Multiple isotope tracers from Permian-Triassic hydrated sulfates: Implications for fluid-mineral interaction

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Abstract – Isotopic compositions of water of crystallization and sulfate anionic group in gypsum and polyhalite were used as tracers for events related to their formation and subsequent evolution, as for example origin of crystallization water and extent of thermal overprint. For this purpose, gypsum and polyhalite from the Permo-Triassic evaporites of the Eastern Alps, were analysed for isotope composition of sulfate anionic group (δ34S and δ18OSO4) and water of crystallization (δD and δ18O). For comparison, water of crystallisation of polyhalite samples of similar age from New Mexico (USA), Klodawa (Poland) and Hattberg, Hesse (Germany) were also investigated. Estimated δ18O and δD values of polyhalite formation brines vary from 14.4 to 3.4‰ and 42.5 to −6.1‰, respectively. Gypsum formation brines show different δ18O and δD values, from −5.7 to −15‰ and −30.9 to −88.8‰, respectively. The measured δ18OSO4 values of sulfate group are compatible with a thermal overprint at 100°–200°C for both minerals. The thermal overprint documented for the Eastern Alps led to gypsum but not to polyhalite dehydration. The isotopic composition of water of crystallization suggests that polyhalite is preserving the isotopic signature of an enriched brine. During a subsequent event, anhydrite rehydrated to gypsum, with the isotopic composition of water of crystallisation indicating lower (δD and δ18O) values than the present-day meteoric water ones. Due to their distinct mineral structure and, as a result, different temperature of dehydration, gypsum and polyhalite record different histories following precipitation in an evaporative system.

Keywords: sulfates / water of crystallization / stable isotopes / Eastern Alps / Permian-Triassic

Résumé – Traceurs isotopiques multiples à partir de sulfates hydratés de Permien-Trias : implications pour l’interaction fluide-minéral. Les compositions isotopiques d’eau de cristallisation et des ions sulfate dans le gypse et la polyhalite ont été utilisées comme traceurs des événements liés à leur formation et à leur évolution ultérieure, comme par exemple l’origine de l’eau de cristallisation et de la surimpression thermique. À cette fin, le gypse et la polyhalite des evaporites permo-triassiques des Alpes orientales ont été analysés pour déterminer la composition isotopique des ions sulfate (δ34S et δ18OSO4) et de l’eau de cristallisation (δD et δ18O). À titre de comparaison, des eaux de cristallisation d’échantillons de polyhalite d’âge similaire du Nouveau-Mexique (États-Unis), Klodawa (Pologne) et Hattberg, Hesse (Allemagne) ont également été étudiées. Les valeurs estimées du δ18O et du δD des saumures de formation de la polyhalite varient respectivement de 14,4 à 3,4‰ et de 42,5 à −6,1‰. Les saumures de gypse présentent des valeurs de δ18O et δD différentes, de −5,7 à −15‰ et de −30,9 à −88,8 respectivement. Les mesures de δ18OSO4 des ions sulfate sont compatibles avec une surimpression thermique à 100–200°C pour les deux minéraux. La surimpression thermique documentée pour les Alpes orientales a conduit au gypse mais pas à la déshydratation des polyhalites. La composition isotopique de l’eau de cristallisation suggère que la polyhalite préserve la signature isotopique d’une saumure enrichie isotopiquement. Au cours d’un événement ultérieur, l’anhydrite s’est réhydratée en gypse, la composition isotopique de l’eau de cristallisation indiquant

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1 Introduction

Evaporites consist mostly of ionic salts containing the major ions Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), K\(^+\), Cl\(^-\), (SO\(_4\))\(^{2-}\), and (CO\(_3\))\(^{2-}\), structural water as well as other ionic constituents like Ba\(^{2+}\), Sr\(^{2+}\), Br\(^-\), Li\(^+\), I\(^-\), B\(^{3+}\). Approximately eighty different salt minerals have been identified for evaporite deposits, although only few of them are considered important rock formers (Holland, 1984). MgSO\(_4\) bearing marine evaporites are relatively rare in the geologic record and restricted to the late Precambrian, Pennsylvanian-Triassic, and Cenozoic (Eocene to modern) (Hardie, 1996). Generally, in evaporite deposits, minerals precipitate from sea water in reverse order of their solubilities: carbonates first, followed by sulfates, and finally chloride minerals. Polyhalite triple-cationic salt, K\(_2\)Ca\(_2\)Mg(SO\(_4\))\(_4\)-2H\(_2\)O, has a higher solubility than gypsum, polyhalite forming as near end member mineral in evaporite sequences, even after precipitation of halite.

Upper Permian potash-bearing rocks, including primary formed polyhalite and carnallite K\(_2\)MgCl\(_4\)-6H\(_2\)O, are found in the Delaware basin in the western Texas and south-eastern New Mexico (Lowenstein, 1988; Barker and Austin, 1993) as well as in NE England (Armstrong et al., 1951; Kemp et al., 2016) and the Zechstein basin of Germany (Kampschulte et al., 1998). The origin of polyhalite of Permian age from the Zdrada platform and Peribaltic Basin of Poland was investigated by Peryt et al. (1998) and Peryt et al. (2005), the authors concluding that it formed by reaction of anhydrite with marine brines. By determining the age of polyhalite by \(^{40}\)Ar/\(^{39}\)Ar method, Schorn et al. (2013) and Leitner et al. (2013) linked tectonic events and mineral textures from the Northern Calcareous Alps.

Recently, formed diagenetic polyhalites replacing gypsum or anhydrite were investigated from Baja California, Mexico (Holser, 1966). Polyhalite may form as a back reaction between brine and glauberite Na\(_2\)Ca(SO\(_4\))\(_2\), as demonstrated for the drill holes from the Lop Nor basin, China (Ma et al., 2010). Polyhalite occurs as end member precipitate in a recent playa lake of La Mancha, Spain (Pena et al., 1982) or in the evaporitic sequence of the Salt Lake, Tuz Gölü basin, Turkey (Camur and Mutulu, 1996). Potash salts, including polyhalite, form today also in the Qaidam basin, China (Lowenstein et al., 1989) or Sambhar Lake, Thar Desert, India (Sinha and Raymahashay, 2004).

Once formed, gypsum and polyhalite record in their texture or isotopic composition primary and/or secondary events, the last ones occurring much latter than their formation age. For example, for the Carpathian Foredeep, Halas and Krouse (1982) investigated for Miocene gypsum the isotopic composition of water of crystallization and demonstrated that during the last glacial, isotopically depleted meteoric water was incorporated in gypsum as water of crystallization. Matsubaya and Sakai (1973) demonstrate that anhydrites and gypsum were rehydrated subsequently by various mechanisms. By using a different method, namely the \(^{40}\)Ar/\(^{39}\)Ar dating, Leitner et al. (2013) conclude that the radiogenic system of Permian polyhalites from the Eastern Alps is not recording formation ages but subsequent Permian and Alpine events.

In the present study, we investigate mineral formation and subsequent events recorded in hydrated sulfates deposits by using multiple isotope systems recorded in the sulfate anionic group and water of crystallization. The investigated minerals are: gypsum and polyhalite of Upper Permian and Triassic age from the most prominent evaporitic sequences of the Alps and, in order to compare the effect of contrasting thermal history on the isotope composition of water of crystallization, selected samples from New Mexico (USA) and Klodawa mine (Poland) and Hattberg, Hesse (Germany).

2 Geological setting

Sulfates occur in the halite and gypsum deposits of the Northern Calcareous Alps and in the so-called Central Alpine Mesozoic (Fig. 1). The two units of the Eastern Alps are characterised by the presence of representative and well exposed Permian-Triassic evaporitic deposits (Schorn et al., 2013; Leitner et al., 2013). Description of samples from various locations, mineralogy, texture as well as the age of the deposits are given in the supplementary material. Systematic presentation of the mineral deposits is given in Bojar et al. (2016).

Additionally, we analysed two polyhalites from New Mexico (Barker and Austin, 1993). Two others polyhalite samples are from the Zechstein facies of Europe, namely one from the Klodawa Mine, Poland (Burliga, 2014) and the other from Hattdorf, Hesse, Germany (Kampschulte et al., 1998).

3 Analytical methods

The stable isotope data of sulfates were obtained on a dual inlet and triple collector mass spectrometer on SO\(_2\) prepared from the supplied BaSO\(_4\) samples by the method published by Halas and Szaran (2001) in the case of \(\delta^{34}\)S measurements, and on CO\(_2\) prepared from these BaSO\(_4\) samples by the method of Halas et al. (2007) in the case of \(\delta^{18}\)O\(_{SO_4}\) measurements. NBS-127 was used as internal standard. Results are reported with respect to the international standards Canyon Diablo Troilite (V-CDT) and Standard Mean Ocean Water (V-SMOW), respectively, with standard deviation better than \(\pm 0.2\)‰.

Water of crystallization was extracted by heating the samples in vacuum. Firstly, the samples were treated in vacuum by heating at 50°C for two hours in order to remove
absorption water (Halas and Krouse, 1982). Crystallization water was then collected by heating gypsum at 250 °C and polyhalite at 400 °C. The cryogenically trapped water was subsequently analysed for δ18O and δD on a Picarro L2120-i Analyzer. Laboratory standards, previously calibrated to the V-SMOW-V-SLAP scale were OH-13 (δD = +2.84‰, δ18O = +0.96‰) and OH-16 (δD = −114.68‰, δ18O = −15.43‰) (Bojar et al., 2017). These standards were used to normalize the results to the V-SMOW-V-SLAP scale. The isotopic compositions of water of crystallization were synchronously measured, with a standard deviation of ±0.1‰ for δ18O and ±0.4‰ for δD.

4 Results and Interpretation

4.1 Results

For the present study, the measured δ34S and δ18O values of sulfates and δ18O and δD of water of crystallization are given in Tables 1 and 2, respectively. For the Northern Calcareous Alps, δ34S values for both gypsum and polyhalite of Late Permian age, fall in a narrow range between 10 and 13‰, except one sample with 14‰ (Tab. 1). Triassic (Carnian-Norian) sulfates from the Central Alpine Mesozoic, consistently show a more enriched isotopic composition, with δ34S values between 14 and 15‰. In contrast to sulfur, the δ18OSO4 values of gypsum and polyhalite show a broader distribution between 12 and 20‰, with one exception (H_5) showing 6.5‰ (Tab. 1).

The δ18O and δD values from gypsum crystallisation water vary from −1.8 to −11.1‰ and from −50.3 to −107‰, respectively (Tab. 2). Polyhalite δ18O and δD values vary from 13.3 to 7.4‰ and from −1.2 to −26‰, respectively.

| Sample | Mineral | δ34S sulfates (V-CDT) | δ18O sulfates (V-SMOW) |
|--------|---------|----------------------|-----------------------|
| Salt, NCA |         |                      |                       |
| *HT_2, Hall in Tyrol | Gypsum | 10.2 | 13.1 |
| D_4, Hallein | Polyhalite | 13.1 | 13.6 |
| D_2, Hallein | Polyhalite | 11.6 | 17.8 |
| *H_4, Hallstatt | Gypsum | 10.4 | 14.5 |
| *H_1, Hallstatt | Polyhalite | 10.3 | 16.0 |
| H_5, Hallstatt | Polyhalite | 10.0 | 6.2 |
| *A_5, Altaussee | Gypsum | 12.7 | 17.1 |
| *A_1, Altaussee | Polyhalite | 11.5 | 18.8 |
| A_6, Altaussee | Polyhalite | 11.2 | 14.8 |
| BI_3, Bad Ischl | Polyhalite | 10.3 | 13.9 |

Gypsum, NCA

| Sample | Mineral | δ34S sulfates (V-CDT) | δ18O sulfates (V-SMOW) |
|--------|---------|----------------------|-----------------------|
| *G_4, Golling | Gypsum | 11.7 | 19.8 |
| *W_9, Wiernern | Gypsum | 11.1 | 14.7 |
| *T_8, Tragöß | Gypsum | 14.0 | 11.5 |
| *WD_1, Seewiesen | Gypsum | 11.3 | 14.9 |
| *WD_2, Seewiesen | Gypsum | 11.3 | 14.3 |

Gypsum, CAM

| Sample | Mineral | δ34S sulfates (V-CDT) | δ18O sulfates (V-SMOW) |
|--------|---------|----------------------|-----------------------|
| *GT_2, Götztritz | Gypsum | 15.5 | 15.6 |
| *GT_4, Götztritz | Gypsum | 15.1 | 20.8 |
| *ST_2, Stanz | Gypsum | 14.2 | 14.7 |

The samples with an asterisk are from Bojar et al., 2016.
Table 2. Isotopic composition of water of crystallization and brine.

| Sample                  | Altitude (m) | Mineral       | $\delta^{18}$O crystallization water (V-SMOW) | $\delta^2$D crystallization water (V-SMOW) | $\delta^{18}$O brine (V-SMOW) | $\delta^2$D brine (V-SMOW) |
|-------------------------|--------------|---------------|---------------------------------------------|------------------------------------------|-----------------------------|----------------------------|
| Salt, NCA               |              |               |                                             |                                          |                             |                            |
| HT_2, Hall in Tirol     | 570          | Gypsum        | $-1.8$                                      | $-50.3$                                  | $-5.7$                      | $-30.9$                    |
| D_4, Hallein            | 450          | Polyhalite    | $7.4$                                       | $-26.0$                                  | $3.4$                       | $-6.1$                     |
| D_2, Hallein            | 450          | Polyhalite    | $10.1$                                      | $-10.0$                                  | $6.0$                       | $10.3$                     |
| H_4, Hallstatt          | 510          | Gypsum        | $-6.7$                                      | $-84.2$                                  | $-10.6$                     | $-65.5$                    |
| H_1, Hallstatt          | 510          | Polyhalite    | $12.4$                                      | $-1.2$                                   | $8.4$                       | $19.2$                     |
| H_5, Hallstatt          | 510          | Polyhalite    | $10.4$                                      | $4.7$                                    | $6.4$                       | $25.2$                     |
| A_5, Altaussee          | 710          | Gypsum        | $-7.2$                                      | $-91.7$                                  | $-11.1$                     | $-73.2$                    |
| A_1, Altaussee          | 710          | Polyhalite    | $13.3$                                      | $-3.0$                                   | $9.3$                       | $17.3$                     |
| A_6, Altaussee          | 710          | Polyhalite    | $12.8$                                      | $1.9$                                    | $8.7$                       | $22.3$                     |
| BI_3, Bad Ischl         | 470          | Polyhalite    | $12.4$                                      | $8.7$                                    | $8.4$                       | $29.3$                     |
| Gypsum, NCA             |              |               |                                             |                                          |                             |                            |
| G_4, Golling            | 480          | Gypsum        | $-11.1$                                     | $-101.3$                                 | $-15.0$                     | $-82.9$                    |
| W_9, Wiernern           | 730          | Gypsum        | $-8.7$                                      | $-101.4$                                 | $-12.6$                     | $-83.0$                    |
| T_8, Tragoß             | 790          | Gypsum        | $-9.1$                                      | $-94.2$                                  | $-13.1$                     | $-75.7$                    |
| WD_1, Seewiesen         | 970          | Gypsum        | $-10.9$                                     | $-89.8$                                  | $-14.8$                     | $-71.2$                    |
| WD_2, Seewiesen         | 970          | Gypsum        | $-9.2$                                      | $-96.4$                                  | $-13.2$                     | $-78.0$                    |
| Gypsum, CAM             |              |               |                                             |                                          |                             |                            |
| GT_2, Göstritz          | 800          | Gypsum        | $-9.5$                                      | $-93.2$                                  | $-13.5$                     | $-74.7$                    |
| GT_4, Göstritz          | 800          | Gypsum        | $-9.3$                                      | $-92.1$                                  | $-13.3$                     | $-73.5$                    |
| ST_2, Stanz             | 650          | Gypsum        | $-11.0$                                     | $-107.0$                                 | $-14.9$                     | $-88.8$                    |
| NM1, New Mexico, USA    | 1100         | Polyhalite    | $13.4$                                      | $5.2$                                    | $9.36$                      | $25.7$                     |
| NM2, New Mexico, USA    | 1100         | Polyhalite    | $18.44$                                     | $21.6$                                   | $14.38$                     | $42.5$                     |
| K1, Kłodawa Mine, Poland| 100          | Polyhalite    | $14.9$                                      | $16.1$                                   | $10.81$                     | $36.9$                     |
| HH1, Hattendorf, Hesse, Germany | 300 | Polyhalite    | $9.8$                                       | $16.4$                                   | $5.8$                       | $37.1$                     |

4.2 Interpretation

4.2.1 Isotopic fractionation between hydrated salts and water

4.2.1.1 Fractionation between water of crystallisation in gypsum and brine

According to Gonfiati and Fontes (1963), the fractionation factor for oxygen is $\alpha = 1.0037$; Fontes and Gonfiatintini (1967) determined the fractionation factor for hydrogen as $\alpha = 0.98$, both fractionation factors being not temperature-dependent.

For gypsum, a summary of available fractionation factors between oxygen in brine and oxygen in water of crystallization is given by Herwartz et al. (2017). The authors also determined a fractionation factor of 1.0034, but used for their calculations the factor of 1.0037 as determined by Gonfiati and Fontes (1963). Herwartz et al. (2017) mention that by using one of the already determined factors of 1.0034 to 1.004 the calculated oxygen composition of brines will not significantly change. Concerning hydrogen, Gazquez et al. (2017) determined a fractionation factor in good agreement to Fontes and Gonfiatintini (1968). In the present case, the small temperature dependence found by Gazquez et al. (2017) does not change our interpretation. The fractionations of Gonfiati and Fontes (1963) and Fontes and Gonfiatintini (1967) approximate better the present situation where we have not precise constrains for temperature.

4.2.1.2 Fractionation between water of crystallisation in polyhalite and brine

Hydrogen isotope fractionation between hydroxyl bearing minerals and water is for most of the determined minerals less than 1 (Chako et al., 2001 and reference therein). It has been shown that salt hydrates crystallization causes deuterium enrichment of brine (Barrer and Denny, 1964; Horita, 1989). For sulfate bearing minerals, both hydrogen from the hydroxyl group as well as from water of crystallization are deuterium depleted in respect to brine (Seal et al., 2000). The hydrogen isotopic fractionation of crystallization water for the complex polyhalite structure is not precisely determined. If we consider a fractionation factor less than one, for example in the range determined for alunite-jarosite for the hydroxyl group (Seal et al., 2000), than the calculated values of brines in the present study will not change in order to affect conclusions. The fractionation factor for hydrogen in gypsum ($\alpha = 0.98$) is between those determined for structural water in alunite ($\alpha = 1.004$) and jarosite ($\alpha = 0.050$). The number of determined $^{18}$O fractionation for salt hydrates are even smaller (Horita, 1989; Seal et al., 2000) and in the order of magnitude of this
factors for oxygen (compositions of brines are shown in Table 2. The equation for the fractionation factor is given by (1967) for hydrogen (overprint shown by for both minerals, gypsum and polyhalite, suggesting that thermal overprint by “trend 1” affected both to similar extent. Isotherm calculation was done according to Zeebe (2010). Blue horizontal line represents Permian oxygen isotopic composition in sulfates: blue dots represent gypsum and red polyhalite isotopic compositions.

5.2 Isotopic composition of sulfur and oxygen in the sulfate group; extent of thermal overprint

Sulfur isotope chemostratigraphy curve constructed with sulfates recovered from marine evaporites and marine carbonate deposits were for example constructed by Claypool et al. (1980), Kampschulte et al. (1998), Paytan and Gray (2012), Sial et al. (2015). The sulfur isotope data from Tab. 2 suggest that sulfates largely preserve their initial marine sulfur isotopic composition, a discussion for the Alpine realm is included for example in Longinelli and Flora (2007), Boschetti et al. (2011), Bojar et al. (2016) and references inside.

As temperature of dehydration is important for the interpretation of the results, data regarding this aspect will be discussed in the following paragraph for the two investigated minerals, gypsum and polyhalite.

5.1 Dehydration temperature of gypsum and polyhalite

Polyhalite loses crystallization water at approximately 285 °C (Fisher et al., 1996), its structure being more stable than that of gypsum, which loses crystallization water at 200 °C (Kemp, 1999). According to Wollmann et al. (2008), polyhalite dehydration starts at ~255 °C, the reaction being completed at ~343 °C. Polyhalite precipitates from saturated solutions at more elevated temperature than normal laboratory conditions of ~20 °C, increase of temperature to boiling driving crystallization (D’Ans, 1908). In this context, we consider that temperature of polyhalite crystallization is an additional factor for determining the geological time-period when polyhalite mineral deposits formed. For example, large volumes of polyhalite are known for Permian. In addition to the sulfate-rich oceans present at that time, brine temperatures around 50 °C (Halas et al., 2015) may have further enhanced the formation of the mineral.
sulfates precipitated at ambient temperatures, the measured oxygen isotope composition is largely in disequilibrium with the oxygen isotope composition of water (Chiba and Sakai, 1985). Halas and Pluta (2000) demonstrate that in the case of long residence time, the isotopic re-equilibration process between oxygen in gypsum sulfate group and oxygen in water molecules of brines may start at temperatures of 30–35°C, their findings being in accordance with Zeebe (2010). For isotherm calculations, we consider the oxygen fractionation factor between dissolved sulfate and water of Zeebe (2010) similar to that of Halas and Pluta (2000), for details see also Boscetti (2013). During calculation, we also included the precipitation effect on oxygen isotopes considering a fractionation factor of approximately 3% between precipitated and dissolved sulfates (Lloyd, 1968; Szaran et al., 1998). The position of isothersms will not significantly change if we use for 18O in sulfate one of the following fractionation factors: anhydrite-water (Chiba et al., 1981), alunite-jarosite-water (Stoffregen et al., 1994; Rye and Stoffregen, 1995) or barite-water (Kusakabe and Robinson, 1977). In the present case, we interpreted the shift of δ18OSO4 toward higher values than these typical for marine evaporites of Permian-Triassic age resulting from partial equilibration of oxygen in sulfates with a brine, for example, this resulted from the dehydration of gypsum during the thermal overprint (Fig. 2).

5.3 Isotopic composition of water of crystallization and brine

The δ18O values of calculated brines using water of crystallization (x-axis) versus δ18OSO4 values (y-axis) are displayed in Figure 2. Gypsum and polyhalite plot in two distinct groups, with gypsum showing negative oxygen isotope values and polyhalite showing positive values of brines. Considering the measured δ18OSO4 values, the isotopic values of water of crystallisation and the isothersms presented in Figure 2, we may distinguish between several processes. Oxygen isotopic composition of gypsum shows partial equilibration of sulfate group with local brines, as their δ18OSO4 values are higher than those of the Permian marine sulfate, and this is indicated as “trend I” (Fig. 2). Polyhalites show a similar trend of partial equilibration between oxygen in the sulfate group with brine oxygen. A compact, fine-grained polyhalite (H 5) shows also thermal overprint, in this case at higher temperatures. The calculated value of ~300°C is too high and should be considered qualitatively, as indicating preservation of peak temperatures during the overprint event. A vein polyhalite (D 4) and a coarse crystalline polyhalite (D 2) show partial equilibration of sulfate oxygen isotopic composition with brines at temperatures between 100° and 200°C (Fig. 2). In contrast, oxygen and hydrogen isotopic composition of brines plot on a mixing line suggesting a meteoric component (Fig. 3).

Considering the available samples, we may distinguish for polyhalite between:

- coarse polyhalite recording isotopic composition similar to evaporation brines evolving from marine water. The most enriched isotopic compositions are shown by samples NM1, NM2 (New Mexico) followed by K1 (Klodawa Mine), sampled from evaporitic deposits, which were not deformed and thermal overprint in contrast to the evaporites of the Eastern Alps. In this frame, the samples from New Mexico and Klodawa Mine may represent the isotopically enriched end-member of primary brines (Fig. 3);
- recrystallized orange polyhalites (D_2, H_5, D_4), which indicate either isotopic equilibration between meteoric waters and polyhalite or incorporation of meteoric waters into crystal lattice of the salt; H_5 shows an unrealistic high temperature of ~300°C, higher than polyhalite dehydration limit;
- fibrous polyhalite (HH1, A_6, H_1) formed in veins from salt rock. These samples record a latter imprint at estimated temperatures between 100° and 200°C;
- granular polyhalites grown on anhydrite or mud, which also indicate a higher temperature imprint (A_1, B1_3).

Monitoring of brines from Klodawa Mine (Dulinski et al., 2014) has shown that enriched syngenetic water of Zechstein age is still present in closed salt pockets. The oxygen and hydrogen isotopic compositions of syngenetic brine from which Klodawa polyhalite formed is shown in Figure 3, its composition plotting in the field of the measured brines from the salt pockets (Dulinski et al., 2014).

Permian-Triassic sulfates of Eastern Alps were thermally overprinted (Lettnier et al., 2013; Bojar et al., 2016). Using illite crystallinity, vitrinite reflectance and fluid inclusions in anhydrite, Lettnier et al. (2013) estimated peak overprint temperatures affecting polyhalite bearing deposits at c. 200°C. For evaporite deposits from the Eastern Alps, Bojar et al. (2016) estimated overprint temperatures using sulfate-sulfide isotope thermometers between 190° and 260°C (except for Tragöß gypsum deposit). As polyhalites were not thermally overprinted over 275°C, they have preserved their water of crystallization and rather (re)crystallized at temperatures between 100° and 200°C. On the other hand, secondary growth features were found for polyhalite of the Eastern Alps (Lettnier et al., 2013; Bojar et al., 2016) showing recrystallizations younger than Permian. We may assume that during a latter process partial equilibration and/or incorporation of low amount of meteoric fluid (up to 10% for the data acquired in this study) took place at temperatures closed to ambienal ones. For example, Halas and Krouse (1982) and Kasprzyk and Jasińska, (1998) identified various amounts of meteoric water in the crystallization water of Miocene gypsum from the Carpathian realm. Tan et al. (2014) showed that isotopic compositions of Quaternary gypsum formed in Qaidam basin in an arid environment plot on a mixing line between lake brine and recharge river water.

5.4 Relationship between the measured water of crystallization, calculated brines and local meteoric water line

Alpine overprint temperatures over 200°C were high enough in order to drive dehydration of gypsum to anhydrite. Rehydration to gypsum is possible if fluids are available and temperature falls below the dehydration limit of the mineral. The calculated isotopic compositions of brine (using the oxygen and hydrogen isotopic compositions of gypsum crystallization water) indicate that during rehydration/recryst-
tallization calcium sulfate (gypsum, anhydrite) incorporated meteoric water, as shown in Figure 2 by “trend 2”. The altitudes from which gypsum samples were collected for this study range between 480 and 970 m (Tab. 2). Incorporated meteoric water has δ18O values from −5.7 to −15‰ and −30.9 to −89‰, respectively (Fig. 3), the isotopic values do not correlate with the altitude (Tab. 2). According to Froehlich et al. (2008), for similar altitudes, weighted annual mean δ18O values are from −10.3 to −10.6‰. These values are higher than those measured for the water of crystallization in the investigated gypsum samples. The water of crystallization for the gypsum samples is also plotting to the left of the Local Meteoric Water Line (LMWL) (Fig. 3). It has been documented that late-glacial meteoric water has lower isotopic composition than the late-Holocene one, with δ18Olate-Holocene > δ18Olate-glacial by more than 3‰ (Jasechko et al., 2015). Moreover, the Younger Dryas period represents the last major period of aquifer refill (Bath et al., 1979). In light of these findings, the lower isotopic values of crystallization water plotting left of the meteoric water line suggest that meteoric water was incorporated in gypsum in a period cooler and dryer than today, possible during the Younger Dryas, if not earlier. An alternative explanation could consider that gypsum crystallization water records the isotopic signature of meteoric water percolating downward from a much higher elevation than today into subsurface, thereby reaching the sulfate deposit. The incorporation of water characterized by lower isotopic values than present one was put in evidence also for Miocene sulfates (Halas and Krouse, 1982). In Figure 3, gypsum samples from the halite type deposits, HT_2, H_4, A_5 (all transparent gypsum crystals, see supplementary material) show an isotopic composition of crystallization water close to the present global meteoric water line, suggesting late crystal growth.

6 Conclusions

Polyhalite and gypsum from the Eastern Alps are of marine origin, as suggested by their sulfur isotopic composition. As the δ34S values are in the same range for gypsum and polyhalite, the thermal overprint of 100 to 200 °C affected both minerals to similar extent.

The two minerals plot in two distinct groups (Figs. 2 and 3), which are not related to different precipitation stages in the marine evaporitic sequence but to different source for the incorporated crystallization water. Polyhalites from Carlsbad potash district, New Mexico and those from Kłodawa Mine (Poland) preserve an enriched syngenetic isotopic composition, characteristic for brines emerging from marine water. Polyhalites from the Eastern Alps indicate a narrow range for δD and δ18O of syngenetic brines with enriched oxygen and hydrogen isotopic composition. For a few samples mixture with meteoric water was involved, as indicated by the shift of values toward the meteoric water line.

In the case of the Eastern Alps, the crystallization water of gypsum records incorporation of meteoric water during a later event when, related cooler conditions meteoric water was depleted in heavy isotopes. A few gypsum crystals contain crystallization water whose isotopic compositions (δD and δ18O) are close to those of the present-day MWL.

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