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1 Origin of the Gypsum Veins Associated with the Diagenetic Dolomite Nodules from the
2 Neogene Marls of South-East Spain.

3

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9

10 Abstract

11 The late Neogene marls from the Lorca, Murcia and Vera basins in S-E. Spain contain
12 abundant dolomite nodules that were formed due to intense methane-rich fluid migration. The
13 pathways for these fluids are evidenced by dense networks of fractures that are crossing the
14 sedimentary layers and eventually the dolomite nodules. The fractures are generally filled by
15 secondary fibrous gypsum that form veins of a few cm thick.

16 The oxygen and sulfur isotopic compositions of the gypsum veins exhibit wide
17 ranges ($-2.2 < \delta^{18}\text{O}\text{‰ VSMOW} < 6.7$; $-22.3 < \delta^{34}\text{S}\text{‰ VCDT} < 10.5$) that are far away from
18 the average δ values of Tortonian-Messinian gypsum from the basins of Lorca, Fortuna and
19 Sorbas ($\delta^{18}\text{O} = 13.8 \pm 2.3\text{‰}$; $\delta^{34}\text{S} = 21.3 \pm 1.0\text{‰}$) precipitated from the late Neogene
20 seawater sulfate. These low δ values of the gypsum veins clearly indicate their diagenetic
21 origin that would have resulted from sulfide oxidation with ^{18}O -depleted water. The isotopic
22 compositions of the diagenetic dolomite nodules close to the gypsum veins ($-0.7 <$
23 $\delta^{18}\text{O}\text{‰ VPDB} < 3.7$; $-11.9 < \delta^{13}\text{C}\text{‰ VPDB} < 7.3$) are indicative of their formation in
24 methane-rich fluids. In this context, the formation of sulfide is related to the bacterial sulfate
25 reduction that is associated with the anaerobic oxidation of methane. During this process,
26 pyrite coprecipitated with dolomite, either within the dolomite framework or within conduits
27 where the fluids were seeping. The pyrite oxidation occurred later during diagenesis when
28 more or less oxygenated groundwaters circulated within the fractures during the sealevel

29 drawdown of the Messinian Salinity Crisis and after the regional uplift of the sedimentary
30 deposits in relation with the Betic cordillera tectonics.

31 1. Introduction

32 The Tortonian, Messinian and lower Pliocene marls outcropping in S.E. Spain basins
33 are predominantly located in the internal zone of the Betic cordillera (Murcia, Aledo, Lorca,
34 Sorbas, Huercal Overa, Albox, Vera) or at the transition between the internal and external
35 zones (Fortuna) (Fig. 1). They contain abundant authigenic dolomite nodules. Previous
36 studies of these authigenic carbonates (Pierre and Rouchy, 2004; Pierre et al., 2002, 2015,
37 2018) have shown that they were precipitated within the marly sediments due to circulation of
38 fluids of various origin and composition that are recorded by the large variability of the
39 isotopic values ($-7.9 < \delta^{18}\text{O}\text{‰ VPDB} < 6.3$; $-35.5 < \delta^{13}\text{C}\text{‰ VPDB} < 9.8$). These authigenic
40 carbonates are thus considered as archives of the past history of fluid migration during at least
41 11 Ma. During this long period where major paleoenvironmental and tectonic changes
42 occurred in the Mediterranean domain (the successive tectonic events from the formation of
43 the Neogene basins up to their final uplift, the Messinian salinity crisis), these fluids were
44 largely modified by different processes: gas hydrate formation/dissociation, clay minerals
45 dehydration, evaporitic brines, deep-warm fluids, anaerobic oxidation of methane,
46 methanogenesis.

47 In some places the sedimentary series containing the dolomite nodules are intensely
48 faulted and the veins are often infilled with secondary gypsum (Fig. 2A). Secondary gypsum
49 may also occur around and within the dolomite nodules (Figs. 2B, C, D, E). Similar
50 occurrences of dolomite nodules related to diagenesis with methane-rich fluids have also been
51 described in many outcrops, e.g.: the Eocene of North-East Spain (Hoareau et al., 2008), the
52 late Neogene of Northern Apennines and Piedmont in Italy (Dela Pierre et al, 2010; Oppo et
53 al., 2017), the Miocene of New Zealand (Nyman et al., 2010), the Miocene of California
54 (Aiello et al., 2001). These dolomite structures are sometimes associated with secondary veins
55 of celestite, barite and calcite but never with secondary gypsum veins.

56 In the geological context of the S.E. Spain basins during Neogene, the possible
57 relationship of the secondary gypsum veins with the Tortonian-Messinian evaporites, either
58 by circulation of sulfate-rich solutions issued from dissolution of gypsum deposits or from
59 connate brines, might be questioned. The determination of the origin of the secondary
60 gypsum veins by oxygen and sulfur stable isotopes ($\delta^{18}\text{O}$ and $\delta^{34}\text{S}$) would thus provide the

61 clue to bring a better knowledge of the composition and origin of the fluids that were
62 circulating either within the fault networks or percolating through the microfractures and
63 porosity of the sediments.

64 2. Geological background

65 The Betic Cordillera constitutes the northern arm of the Betic-Rifian arcuate belt, which
66 is the westernmost part of the Alpine orogen issued from the collision of the African and
67 Eurasian plates. It is usually divided into an external zone composed of deformed Mesozoic to
68 Tertiary sediments initially deposited on the southern margin of Iberia and an Internal Zone
69 made of a pile of nappes composed of Paleozoic to Mesozoic rocks affected by different
70 degrees of metamorphism (Fig. 1). The Albox, Vera, Lorca and Murcia basins where the
71 studied samples have been collected, belong to a complex system of interconnected
72 intramontane basins that formed after the cessation of the westward drift of the Internal Zones
73 that occurred towards the end of the middle Miocene, and in relation with the development of
74 SW-NE strike-slip fault zones as the Alhama de Murcia faults which extend from Huerca
75 Overa to Alicante and the Palomares faults located in the Almeria-Vera area (Montenat et al.,
76 1987; de Larouzière et al., 1988; Sanz de Galdeano, 1990, 1992) (Fig.1). The most common
77 characteristic of these basins was the intense subsidence with high sedimentation rates during
78 the Tortonian. However, their paleogeography and sedimentary settings evolved differently
79 until the Quaternary under a complex control involving not only the variation of activity of
80 these fault systems under a predominantly compressional regime with episodes of distension
81 (Sanz de Galdeano, 1990; Sanz de Galdeano and Vera, 1992), but also their position within
82 the organisation of the Betic substrate and their proximity to the deep central Mediterranean
83 Basin. Accordingly, the major subsidence and the final uplift ending by the withdrawal of the
84 sea may differ strongly from a basin to another.

85 In the Vera and Murcia basins, which occupied the more proximal position with regard
86 to the deep Mediterranean, marine conditions persisted through the whole Tortonian until the
87 early Pliocene (Fig. 3). The Messinian Salinity Crisis impacted directly these two basins with
88 deposition of gypsum in the eastern part of the Murcia Basin (San Miguel de Salinas area) and
89 in the Vera Basin where it has been removed as a megabreccia during the final drawdown of
90 the Mediterranean sea level responsible, in the two basins, for an important erosional surface
91 at the Messinian/Zanclean transition (Montenat et al., 1976, 1977; Pierre et al., 2006; Corbí et
92 al., 2016; Caruso et al., 2020) (Fig. 3). In the Albox basin located at the SW end of the

93 Alhama de Murcia fault system, marine deposition ceased at the end of Tortonian in response
94 to tectonic uplift, the last Messinian marine deposits being known only in the nearby Huercal
95 Overa basin to the east (Guerra-Merchán and Serrano, 1993; ^[11]_{SEP}Meijninger and Vissers, 2006;
96 Pedrera et al., 2010). The Lorca basin close to the boundary with the External Zones had a
97 more complex sedimentary evolution. It underwent an earlier marine restriction during late
98 Tortonian/early Messinian responsible for the deposition of a sequence composed of silicified
99 dolostones grading upward into an organic-rich diatomite-bearing unit and finally to an
100 evaporitic (gypsum and salt) unit (Rouchy et al., 1998; Krijgsman et al., 2006; Playà et al.,
101 2000), (Figs. 2F, 3).

102 2. Material and methods

103 2.1 Gypsum veins

104 In the basins of Murcia, Lorca, Vera, Albox, as in most of the other basins, the
105 dolomite nodules are associated to secondary gypsum that exhibits a wide range of size,
106 morphologies and distribution through the marls and the nodules. These gypsum occurrences
107 commonly appear as veins cm to dm in thickness and up to several meters of length that cut
108 the marls perpendicularly, obliquely or more or less conformably to the bedding of the host
109 sediment and making sometimes a dense network (Fig. 2A). The gypsum veins may also cut
110 irregularly the nodules themselves or form an external envelope around them (Figs. 2B, C, D).
111 Locally, a nodule is crossed by a polygonal network of fissures looking like septarian cracks
112 (Fig. 2B). The gypsum may also display micronodular shapes disseminated within the
113 carbonate nodules or aggregates of larger selenitic crystals, several cm in size filling the
114 central part of nodules (Fig. 2E). In the Lorca basin, the stratigraphic interval containing the
115 nodules ends with a succession of well-stratified beds several dm-thick of opal-CT rich
116 dolostones intercalated with gypsum veins associated with alunite $[(\text{Na},\text{K}) \text{Al}_3 (\text{SO}_4)_2 (\text{OH})_6]$
117 occurrences (Fig. 2F).

118 Eight gypsum samples were collected in the marly deposits that contain also abundant
119 authigenic dolomite nodules, from the late Neogene (Late Tortonian to early Pliocene) of the
120 basins of Lorca, Albox, Murcia and Vera (Table 1). In the Murcia Basin, two sets of samples
121 were collected in the early/middle Tortonian (ES 16.125, ES 16.126, ES 16.127) and near the
122 Tortonian/Messinian transition (ES 17.45, ES 17.46, ES 17.64) along the road between
123 Cabezo de la Plata and Los Ginovinos (Fig. 3). In the Vera basin, the samples come from the
124 early Pliocene (Zanclean) marls located near the Vera graveyard, and at Albox from

125 Tortonian levels in the Olleres outcrops (Fig. 3). In the Lorca Basin, the samples were taken
126 into interval of dolomitic nodules and cherty dolostones and in the overlying organic-rich
127 deposits of the diatomite-bearing unit that crop out in the La Serrata section at the transition
128 between the Tortonian marine marls and the massive gypsum unit (Fig. 3). The gypsum
129 samples generally exhibit fibrous satin-spar lithofacies where the gypsum crystals are oriented
130 perpendicular to the walls of the veins (Rouchy et al., 1994). This facies is characteristic of
131 secondary precipitation of gypsum from circulation of saturated solutions in open fractures.

132 Prior to stable isotope analyses, gypsum was converted to BaSO₄ following the
133 classical procedure described by Longinelli and Craig (1967). Gypsum was dissolved in
134 acidified deionized water; the resulting solution was then filtered (0.8 μm), heated and barium
135 sulfate was precipitated by adding a 1N-BaCl₂ solution. The BaSO₄ precipitate was finally
136 filtered, rinsed with deionized water and dried in an oven at 90°C. Oxygen isotope analyses
137 were conducted on a ThermoScientific Delta V Advantage IRMS at LOCEAN, Sorbonne
138 Université, Paris. The IRMS is coupled with a Conflo IV interface and Flash-EA2000
139 (Thermal Conversion Elemental Analyzer Unit) where pyrolysis (at 1400°C) and combustion
140 (at 1050°C) produce CO and SO₂ for oxygen and sulfur isotopic analyses, respectively. For
141 pyrolysis, about 150μg of BaSO₄ plus 1 mg of AgCl (Boschetti and Iacumin, 2005) are
142 weighted and pressed in a silver capsule. For combustion, about 250μg of BaSO₄ plus 1 mg
143 of V₂O₅ are weighted and pressed in a tin capsule.

144 The δ¹⁸O and δ³⁴S values were calibrated using the IAEA international references
145 [(NBS 127 : δ¹⁸O = +8.5±0.2‰ VSMOW, Boschetti and Iacumin, 2005; δ³⁴S = +21.2
146 ±0.2‰ VCDT, Halas and Szaran, 2001), (S1 : δ³⁴S = -0.3‰ VCDT), (S2 : δ³⁴S = +22.7‰
147 VCDT), (S3 : δ³⁴S = -32.3‰ VCDT)].

148 The oxygen and sulfur isotopic compositions are expressed in the δ notation :

149
$$\delta = (R_{\text{sample}}/R_{\text{reference}} - 1) \times 1000$$

150 where R = ¹⁸O/¹⁶O or ³⁴S/³²S in the sample and in the reference, using the international
151 reference VSMOW (Vienna Standard Mean Ocean Water) and VCDT (Vienna Cañon Diablo
152 Troilite) for δ¹⁸O and δ³⁴S measurements respectively. The analytical precision is ±0.2‰ for
153 δ¹⁸O and δ³⁴S measurements.

154 2.2 Dolomite nodules

155 The dolomite nodules associated to the gypsum veins exhibit the common facies of
156 rounded to elongated massive compact bodies, which diameter generally of a few decimeters
157 may reach up to more than one meter (Figs. 2 B, C, D, E). The bulk mineralogy of the nodules
158 was determined by XRD and was completed by SEM observations of the morphology and
159 composition of the crystals (Fig. 4).

160 The oxygen and carbon isotopic compositions of dolomites were determined on the
161 bulk powdered samples. A fraction of about 100 to 200 μg was reacted at 90°C with
162 orthophosphoric acid using a multicarb system coupled with a dual inlet isotopic ratio mass
163 spectrometer (DI IRMS) VG Isoprime. The $\delta^{18}\text{O}$ values reported in Table 1 were corrected for
164 the phosphoric acid fractionation at 90°C (Rosenbaum and Shepard (1986). The analytical
165 precision 2σ is 0.01‰ and the reproducibility is $\pm 0.2\text{‰}$ for both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values.

166 The oxygen and carbon isotopic compositions are expressed in the δ notation where $R =$
167 $^{18}\text{O}/^{16}\text{O}$ or $^{13}\text{C}/^{12}\text{C}$ in the sample and in the reference, using the international reference VPDB
168 (Vienna Peedee Belemnite) defined by Craig (1957) and revised by Gonfiantini et al.
169 (1995).

170 3. Results

171 3.1 Gypsum veins

172 The microscopic SEM observations of gypsum veins show their internal fabrics where
173 the gypsum crystals exhibit generally platy and fibrous habits (Figs. 4A, B) and include
174 numerous sedimentary particles (detrital silicates, coccolites, calcite and dolomite aggregates)
175 that were cemented during gypsum precipitation. The sedimentary inclusions also contain
176 previous pyrite structures of framboids and octahedra, that are still present but as oxidized Fe-
177 products (Figs. 4C, D, E, F). These occurrences confirm that bacterial sulfate reduction was
178 responsible for pyrite formation during early diagenesis when methane-rich fluids circulated
179 within the sedimentary matrix. Further circulation of oxygenated waters through the
180 sedimentary deposits led to pyrite oxidation that was converted to Fe-oxy-hydroxides and
181 produced sulfate-rich acid solutions from which carbonates were dissolved and gypsum was
182 precipitated. Calcite and dolomite dissolution is evidenced by numerous holes within the
183 crystals (Fig. 4F)

184 The $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of the gypsum veins (Table 1; Fig. 5) vary in large ranges (-
185 $2.2 < \delta^{18}\text{O}\text{‰ VSMOW} < 6.7$; $-22.3 < \delta^{34}\text{S}\text{‰ VCDT} < 10.5$). The highest $\delta^{34}\text{S}$ value is
186 measured in the gypsum of Lorca that is associated with alunite. However, all these values are
187 much lower than those of the Tortonian-Messinian marine gypsum from the SE Spain basins
188 of Sorbas, Lorca and Fortuna ($\delta^{18}\text{O} = 13.8 \pm 2.3\text{‰ VSMOW}$; $\delta^{34}\text{S} = 21.3 \pm 1.0\text{‰ VCDT}$;
189 Evans et al., 2015; Garcia-Veigas et al., 2019).

190 3.2 Dolomite nodules

191 The SEM observations (Figs. 6A, B, C, D) reveal that the dolomite rhombs are always
192 associated with pyrite (mostly as framboids) that may be preserved or oxidized. In some cases,
193 dolomite rhombs show numerous cavities that correspond probably to dissolved pyrite that
194 was included within the dolomite crystals (Fig. 6B).

195 The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the dolomite nodules (Table 1, Fig. 7) vary also in wide
196 ranges ($-0.7 < \delta^{18}\text{O}\text{‰ VPDB} < 3.7$; $-11.9 < \delta^{13}\text{C}\text{‰ VPDB} < 7.3$) that display distinct groups
197 between Vera (with the lowest $\delta^{13}\text{C}$ values), Murcia and Lorca (with the lowest $\delta^{18}\text{O}$ values
198 and the highest $\delta^{13}\text{C}$ values) and Albox (with the highest $\delta^{18}\text{O}$ values).

199 4. Discussion

200 The precipitation of the authigenic minerals (dolomite, pyrite, secondary gypsum,
201 alunite, silica) was controlled by biogeochemical reactions related to complex processes
202 where reducing and oxidizing conditions were occurring at different stages of diagenesis (Fig.
203 8). The isotopic compositions recorded by dolomite and gypsum are indicative of important
204 variations of the composition of the diagenetic fluids that were involved during their
205 precipitation.

206 4.1 The biogeochemical reactions under anoxic conditions

207 4.1.1 Dolomite diagenesis

208 The production of dissolved inorganic carbon (DIC) in pore fluids occurs when anoxic
209 conditions in organic-rich sediments enhance microbial activity, which controls also the
210 cycling of other elements as sulfur and iron (Konhauser, 2007). Because organic matter is
211 depleted in ^{13}C ($\delta^{13}\text{C} \sim -25\text{‰}$), the products of its degradation (biogenic and thermogenic) are
212 also depleted in ^{13}C , especially the most common gas product, CH_4 , which has $\delta^{13}\text{C}$ values

213 varying between -110 and -30‰ (Claypool and Threlkeld, 1983; Whiticar, 1999). During
214 methanogenesis, there is a large isotopic fractionation between the two by-products CH₄ and
215 CO₂, which gives ¹³C-poor CH₄ and ¹³C-rich CO₂ (Whiticar and Faber, 1986; Alperin et al.,
216 1988). In such context, ¹³C-depleted DIC is released during microbial reduction of sulfate
217 with methane (or heavier hydrocarbons), whereas ¹³C-rich DIC is produced during
218 methanogenesis (Fig. 8). The recent review by Meister and Reyes (2019) of the carbon
219 isotope variations in marine environments summarizes the current knowledge of authigenic
220 carbonate precipitation in relation with the microbial processes related to sulfate reduction,
221 AOM and methanogenesis. Moreover, Torres et al. (2020) add complementary information on
222 the major role of silicate weathering for authigenic carbonate precipitation in anoxic
223 environments.

224 The δ¹³C values of the authigenic dolomites associated with the gypsum veins from
225 the Neogene of Spain range between -11.9 and 7.3‰, and they thus display these typical
226 characteristics of ¹³C-poor /¹³C-rich methane-related carbonates. Moreover, as shown by
227 Chatterjee et al (2011), at the Sulfate Methane Transition Zone (SMTZ) where authigenic
228 dolomite precipitates, the upward flux of ¹³C-rich DIC issued from the methanogenesis zone
229 modulates the relative contribution of ¹³C-poor DIC derived from Anaerobic Oxidation of
230 Methane (AOM), thus supporting the large spatial and temporal variability of δ¹³C values of
231 the authigenic dolomites in these environments.

232 The oxygen isotopic fractionation factor between dolomite and water depends on
233 temperature ($1000 \ln \alpha^{18}\text{O} \text{ dolomite-water} = 2.73 \times 10^6 \text{ T}^{-2} + 0.26$; Vasconcelos et al., 2005).
234 This equation is used to estimate the temperature range of 15.6 to 40.3°C (Table 1) for the
235 authigenic dolomites that would have precipitated at equilibrium with seawater-derived fluids
236 characterized by δ¹⁸O values ranging from 0.8 to 1.6‰, which are the values measured in the
237 present-day Western Mediterranean (Pierre, 1999). The estimated equilibrium temperatures of
238 dolomites differ in the studied basins: they are the lowest in Albox (15.6 to 24.4°C),
239 intermediate in Vera (19.6 to 28.5°C) and the highest in Murcia and Lorca (25.6 to 40.3°C).
240 Compared to the present-day Mediterranean bottom water temperature (~13°C), most of the
241 temperature estimations are much warmer, thus indicating that the diagenetic fluids were
242 issued from moderate to relatively great burial depths (up to 1 km for a normal geothermal
243 gradient).

244 4.1.2 Bacterial sulfate reduction

245 The production of hydrogen sulphide during bacterial sulfate reduction promotes the
246 precipitation of sulfide minerals, generally as pyrite, which explains the close association of
247 authigenic dolomite and pyrite that is observed in the dolomite nodules. During the sulfate
248 reduction reaction, there is a large sulfur isotopic fractionation between the produced sulfide
249 and the remaining sulfate that ranges from -46 to -77‰ in natural environments (Brunner and
250 Bernasconi, 2005; Canfield et al., 2010; Meister et al., 2019; Rees, 1973; Rudnicki et al.,
251 2001; Sim et al. 2011; Wortmann et al., 2001). As a result, if the initial source of dissolved
252 sulfate is from seawater, the produced sulfide would have very negative $\delta^{34}\text{S}$ values whereas
253 the residual sulfate would exhibit $\delta^{34}\text{S}$ values higher than the seawater source. The rate of the
254 sulfate reduction reaction has a critical importance in controlling the ratio of the enrichment
255 factors $\epsilon^{34}\text{S}/\epsilon^{18}\text{O}$ in the residual sulfate; it is generally close to 2.5 (Mizutani and Rafter,
256 1973) but it may reach 4 when the amount of remaining sulfate becomes very low (Böttcher et
257 al., 1998; Brunner et al., 2005).

258 The $\delta^{34}\text{S}$ values of the gypsum veins from the Neogene marls of Spain are depleted by
259 10.5 to 43.3‰ relative to evaporitic gypsum precipitated from the Cenozoic seawater sulfate
260 (Evans et al., 2015; Garcia-Veigas et al., 2019); they are thus clearly issued from sulfide that
261 was produced by the bacterial reduction of the initial source of seawater sulfate. Sulfide was
262 probably precipitated as pyrite both within the dolomite framework and in conduits and
263 fractures where fluids circulated in the sediments.

264 4.2 The biogeochemical reactions under oxic conditions

265 Under oxic conditions, pyrite is rapidly oxidized as iron oxy-hydroxides and sulfuric
266 acid that reacts with the carbonate and clay minerals of the sedimentary matrix to produce
267 authigenic sulfate and silica minerals (Fig. 8). Gypsum is the most important product of this
268 oxidation process and it may be associated with alunite and silica. The association of
269 authigenic natroalunite, anhydrite and silica was previously discovered in the middle Miocene
270 evaporites from the Gulf of Suez (Rouchy and Pierre, 1987). Authigenic gypsum was also
271 described in active methane seeps of the West African margin and of the Sea of Marmara
272 where it occurred as euhedral crystals disseminated in the organic-rich sediment in association
273 with methane-derived authigenic carbonates (Crémière et al., 2012; Pierre, 2017).

274 The sulfur isotope fractionation during pyrite oxidation is close to zero (Nakai and
275 Jensen, 1964; Mizutani and Rafter, 1969), so that the $\delta^{34}\text{S}$ values of gypsum are quite similar
276 to those of the pyrite from which they are derived.

277 The oxidation of pyrite occurs either during early diagenesis with oxygen-rich
278 seawater, or later when the deposits are uplifted and flushed by groundwaters and surficial
279 meteoric waters. Because the oxidation of pyrite uses both oxygen of water and molecular
280 dissolved oxygen to produce aqueous sulfate, the relative contribution of these two sources
281 control the oxygen isotopic composition of sulfate. Van Everdingen and Krouse (1965) have
282 defined the following equation that relies the different parameters of the reaction.

$$283 \delta^{18}\text{O}_{\text{SO}_4\text{-ox}} = f (\delta^{18}\text{O}_{\text{water}} + \epsilon_{\text{water}}) + (1-f) (\delta^{18}\text{O}_{\text{O}_2} + \epsilon_{\text{O}_2})$$

284 The enrichment factors during this process ($\epsilon_{\text{water}} = 4.1\text{‰}$, $\epsilon_{\text{O}_2} = -11.2\text{‰}$) were estimated by
285 Lloyd (1967) and Mizutani and Rafter (1969), later revised by Taylor et al (1987). Most
286 experiments have shown that water was the main source of oxygen during the oxidation of
287 sulfide (about 66% for Taylor et al, 1987; from 85 to 92% for Balci et al, 2007). These results
288 indicate that the value of f would range between 1 and ~0.7.

289 For the gypsum veins of SE Spain, the $\delta^{18}\text{O}$ values of water used during pyrite
290 oxidation were estimated using the $\delta^{18}\text{O}$ value of molecular oxygen (23.5‰ VSMOW;
291 Kroopnick and Craig, 1972) and the fraction f of oxygen of water that would range between 1
292 and 0.66. Moreover, it is necessary to consider the isotopic fractionation between the aqueous
293 and solid sulfate ($\epsilon^{18}\text{O} = 3.5\text{‰}$, Lloyd, 1968; $\epsilon^{34}\text{S} = 1.7\text{‰}$, Thode and Monster, 1965), which
294 is the case when gypsum precipitation occurs from gypsum-saturated solutions in open system
295 conditions. These fractionation factors measured by Van Driessche et al. (2016) from gypsum
296 precipitation experiments display significant variations above 20°C and at low salinities, but
297 they are close to those proposed by Lloyd and Thode and Monster below 20°C both in low
298 and high salinities. The results of these estimations are reported in Table 1 and Fig. 9. The
299 $\delta^{18}\text{O}$ values of water assumed for pyrite oxidation range between -9.8 to -0.9 when oxygen is
300 issued only from water, and from -19.1 to -5.6 when oxygen is issued both from water and
301 dissolved oxygen. Such ^{18}O -depleted values are characteristic of meteoric waters. However
302 only some of them would be compatible with the regional hydroclimatic context from SE
303 Spain where the average present-day $\delta^{18}\text{O}$ values of the local meteoric waters vary in the
304 range ~ -6.0‰ in Murcia to ~-4‰ in Almeria (Araguas-Araguas and Diaz Teijeiro, 2005).

305 Lower $\delta^{18}\text{O}$ values of meteoric waters would have been recorded during glacial times due the
306 global decrease of temperatures. Using the Dansgaard equation (1964) for an average 5°C
307 decrease of temperature during glacial times, the $\delta^{18}\text{O}$ values of meteoric waters can be
308 estimated to have ranged from -10.5 to -8.5‰. Finally the few $\delta^{18}\text{O}$ values of water that are
309 higher than the present-day meteoric waters but lower than the present-day seawater, could
310 correspond to mixtures between these two water sources.

311 Overall, these results exclude any relationship of the gypsum veins with the Tortonian-
312 Messinian evaporites. They also prove that the gypsum veins were not produced during early
313 diagenetic pyrite oxidation with seawater, but they clearly indicate late diagenetic oxidation
314 with waters of meteoric origin. The pyrite oxidation process was following the final tectonic
315 uplift of the sedimentary deposits that occurred differently according to the different basins
316 but was completed in the late Pliocene. These deposits were drained with groundwaters more
317 or less oxygenated leading to the precipitation of the gypsum veins along circulation
318 pathways of gypsum-saturated solutions.

319 5. Conclusion

320 Secondary gypsum veins in sedimentary deposits led often to questioning about their
321 origin. They might be related to circulation of gypsum-saturated solutions issued from
322 connate evaporitic brines, dissolution of sulfate evaporite deposits, or oxidation of sulfide ore
323 deposits (Dogramaci et al., 2017). In the present study the oxygen and sulfur isotopic
324 compositions of gypsum were used to characterize the source of sulfate and to replace the
325 diagenetic processes in the sedimentary and tectonic context during the Neogene in SE Spain.
326 The gypsum veins present in the Tortonian, Messinian and Pliocene marls are the ultimate
327 products of the complex history of these basins during this period. This history was marked
328 by the important restriction of the marine environment that caused the deposition of organic-
329 rich sediments, with high sedimentation rates, leading further to intense methanogenesis,
330 responsible of the formation of methane-derived dolomites associated with sulfide minerals
331 (pyrite). The circulation of oxygenated groundwaters in the sedimentary series was
332 responsible for the oxidation of pyrite that was precipitating gypsum in veins networks. This
333 occurred in a first stage of the sea-level drawdown during the Messinian salinity crisis and
334 later after the MSC due to the progressive uplift of the Betic cordillera.

335

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341 Conflict of interest

342 The authors declare that there is no conflict interest with third parties.

343

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532

533 Figure captions

534 Figure 1 : Schematic geological map of the SE Spain. Location of the sampling sites.

535 Figure 2 : Field views of the dolomite nodules and gypsum veins from the Neogene marls of
536 SE Spain. A : Dense network of gypsum veins crossing the lower Pliocene deposits in the
537 Vera Basin. B : dolomite nodule with internal veins of microcrystalline gypsum , Vera Basin ;
538 C : Dolomite nodule surrounded by fibrous gypsum layer, Vera Basin. D : Group of dolomite
539 nodules surrounded by fibrous gypsum layer and within marls crossed by gypsum veins,
540 Albox Basin. E : mega-nodules of dolomite crossed by veins of fibrous gypsum with
541 aggregates of and large selenitic crystals filling a central cavity (arrow), Murcia Basin. F :
542 View of the lower part of the diatomite-bearing unit composed of alternating diatomites,
543 siltstones, and dolomitic carbonate layers with gypsum veins (arrows), and containing alunite
544 nodules, Lorca Basin.

545 Figure 3 : Simplified lithological successions of the Neogene basins of Murcia, Vera, Albox
546 and Lorca in SE Spain where the studied samples have been collected.

547 Figure 4 : Scanning Electron Microscope observations of the microfacies of the gypsum veins
548 from the Neogene marls of SE Spain. A - Sample ES16-127 (Murcia Basin) : Fibrous layers
549 of gypsum with various sedimentary particles cemented and intercalated between the gypsum
550 layers. B - Sample ES16-36 (Vera Basin) : Palisadic layers of gypsum with intercalations of
551 layers of sedimentary particles. C - Sample ES16-22 (Vera Basin) : Group of pyrite (now
552 oxidized) framboids enveloped by silicate particles. D - Sample ES16-36 (Vera Basin):
553 Inclusion of sediment with pyrite (now oxidized) framboids and octahedrons cemented by
554 gypsum. E - Sample ES16-36 (Vera Basin): close-up of a group of pyrite octahedrons. F -
555 Sample ES16-63 (Albox Basin): Pyrite (now oxidized) framboids and calcite crystals with
556 numerous holes of dissolution.

557 Figure 5 : Oxygen and sulfur isotope composition of the gypsum veins from the Neogene
558 marls of SE Spain. The range of the δ values of Tortonian-Messinian evaporitic gypsum from
559 the Lorca, Sorbas and Fortuna basins (Evans et al., 2015; Garcia-Veigas et al., 2019).

560 Figure 6 : Scanning Electron Microscope observations of the microfacies of the dolomite
561 nodules associated with the gypsum veins. A - Sample ES17-58 (Murcia Basin): Group of
562 framboids of pyrite (mostly preserved) within the microcrystalline dolomite matrix containing
563 large silicate particles. B - Sample ES16-13 (Vera Basin): Dolomite rhombs with numerous
564 dissolution holes; small isolated pyrite crystals and one framboid are disseminated within the

565 matrix. C - Sample ES16-58 (Albox Basin): Group of framboids and isolated crystals of
566 pyrite (mostly preserved) within the microcrystalline dolomite matrix. D - Sample ES-
567 62 (Albox Basin): Microcrystalline dolomite matrix containing numerous silicate particles
568 and crossed by a vein filled with framboids of pyrite (now mostly oxidized).

569 Figure 7 : Oxygen and carbon isotope composition of the dolomite of the nodules associated
570 with the gypsum veins from the Neogene marls of SE Spain.

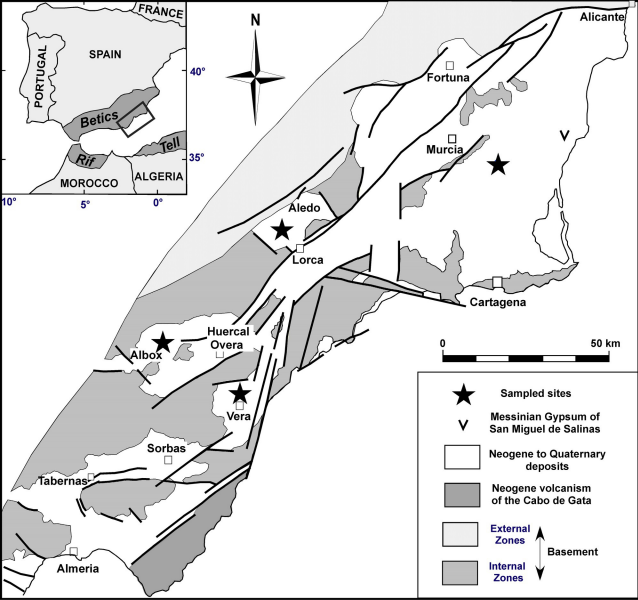
571 Figure 8 : Sequence of the biogeochemical reactions leading to the diagenetic minerals
572 formation.

573 Figure 9 : Estimation of the $\delta^{18}\text{O}$ value of the water of oxidation of pyrite deduced from the
574 $\delta^{18}\text{O}$ value of gypsum. The calculation assumes gypsum precipitation in open system
575 conditions, and pyrite oxidation with only water oxygen ($f = 1$) and with water oxygen ($f =$
576 0.66) and molecular oxygen. The ranges of $\delta^{18}\text{O}$ values of local meteoric waters from SE
577 Spain are indicated for the present-day and extrapolated for glacial periods. The present-day
578 range of $\delta^{18}\text{O}$ values of the West Mediterranean seawater is also given for information.

579

580 Table caption

581 Table 1 : Short description and location of the gypsum veins close to the dolomite nodules
582 sampled in the Vera, Albox, Murcia and Lorca Basins. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of dolomite
583 and $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ values of gypsum are reported in this table. The equilibrium temperatures
584 of dolomite have been estimated for two $\delta^{18}\text{O}$ values of seawater (0.8 and 1.6‰). The $\delta^{18}\text{O}$
585 values of the water assumed for pyrite oxidation are estimated for open system conditions
586 with two values of the fraction f of water (1 and 0.66).

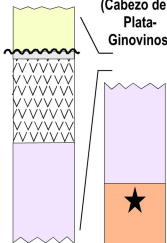




MURCIA

(San Miguel de Salinas)

(Cabezo de la Plata-Ginovinos)



VERA

(Graveyard)



ALBOX

(Olleres)



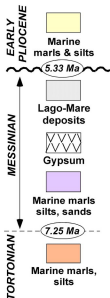
200 m

LORCA

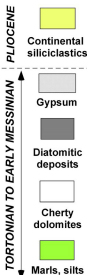
(La Serrata)



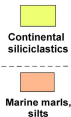
MURCIA & VERA BASINS



LORCA BASIN



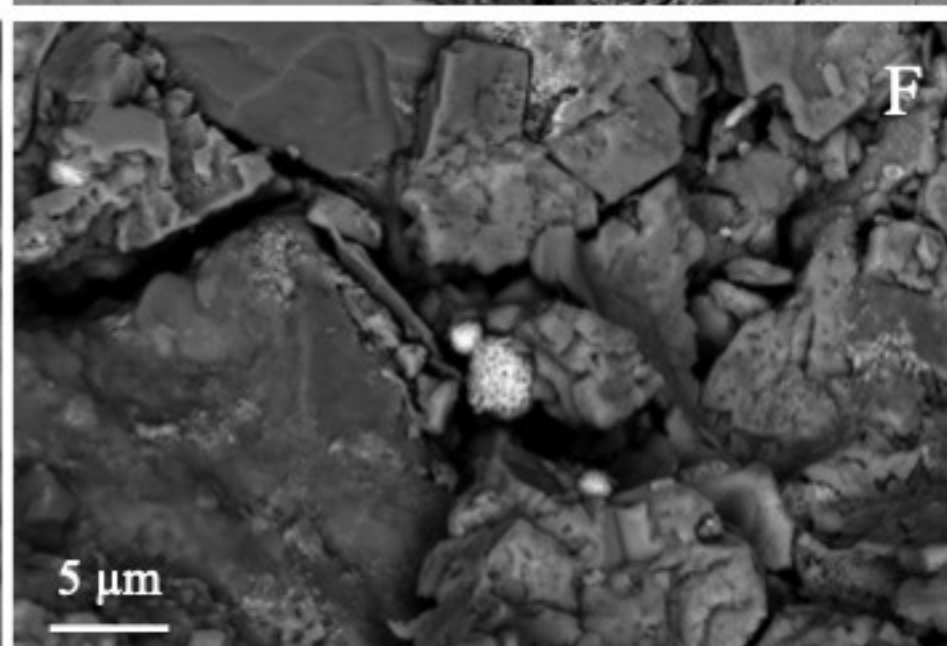
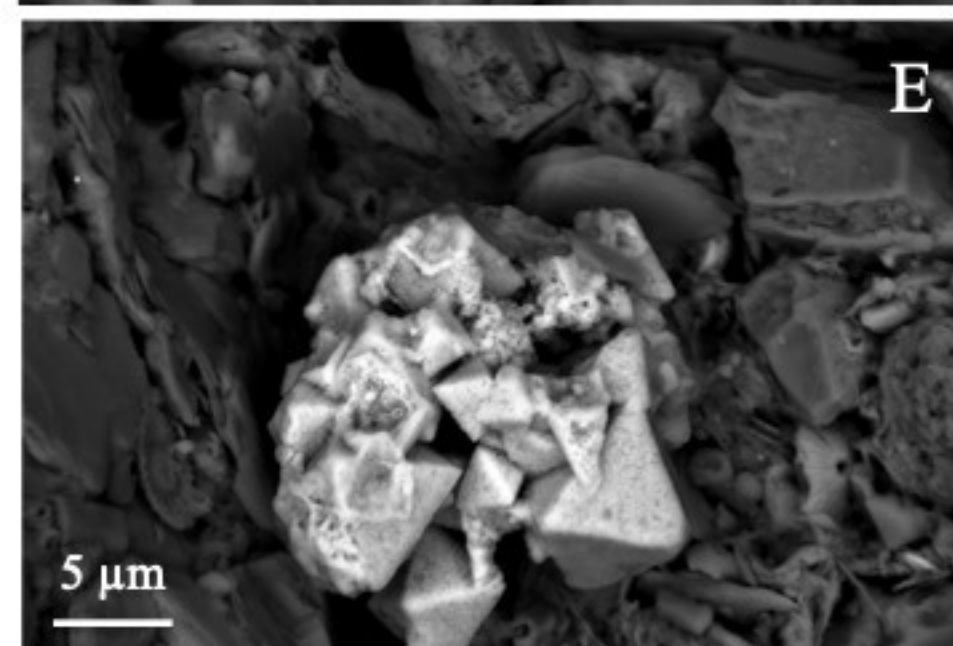
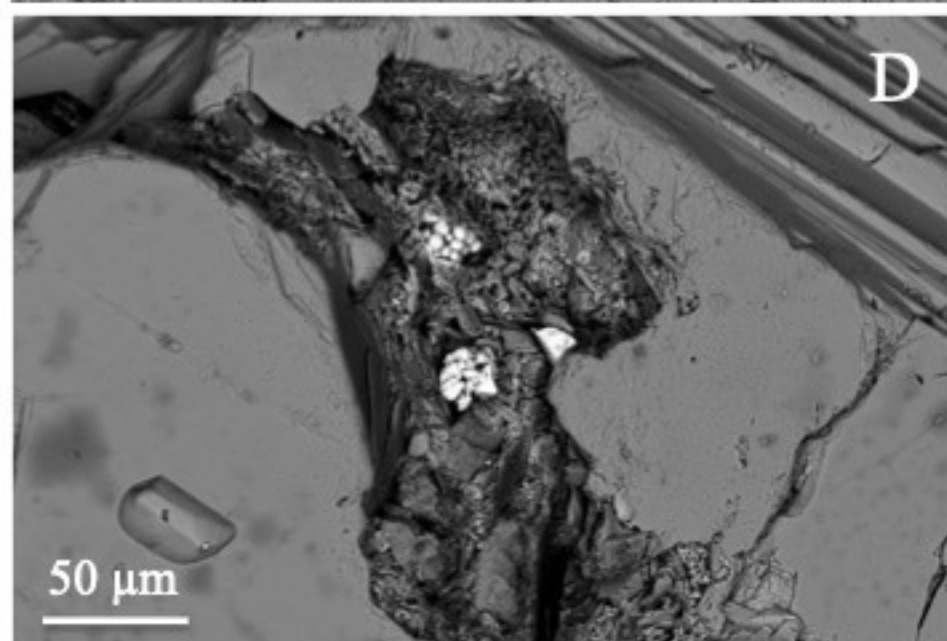
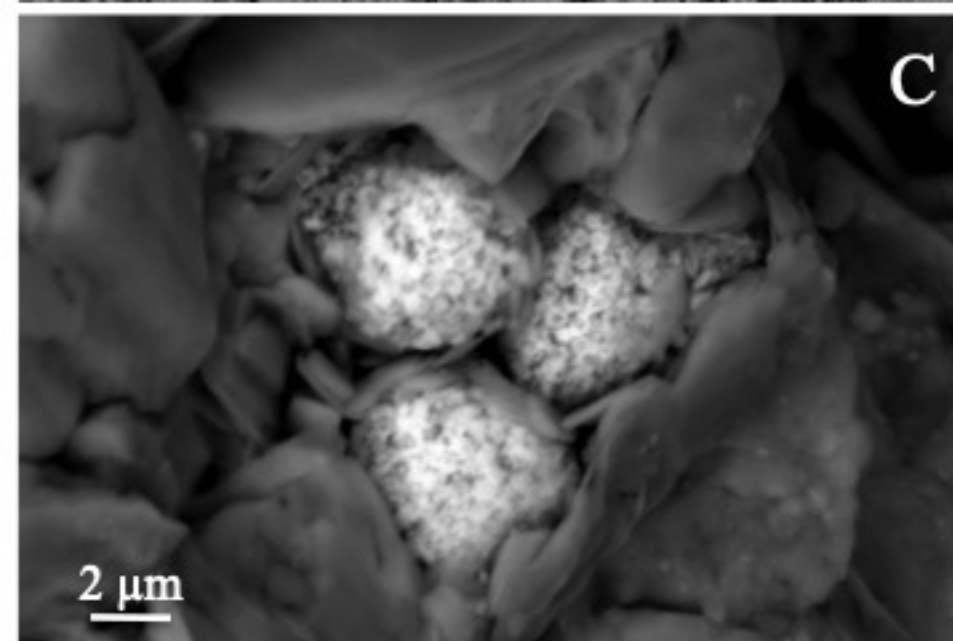
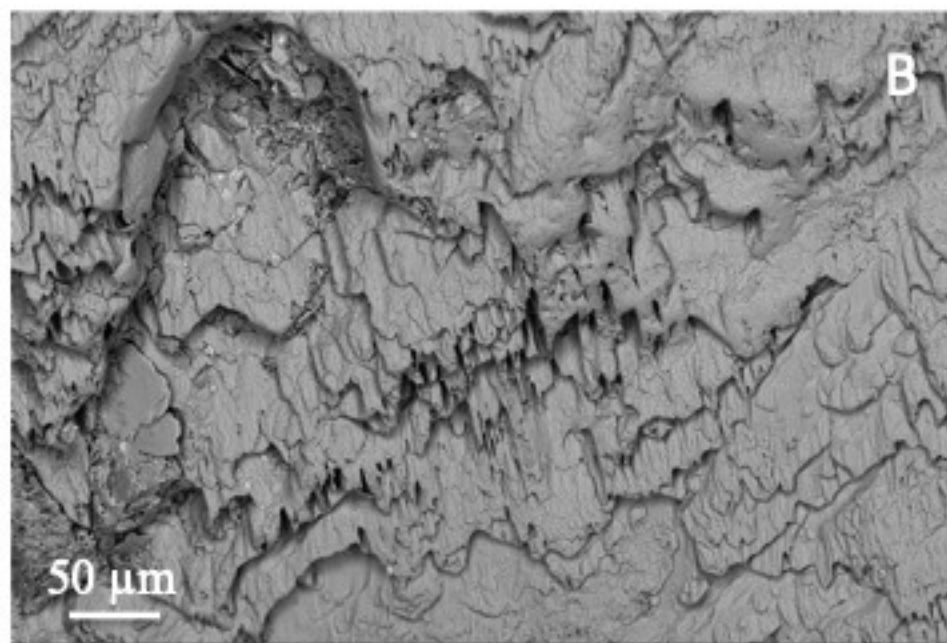
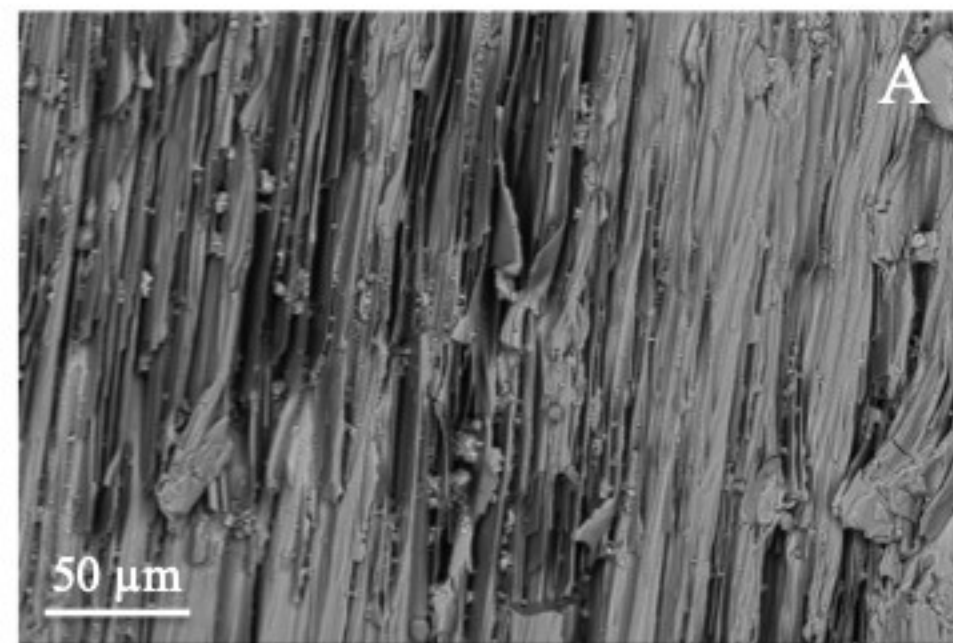
ALBOX BASIN

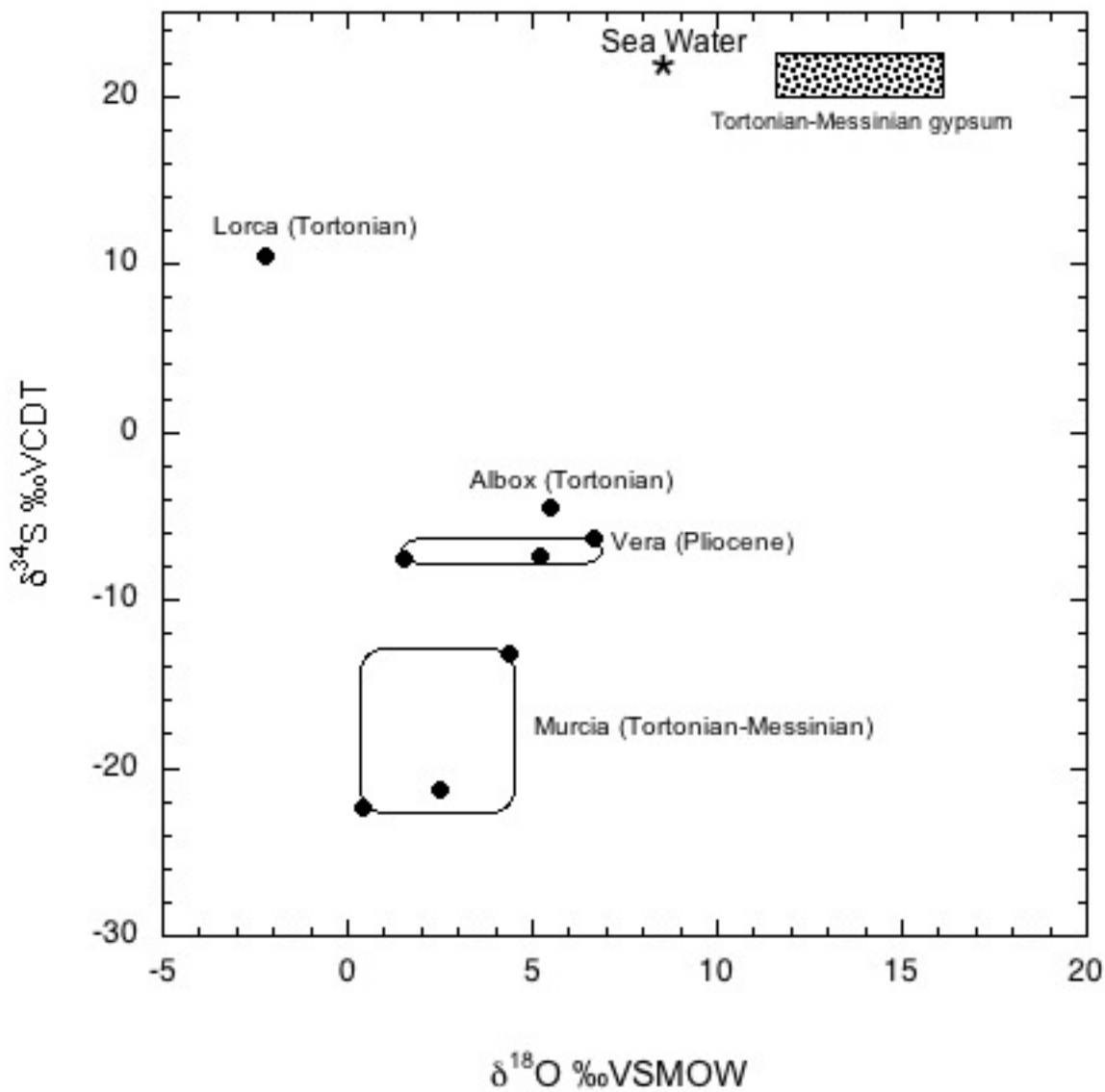


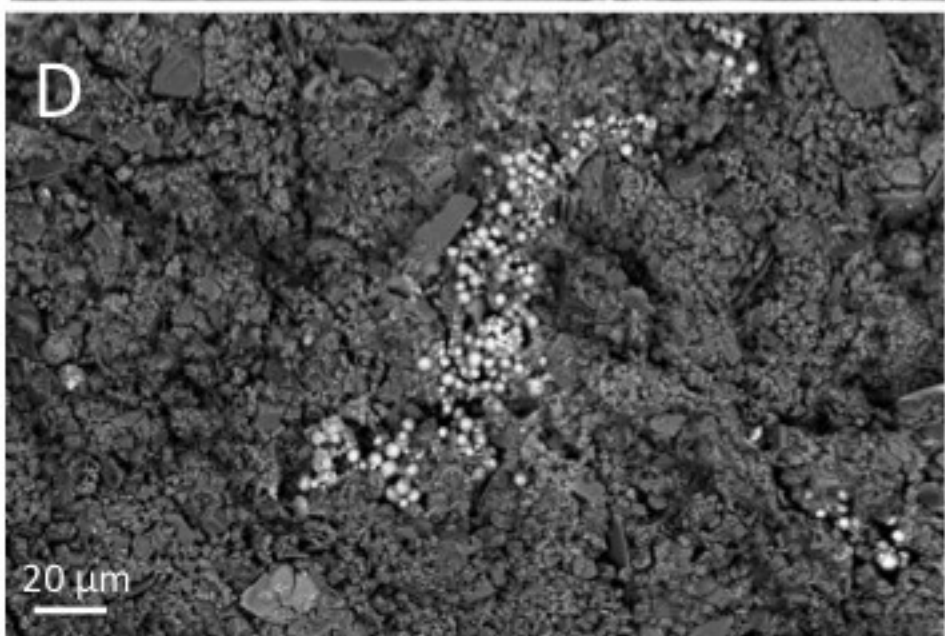
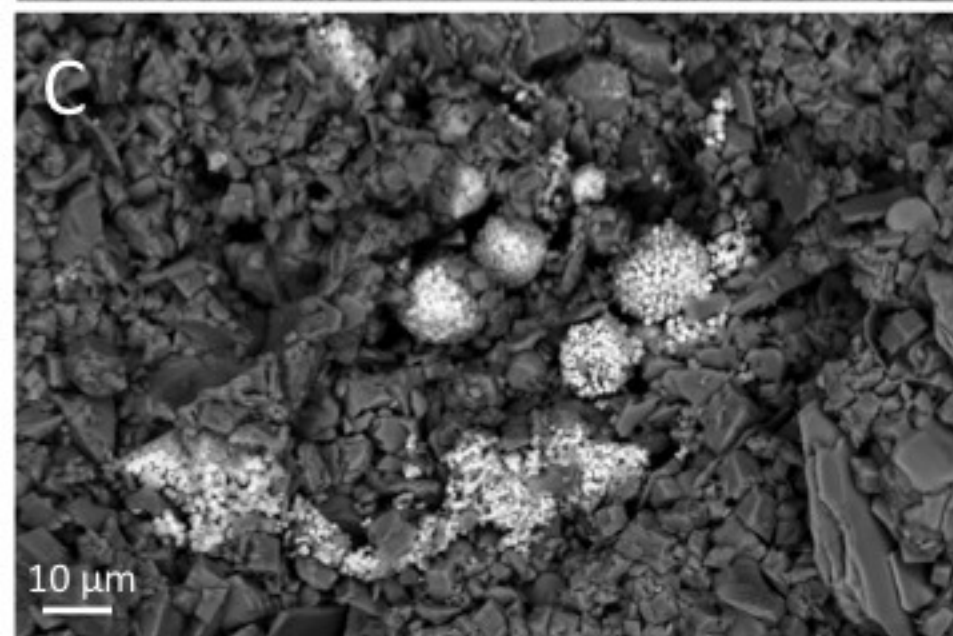
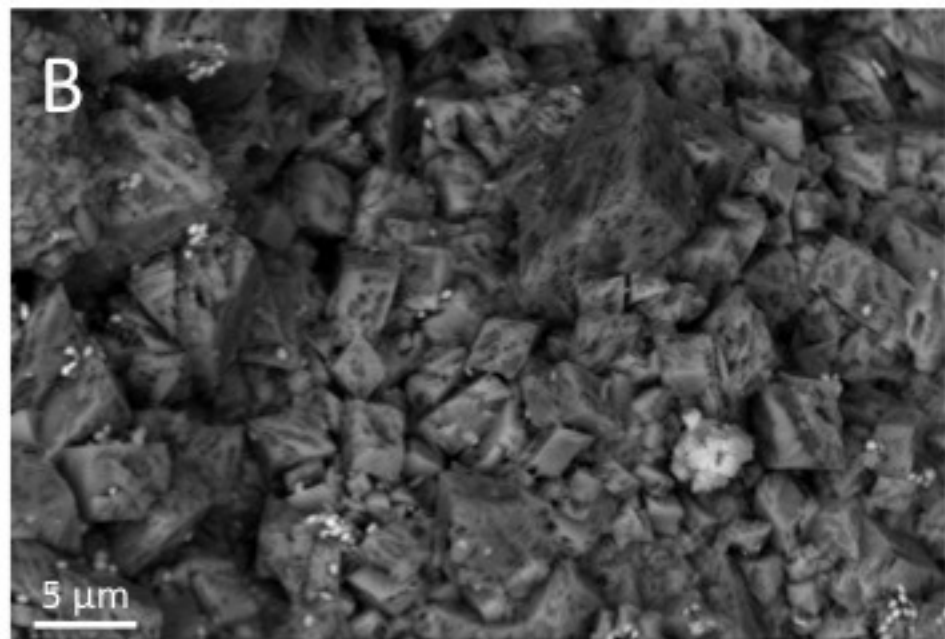
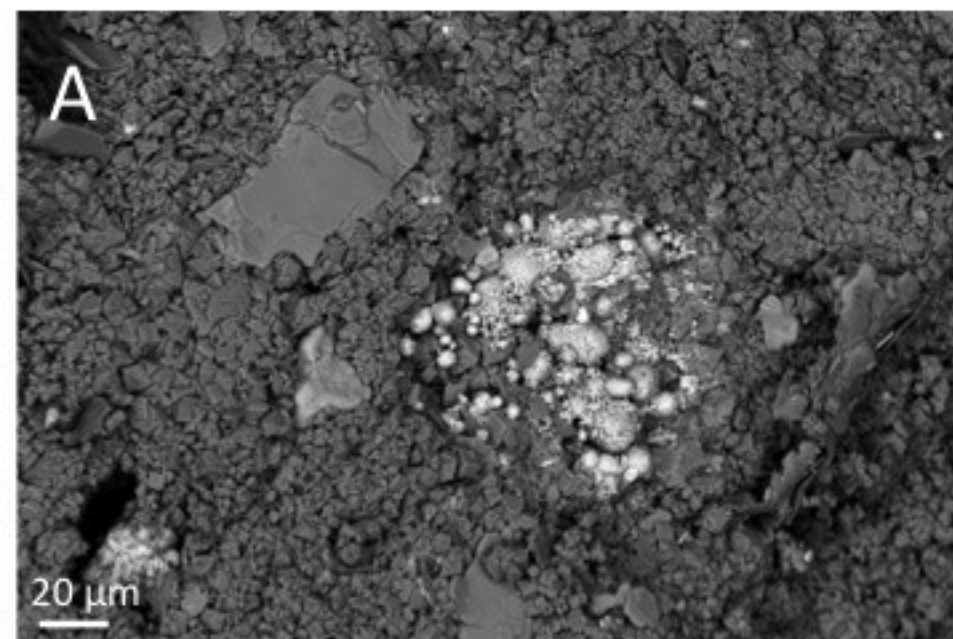
★
Sampled sites

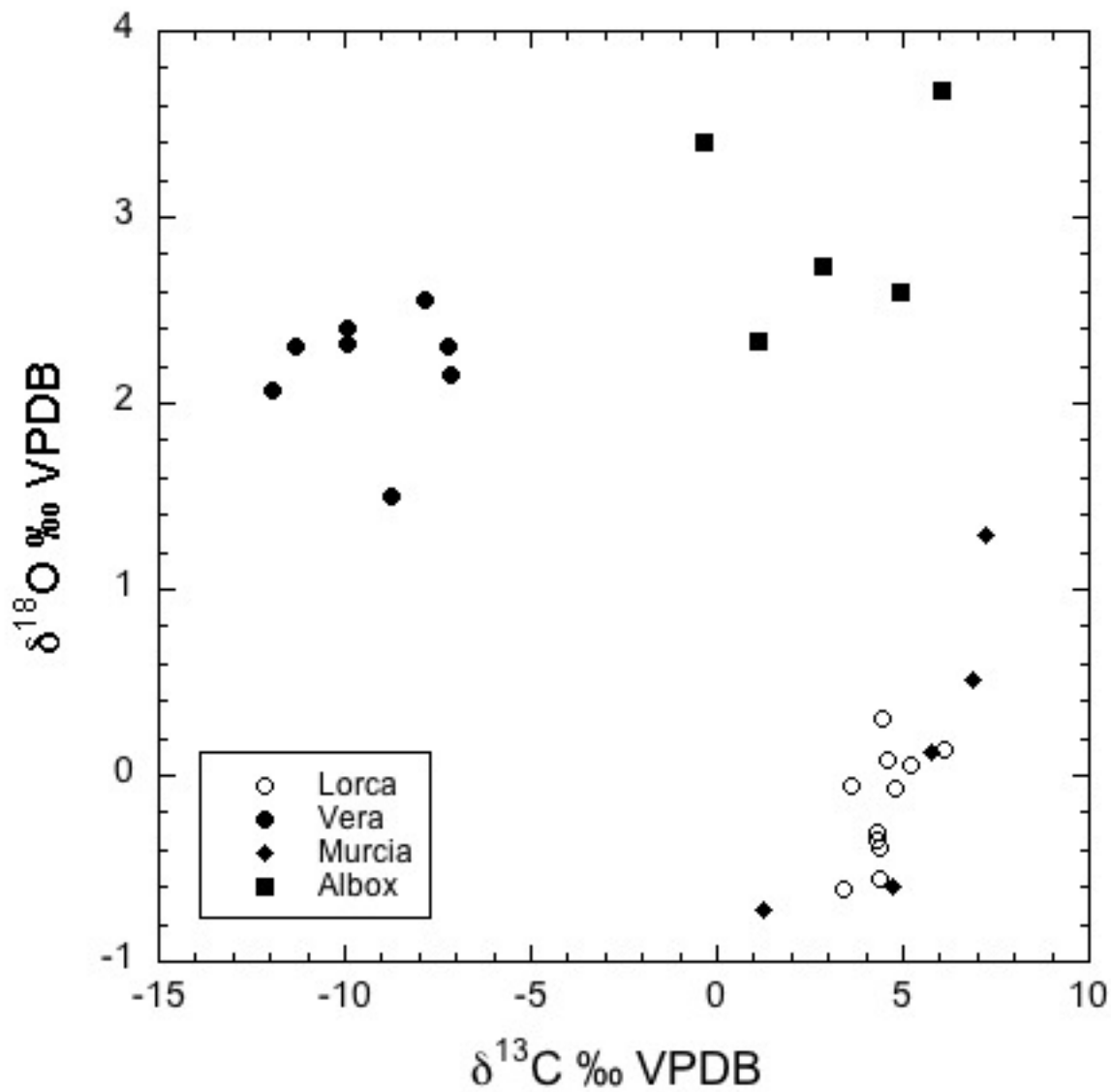
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Messinian erosional surface







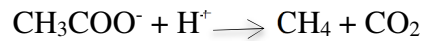




1) Bacterial reduction of sulfate coupled to Anaerobic Oxidation of Methane (AOM)



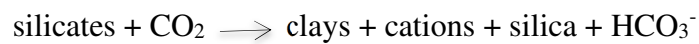
2) Methanogenesis



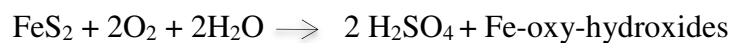
3) Methanogenesis - CO<sub>2</sub> reduction



4) Silicate weathering (with CO<sub>2</sub> produced during methanogenesis)



5) Oxidation of pyrite : sulfuric acid production

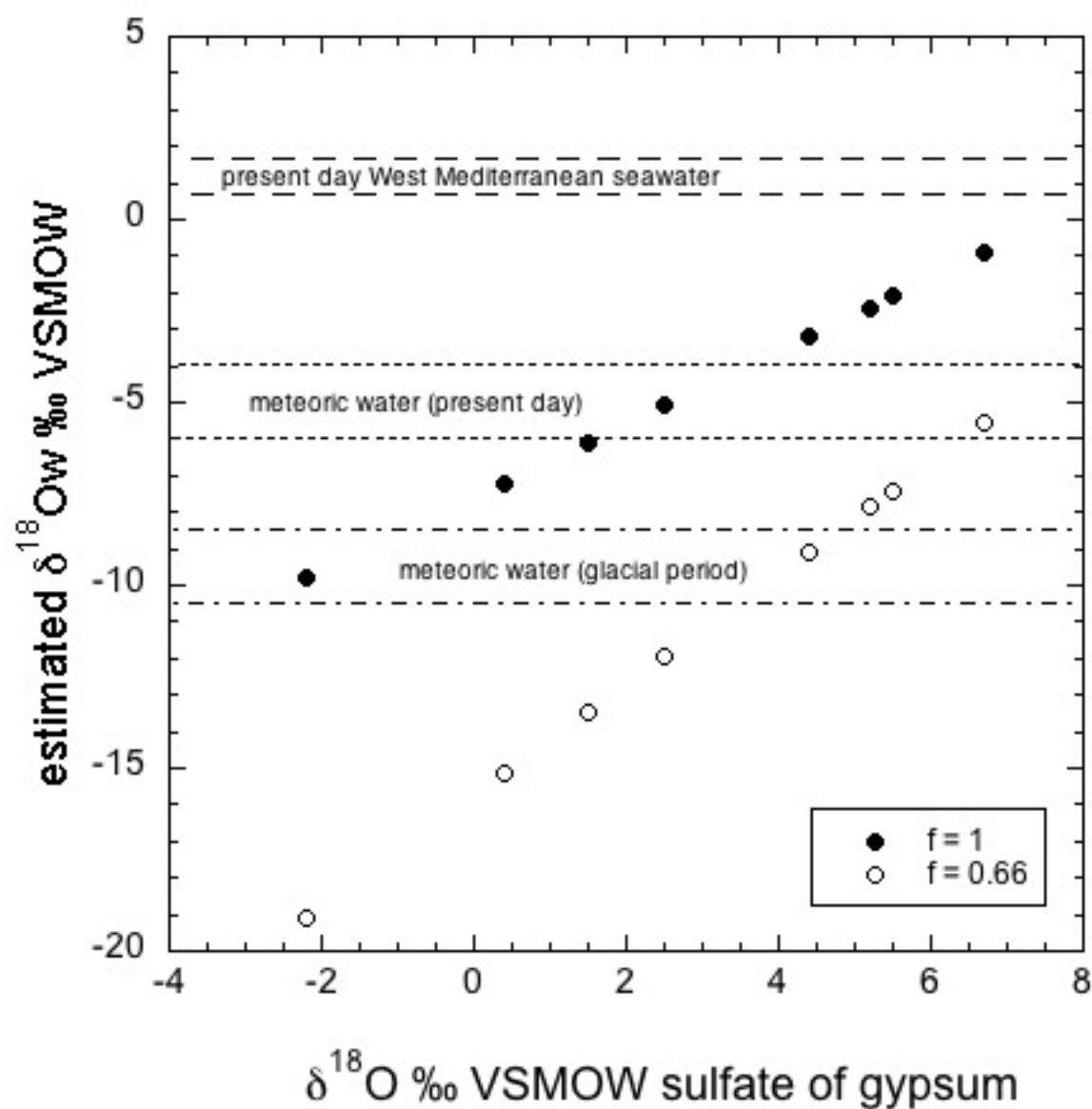


6a) Sulfuric acid weathering of carbonates : diagenetic gypsum formation



6b) Sulfuric acid weathering of clay minerals : diagenetic alunite and silica formation





| Sample   | Age       | Basin | Section                    | Description                       | $\delta^{18}\text{O} \text{‰}$<br>VPDB<br>dolomite | $\delta^{13}\text{C} \text{‰}$<br>VPDB<br>dolomite | Equilibrium<br>temperature °C<br>$\delta^{18}\text{O} \text{ w} = 1.6\text{‰}$ | Equilibrium<br>temperature °C<br>$\delta^{18}\text{O} \text{ w} = 0.8\text{‰}$ | $\delta^{34}\text{S} \text{‰}$<br>VCDT<br>gypsum | $\delta^{18}\text{O} \text{‰}$<br>VSMOW<br>gypsum | estimated<br>$\delta^{18}\text{O}_w$<br>with f=1 | estimated<br>$\delta^{18}\text{O}_w$<br>with f=0.66 |
|----------|-----------|-------|----------------------------|-----------------------------------|----------------------------------------------------|----------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------|---------------------------------------------------|--------------------------------------------------|-----------------------------------------------------|
| ES 16.16 | Pliocene  | Vera  | graveyard                  | Nodule 1-external envelope        | 1.06                                               | -7.01                                              | 30.5                                                                           | 26.5                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.17 | Pliocene  | Vera  | graveyard                  | Nodule 1-internal part            | 1.73                                               | -7.15                                              | 27.3                                                                           | 23.5                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.18 | Pliocene  | Vera  | graveyard                  | Nodule 1-marly intercalation      | 1.5                                                | -8.77                                              | 28.5                                                                           | 24.6                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.19 | Pliocene  | Vera  | graveyard                  | Nodule 1-internal part            | 2,15                                               | -7,12                                              | 25.3                                                                           | 21.5                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.20 | Pliocene  | Vera  | graveyard                  | Nodule 1-lower internal part      | 2.56                                               | -7.81                                              | 23.3                                                                           | 19.6                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.22 | Pliocene  | Vera  | graveyard                  | Gypsum veins around nodule 1      |                                                    |                                                    |                                                                                |                                                                                | -7.6                                             | 1.5                                               | -6.1                                             | -13.5                                               |
| ES 16.30 | Pliocene  | Vera  | graveyard                  | Group of nodules-core of nodule a | 2.31                                               | -11.29                                             | 24.5                                                                           | 20.7                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.31 | Pliocene  | Vera  | graveyard                  | Group of nodules-core of nodule b | 2.32                                               | -9.94                                              | 24.5                                                                           | 20.7                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.32 | Pliocene  | Vera  | graveyard                  | Group of nodules-core of nodule c | 2.30                                               | -7.20                                              | 24.5                                                                           | 20.7                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.33 | Pliocene  | Vera  | graveyard                  | Group of nodules-core of nodule d | 2.41                                               | -9.92                                              | 24.0                                                                           | 20.3                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.34 | Pliocene  | Vera  | graveyard                  | Group of nodules-core of nodule e | 2.07                                               | -11.93                                             | 25.7                                                                           | 21.9                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.36 | Pliocene  | Vera  | graveyard                  | Gypsum veins                      |                                                    |                                                    |                                                                                |                                                                                | -7.4                                             | 5.2                                               | -2.4                                             | -7.8                                                |
| ES 16.37 | Pliocene  | Vera  | graveyard                  | Conduit with gypsum veins         |                                                    |                                                    |                                                                                |                                                                                | -6.5                                             | 6.7                                               | -0.9                                             | -5.6                                                |
| ES 16.57 | Tortonien | Albox | between Albox and Saliente | Group of nodules-core of nodule 1 | 2.34                                               | 1.11                                               | 24.4                                                                           | 20.6                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.58 | Tortonien | Albox | between Albox and Saliente | Group of nodules-core of nodule 2 | 3.41                                               | -0.32                                              | 19.4                                                                           | 15.8                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.59 | Tortonien | Albox | between Albox and Saliente | Group of nodules-core of nodule 3 | 2.73                                               | 2.85                                               | 22.5                                                                           | 18.8                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.61 | Tortonien | Albox | between Albox and Saliente | Group of nodules-core of nodule 4 | 3.68                                               | 6.07                                               | 18.1                                                                           | 14.6                                                                           |                                                  |                                                   |                                                  |                                                     |

| Sample       | Age          | Basin  | Section                    | Description                            | $\delta^{18}\text{O} \text{‰}$<br>VPDB<br>dolomite | $\delta^{13}\text{C} \text{‰}$<br>VPDB<br>dolomite | Equilibrium<br>temperature °C<br>$\delta^{18}\text{O} \text{ w} = 1.6\text{‰}$ | Equilibrium<br>temperature °C<br>$\delta^{18}\text{O} \text{ w} = 0.8\text{‰}$ | $\delta^{34}\text{S} \text{‰}$<br>VCDT<br>gypsum | $\delta^{18}\text{O} \text{‰}$<br>VSMOW<br>gypsum | estimated<br>$\delta^{18}\text{O}_w$<br>with f=1 | estimated<br>$\delta^{18}\text{O}_w$<br>with f=0.66 |
|--------------|--------------|--------|----------------------------|----------------------------------------|----------------------------------------------------|----------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------|---------------------------------------------------|--------------------------------------------------|-----------------------------------------------------|
| ES 16.62     | Tortonien    | Albox  | between Albox and Saliente | Group of nodules-core of nodule 5      | 2.60                                               | 4.91                                               | 23.1                                                                           | 19.4                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.63     | Tortonien    | Albox  | between Albox and Saliente | Gypsum veins                           |                                                    |                                                    |                                                                                |                                                                                | -4.5                                             | 5.5                                               | -2.1                                             | -7.4                                                |
| ES 16.125    | Tortonien II | Murcia | Camino de los Gonzalez     | Group of nodules-core of nodule 1      | 1.29                                               | 7.26                                               | 29.6                                                                           | 25.6                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.126    | Tortonien II | Murcia | Camino de los Gonzalez     | Group of nodules-conduit intra nodules | -0.72                                              | 1.25                                               | 40.3                                                                           | 35.9                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 16.127    | Tortonien II | Murcia | Camino de los Gonzalez     | Gypsum vein                            |                                                    |                                                    |                                                                                |                                                                                | -21.3                                            | 2.5                                               | -5.1                                             | -11.9                                               |
| ES 17-45     | Tortonien    | Murcia | Ginovinos, road RF-M 56    | Nodule 2-central part                  | 0.13                                               | 5.78                                               | 35.6                                                                           | 31.4                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES 17-46     | Tortonien    | Murcia | Ginovinos, road RF-M 56    | Gypsum vein around Nodule 2            |                                                    |                                                    |                                                                                |                                                                                | -22.3                                            | 0.4                                               | -7.2                                             | -15.1                                               |
| ES 17-64     | Tortonian    | Murcia | Ginovinos, road RF-M 56    | Gypsum veins                           |                                                    |                                                    |                                                                                |                                                                                | -13.2                                            | 4.4                                               | -3.2                                             | -9.1                                                |
| ES-94-5      | Tortonian    | Lorca  | median part                | layered dolomite                       | 0.14                                               | 6.08                                               | 35.6                                                                           | 31.3                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-94-49     | Tortonian    | Lorca  | median part                | layered dolomite                       | 0.08                                               | 4.59                                               | 35.9                                                                           | 31.7                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-94-46     | Tortonian    | Lorca  | median part                | layered dolomite                       | -0.06                                              | 3.64                                               | 32.4                                                                           | 28.3                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-94-39     | Tortonian    | Lorca  | median part                | layered dolomite                       | 0.30                                               | 4.46                                               | 34.7                                                                           | 30.5                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-98.2-116  | Tortonian    | Lorca  | median part                | layered dolomite                       | -0.34                                              | 4.32                                               | 38.2                                                                           | 33.9                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-98.2-114  | Tortonian    | Lorca  | median part                | layered dolomite                       | -0.61                                              | 3.42                                               | 39.7                                                                           | 35.3                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-98-4      | Tortonian    | Lorca  | median part                | layered dolomite                       | -0.55                                              | 4.40                                               | 39.3                                                                           | 35.0                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-98.2 -80  | Tortonian    | Lorca  | median part                | layered dolomite                       | -0.07                                              | 4.79                                               | 36.7                                                                           | 32.4                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-98 -2     | Tortonian    | Lorca  | median part                | layered dolomite                       | -0.39                                              | 4.39                                               | 38.4                                                                           | 34.1                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-98.2 -101 | Tortonian    | Lorca  | median part                | layered dolomite                       | -0.31                                              | 4.31                                               | 38.0                                                                           | 33.7                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-98 -3     | Tortonian    | Lorca  | median part                | layered dolomite                       | 0.05                                               | 5.20                                               | 36.0                                                                           | 31.8                                                                           |                                                  |                                                   |                                                  |                                                     |
| ES-97-84     | Tortonian    | Lorca  | median part                | Gypsum veins                           |                                                    |                                                    |                                                                                |                                                                                | 10.5                                             | -2.2                                              | -9.8                                             | -19.1                                               |