditions, the oxidation of pyrite yields a sulphate with isotopically light $\delta^{18}$O values equal or very close to the $\delta^{18}$O of environmental water. According to the conclusions by Balci et al. (2007) water is practically the only oxygen source of sulphate either during anaerobic or aerobic, biological or abiotic conditions of pyrite oxidation.

In the presence of molecular oxygen, the $\delta^{18}$O of the resulting sulphate is considered to shift towards heavy values. However, the possibility of an exchange of oxygen atoms of intermediate anions like $SO_3^{2-}$and/or $HSO_3^-$complicates the oxidation processes introducing a further variable that may affect the final oxygen isotopic composition of the resulting sulphate. In the case of our samples and of most of the U. Triassic samples, a preferential addition to seawater of a sulphate from oxidation processes whose main oxygen source was water can be envisaged. However, variations of the $\delta^{18}$O of the dissolved marine sulphate and of the precipitated evaporites can take place in different basins because homogeneous oxygen isotope values are not necessarily found in the oceans as probably happens in modern seawater sulphate, also because the turnover time for oxygen in marine sulphate is far shorter than the sulphate residence time (Bottrell and Newton, 2006).

It should be pointed out that from about mid-Triassic to recent time, the oxygen isotopic composition of marine evaporites, according to the age curve in Claypool et al. (1980), only underwent minor variations, most of the results remaining within the interval 14.0± 1‰. This could be somewhat surprising considering the huge range of $\delta^{18}O(SO_4^{2-})$ values measured in the case of Messinian evaporites (e.g. Longinelli, 1979/1980), ranging from −6.9‰ to +19.4‰ only within the VII cyclothem of the Eraclea Minoa sequence (Sicily, Italy). The environmental conditions of deposition in the latter case must have been extremely heterogeneous since anomalous $\delta^{18}O(SO_4^{2-})$ values are found with equally anomalous $\delta^{34}S(SO_4^{2-})$ values ranging from −28.3‰ to +22.4‰ (vs. CDT), the two variables not always varying sympathetically. According to Pierre and Fontes (1978) and Fontes and Pierre (1978) these values may result from repeated processes of evaporite dissolution and re-precipitation in fresh water/brine water environments as well as from redox variations through the brine-sediment interface. Strongly reducing bacterial activity could take place at the bottom of the evaporating basin followed by the diffusion of sulphide into the overlying water and its oxidation under variable environmental conditions which could range from fresh water/brackish water plus molecular dissolved oxygen to highly evaporated seawater at relatively elevated temperature with low concentrations of molecular dissolved oxygen. However, fractionation effects as large as those observed in the VII section of Eraclea Minoa are not easily attributable even to extreme conditions and to repeated epidiagenetic processes: the addition of secondary sulphate by inflowing continental waters is at least very probable. The anomalous values indicate that some gypsum layers must be considered of secondary origin since selenite layers that are considered of primary origin, directly deposited from evaporating seawater brines, show homogeneous and "normal" isotope values. This case is perhaps the most impressive from the point of view of the huge environmental changes that may take place during the deposition of an evaporitic sedimentary sequence. This is often found in the case of Messinian evaporites and may happen because some evaporites may not be of marine origin, some may have been deposited in marginal basins where the dissolved sulphate may have been quite different from open ocean sulphate, and some may have been affected by complicated post-depositional processes including addition of secondary sulphate.

Apparently, this is not the case with our samples (and with other evaporite sequences) that, apart from the few light samples of Triassic age, show rather homogeneous isotopic values. If we are dealing with primary gypsum, it did not undergo diagenetic processes: if, on the contrary, we are dealing with primary anhydrite its hydration process was homogeneous and the newly formed gypsum did not undergo further important modification processes. Unfortunately, because of the geologic age of the samples studied, the isotopic measurement of the water of crystallization would be of no help in identifying the primary or the secondary origin of gypsum, because of the relatively weak bond between the water molecules and the sulphate molecule and the facility of diagenetic changes of these water molecules.

## 4. Conclusions

1. Both the oxygen and sulphur signatures of the measured Permian and Triassic gypsum samples seem to be well preserved, despite the intense tectonic activity which took place in this area during Upper Triassic;
2. the reported isotopic values are in fairly good agreement with previously published results obtained from evaporites of similar geologic age even though precise age correlations cannot be made;
3. the evolution of the palaeoenvironmental conditions that produced the reported data can be traced, according to the processes that control oxygen and sulphur isotope compositions of marine sulphate;
4. the oxygen and sulphur isotopic values obtained seem to be quite reliable and, consequently, to represent the isotopic composition of ocean water dissolved sulphate during the related geologic periods.

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