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**From deep to shallow fluid reservoirs: evolution of fluid sources during exhumation of the Sierra Almagrera (Betics, Spain)**

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Key words:	Metamorphic Core Complex, Metamorphic brines, Fluid inclusions, Stable isotopes, Betic Cordillera, Trans-alboran fault

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2           2       **exhumation of the Sierra Almagrera (Betics, Spain)**

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4           3  
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21          20       **Keywords**

22          21       Metamorphic Core Complex / Metamorphic brines / Fluid inclusions / Stable isotopes / Betic  
23          22       Cordillera / Trans-alboran fault

24          23       **Abstract**

25          24       The combination of structural, geochemical and paleotopographic data proves to be an  
26          25       efficient tool to understand fluid transfers in the crust. This study discriminates shallow and deep  
27          26       fluid reservoirs on both sides of the brittle-ductile transition under an extensional regime, and points  
28          27       out the role of major transcurrent fault activity in this paleo-hydrogeological setting.

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28 Paleo-fluids trapped in quartz and siderite-barite veins record the transfer of fluids and metal  
29 solute species during the Neogene exhumation of the Sierra Almagrera metamorphic belt. Ductile  
30 then brittle-ductile extensional quartz veins formed from a deep fluid reservoir, trapping  
31 metamorphic secondary brines containing low-density volatile phases derived from the dissolution  
32 of Triassic evaporites. During exhumation, low-salinity fluids percolated within the brittle domain,  
33 as shown by transgranular fluid inclusion planes affecting previous veins. These observations  
34 indicate the opening of the system during Serravalian to early Tortonian times, and provide  
35 evidence for the penetration of surficial fluids of meteoric or basinal origin into the upper part of the  
36 brittle-ductile transition.

37 During exhumation, syndimentary transcurrent tectonic processes occurred from Late  
38 Tortonian times onwards, while marine conditions prevailed at the Earth's surface. At depth in the  
39 brittle domain, quartz veins associated with hematite record a return to high-salinity fluid  
40 circulation suggesting an upward transfer fed from the lower reservoir. During the Messinian,  
41 ongoing activity of the Trans-Alboran tectono-volcanic trend led to the formation of ore deposits.

42 Reducing fluids led to the formation of siderite and pyrite ores. The subsequent formation of  
43 galena and barite may be related to an increase of temperature. The high salinity and Cl/Br ratio of  
44 the fluids suggest another source of secondary brine derived from dissolved Messinian evaporites,  
45 as corroborated by the  $\delta^{34}\text{S}$  signature of barite. This constrains the age of the mineralizing event at  
46 around 5.65 Ma, prior to the main Messinian salinity crisis.

## 47 **1. Introduction**

48 Fluids are vectors of heat and solute species. Migration of fluids is linked to local and  
49 regional geology, and permeability is a key factor in controlling fluid flow (Manning & Ingebritsen,  
50 1999, Ingebritsen & Manning, 2002). Permeability is a function of time, heterogeneity-anisotropy  
51 and scale (Manning & Ingebritsen, 1999). The Sierra Almagrera (southern Spain) is a favourable  
52 terrain to evaluate the conditions of fluids migration within the Earth's lithosphere. Because this

1  
2 53 area is located in a context of exhumation disturbed by the trans-Alboran transcurrent fault system,  
3  
4 54 fluid flows can be studied through time across the brittle-ductile transition.

5  
6 55 Fluid analysis can focus on the exhumation of metamorphic rocks occurring in wedges  
7  
8 56 undergoing active thickening, owing to the intense erosion of the hanging-wall overlying thrust  
9  
10 57 systems (Menzies *et al.*, 2014). Within Basin and Range type provinces, studies of fluids can also  
11  
12 58 elucidate the exhumation of rocks from the footwall during thinning processes as revealed by the  
13  
14 59 presence of crustal detachments associated with low-angle and high-angle normal faults (Wernicke  
15  
16 60 & Burchfiel, 1982, Lister & Davis, 1989, Vanderhaeghe & Teyssier, 2001). In both geological  
17  
18 61 settings, the location of the brittle-ductile transition plays a major role. In extensional settings, this  
19  
20 62 rheological transition may localize detachment and decollement layers where normal faults are  
21  
22 63 generally rooted. There is currently much debate about the hydrogeological role of the brittle-  
23  
24 64 ductile transition. The rheological change occurring at this transition may separate a deep reservoir,  
25  
26 65 which is accessible to metamorphic and/or magmatic and mantle fluids confined under lithostatic  
27  
28 66 conditions, from a shallower reservoir accessible to surficial fluids (meteoric, marine or basinal)  
29  
30 67 circulating under lithostatic to hydrostatic conditions (Morrison & Anderson, 1998, Famin &  
31  
32 68 Nakashima, 2004). These two reservoirs may interact through tectonic and magmatic processes.  
33  
34 69 Surficial fluids may reach the upper part of the deeper reservoir under contractional regimes  
35  
36 70 (Menzies *et al.*, 2014) as well as under extensional regimes (Mulch *et al.*, 2004, Famin *et al.*, 2005,  
37  
38 71 Siebenaller *et al.*, 2013). Alternatively, deeper fluids may access the upper brittle crust and mix  
39  
40 72 with fluids closer to the Earth's surface (Boiron *et al.*, 2003), a process which may also be triggered  
41  
42 73 by magma ascent. Such fluid circulation events are commonly associated with hydrothermal  
43  
44 74 processes (metasomatism and mineralization) (Beaudoin, 1994), and it is then necessary to decipher  
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46 75 the role played by the different reservoirs and fluids during the tectonic and magmatic events.  
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52  
53 76 The convergence between Africa and Europe resulted in a complex geotectonic history with  
54  
55 77 subduction of upper continental crust (Eocene to Middle Miocene), followed by extensional  
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57 78 tectonics. This early extension triggered the exhumation of metamorphic cores in the internal zones  
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1  
2 79 of the Betic cordillera during the Miocene (between 18 to 14 Ma: Gomez-Pugnaire *et al.* (2004),  
3  
4 80 Platt *et al.* (2006) and Gomez-Pugnaire (2012), and possibly even earlier (Augier *et al.*, 2005b).  
5  
6 81 Further exhumation has occurred under compressional regimes since the late Miocene due to  
7  
8 82 erosional processes affecting the uplifting metamorphic cores. The different mountain ranges have  
9  
10 83 been also partly dissected by a major transcurrent fault system, which has led to the formation of  
11  
12 84 synsedimentary continental to marine basins (Weijermars, 1985, Booth-Rea *et al.*, 2003).  
13  
14 85 Volcanism occurred later in the evolution of the Betics, reflecting mantle and crust processes as  
15  
16 86 well as mantle-crust interactions at depth (e.g. Benito *et al.* (1999); Turner *et al.* (1999); Duggen *et*  
17  
18 87 *al.* (2004)). A major erosional event allowed the uplift of ranges during the Messinian salinity crisis.  
19  
20 88 Deposition of evaporites in the central Mediterranean Sea and incision features affected the  
21  
22 89 bordering slopes. Prior to the main sea-level drop (5.60-5.46 Ma), a first stage of deposition of  
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24 90 evaporites with controversial ages (7.20 Ma / 5.96-5.67 Ma) has been recorded in some basins of  
25  
26 91 the Betics (Fortuna, Lorca, Guadix-Baza, Granada and Sorbas) (Clauzon, 1980, Gautier *et al.*, 1994,  
27  
28 92 Garcés *et al.*, 1998, Rouchy *et al.*, 1998, Krijgsman *et al.*, 1999, Seidenkrantz *et al.*, 2000,  
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30 93 Krijgsman *et al.*, 2000, Gargani *et al.*, 2008, Bourillot *et al.*, 2009, Omodeo Salé *et al.*, 2012).  
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35 94 The Sierra Almagrera metamorphic core exhibits a sequence of quartz vein formation. A  
36  
37 95 series of siderite and barite base metal-bearing ore veins, as well as quartz and carbonate barren  
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39 96 veins in the brittle domain, are associated with the transcurrent tectonics. Study of the different  
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41 97 fluids trapped as inclusions in this vein sequence allows the characterization of the deep reservoir  
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43 98 fluids in equilibrium with the rocks during the ductile stage and the evolution of the fluids within  
44  
45 99 the same reservoir during its exhumation towards exposure at the present day. This reservoir was  
46  
47 100 subject to different deformation styles, from ductile to brittle, and records the Neogene evolution of  
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49 101 this part of the Betic orogenic wedge.  
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52  
53 102 In this study, we combine structural, paleogeographical and geochemical data to propose a  
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55 103 scenario of hydrogeological evolution during exhumation across the brittle-ductile transition in the  
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57 104 Sierra Almagrera. In addition, we discuss the hydrogeological influence of the brittle ductile  
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1  
2 105 transition on the lower and upper crustal reservoirs during the Miocene extensional tectonics, the  
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4 106 effect of transcurrent deformation on the hydrogeological configuration, the possible fluid sources  
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6 107 at the various stages of this evolution and the timing of mineralizations in the region.  
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## 9 108 **2. Geological context**

### 10 111 **2.1. The Betic Cordillera (SE Spain)**

11 112 The Betic Cordillera results from the convergence between the Africa and Eurasia plates  
12 113 since the Eocene, and forms an alpine tectonic wedge reaching a thickness of about 60 km (Platt &  
13 114 Vissers, 1989, Lonergan & White, 1997, Platt, 2007, Jolivet et al., 2008). The internal Alboran  
14 115 domain can be divided into three main tectono-metamorphic nappes, from bottom to top (Figure 1):  
15 116 (i) the Nevado-Filábride nappe, itself divided into three sub-units from bottom to top: Ragua (not  
16 117 represented on Figure 1, to the W), Calar-Alto and Bedar-Macael (De Jong, 1991, Martínez-  
17 118 Martínez et al., 2002), (ii) the Alpujarride nappe, and (iii) the Malaguide nappes (Egeler & Simon,  
18 119 1969). In addition to isostatic uplift, these units were also exhumed due to tectonic unroofing  
19 120 (Lonergan & Mange-Rajetzky, 1994). The associated WSW-ENE-striking tectonic extension  
20 121 related to exhumation of the metamorphic continental crust is supposed to have resulted from partial  
21 122 or complete removal of the lithospheric mantle (Platt & Vissers, 1989). Arguments have also been  
22 123 put forward for other mechanisms, such as subduction zone rollback (Lonergan & White, 1997,  
23 124 Bezada et al., 2013). The contacts observed between structural units exhibiting different degrees of  
24 125 metamorphism are attributed to major detachment faults (Figure 1-a): (1) The Malaguide-  
25 126 Alpujarride contact: unmetamorphosed Malaguide lithologies overlie the medium-pressure  
26 127 medium-temperature metamorphic rocks of the Alpujarride nappe (Sierra Estancias, Figure 1-a), (2)  
27 128 The Filabres major detachment: higher grade Nevado-Filábride metamorphic rocks, which were  
28 129 exhumed during the Miocene, lie beneath the Alpujarride nappes. Ductile shearing related to this  
29 130 exhumation affected the footwall and currently shows a transport direction top towards WSW to  
30 131 SW (Crespo-Blanc et al., 1994, Martínez-Martínez & Azañón, 2002, Platt, 2007). According to the  
31 132 extensional tectonics expressed in the ductile fabrics, the metamorphic nappes reached the brittle  
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2 131 domain during the ongoing exhumation. From the late Miocene, exhumation was mainly the result  
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4 132 of erosion since both the metamorphic cores and the sedimentary cover were affected by regional  
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6 133 compressional and local transcurrent tectonics. The Trans-Alboran transcurrent fault system  
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8 134 generated domains with both releasing and restraining deformation, which created juxtaposed zones  
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10 135 with opposite vertical motions (subsidence and uplift). The ranges (sierras) were separated by  
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12 136 basins either filled by continental or marine sediments according to time and location. This major  
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14 137 tectono-volcanic trend can be followed off-shore to the other side of the Mediterranean in Morocco  
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16 138 (Hernandez et al., 1987).

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19 139 The volcanism linked to lithospheric thinning shows a gradual transition and great  
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21 140 geochemical diversity. The age of this volcanism varies from 34 Ma (tholeiitic dykes in Malaga  
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23 141 province) to 2 Ma (alkali basalts in Murcia province). There is a gap between the oldest volcanic  
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25 142 events in Malaga and the main magmatic activity in SE Spain and the Alboran Basin, which took  
26  
27 143 place between 12.6 and 7.5 Ma with tholeiitic and calc-alkaline affinities (Bellon *et al.*, 1983). Very  
28  
29 144 locally in the Sierra Cabrera, Miocene plutonism is recorded related to the retrograde  
30  
31 145 metamorphism and associated ductile deformation (Westra, 1969, Bolze *et al.*, 1986). Since the  
32  
33 146 reappearance of volcanism during the Serravalian, other episodes of magmatic activity occurred  
34  
35 147 inland in SE Spain mainly between 10 and 6.2 Ma, showing high-K calc-alkaline, shoshonitic and  
36  
37 148 ultrapotassic affinities (Bellon *et al.*, 1983, Turner *et al.*, 1999, Zeck *et al.*, 2000, Duggen *et al.*,  
38  
39 149 2004, Duggen *et al.*, 2005, Cesare *et al.*, 2009). Heterogeneous sources and various processes are  
40  
41 150 implied in the magma genesis, including: (i) various degrees of partial melting, (ii) metasomatism  
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43 151 (i.e. oceanic and continental crust, sediments), (iii) anatexis of crustal metasedimentary basement  
44  
45 152 (Benito *et al.*, 1999, Duggen *et al.*, 2004, Duggen *et al.*, 2005, Prelevic *et al.*, 2008, Álvarez-Valero  
46  
47 153 & Kriegsman, 2008, Conticelli *et al.*, 2009).

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49  
50 154 The Neogene evolution of the Betics is associated with a series of base and precious metal-  
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52 155 bearing hydrothermal ore systems developed mainly in the calc-alkaline volcanic rocks of the Cabo  
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54 156 de Gata range, but also in sedimentary and metamorphic basement lithologies (Figure 1).



1 157 Epithermal ore deposits are hosted by intermediate to acid volcanics ranging in age from 12 to 10  
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4 158 Ma; these deposits are found in a number of different mining districts, for example, Zn-Pb-Cu(-Ag-  
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6 159 Au) at San José (Demoustier *et al.*, 1998, Esteban-Arispe *et al.*, 2009), Au(-Cu-Te-Sn) at  
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8 160 Rodalquilar (Arribas *et al.*, 1995) and Cu-Au-Ag at Carboneras (Morales Ruano *et al.*, 2000,  
9  
10 161 Carrillo-Rosúa *et al.*, 2009). Ba-Ag mineralizations are found in sedimentary rocks, close to high-K  
11  
12 162 calc-alkaline and shoshonitic volcanics within the Vera Basin (Alvado, 1986, Martínez-Frías,  
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14 163 1998). Certain ore deposits are hosted by metamorphic rocks, including the occurrences of Pb-Zn-  
15  
16 164 Fe-Cu (Al) at Cartagena (Graeser & Friedrich, 1970, Oen *et al.*, 1975, Arribas *et al.*, 1983) and Pb-  
17  
18 165 Zn-Ag-Fe at Sierra Almagrera and Sierra Aguilon (Martinez Frias *et al.*, 1989, Morales Ruano *et*  
19  
20 166 *al.*, 1993). Samples from the Sierra Almagrera mining district allow us to reconstruct the fluid  
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22 167 history described below.  
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## 26 168 **2.2. Geology of the Sierra Almagrera (Figure 1-b)**

27  
28  
29 169 The metamorphic range of the Sierra Almagrera exposes a Nevado Filabres unit largely  
30  
31 170 composed of graphitic quartz-rich chloritoid-schists (Booth-Rea *et al.*, 2004) and quartzites.  
32  
33 171 Locally, carbonates and gypsum are found north of the Sierra Almagrera within an Alpujarride unit  
34  
35 172 (Álvarez & Aldaya, 1985). The present-day geomorphology of the Sierra Almagrera mainly results  
36  
37 173 from sinistral strike-slip faulting in the area that generated several fault segments at various scales.  
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39 174 The Palomares Fault Zone results in an approximately 16 km North-South trending left-lateral  
40  
41 175 relative displacement (Booth-Rea *et al.*, 2004). This transcurrent faulting may have started during  
42  
43 176 the late Tortonian (around 7.2 Ma), but was mainly active during the Messinian. The evolution of  
44  
45 177 this faulting associated with a vertical component (oblique faulting) caused the recent uplift, thus  
46  
47 178 leading to erosion and exhumation of the Sierra Almagrera during the Plio-Quaternary. The  
48  
49 179 southern segments of the Palomares Fault Zone dip towards the West. Their transtensional activity  
50  
51 180 favoured the subsidence of the western block. By contrast, the northern segments, which are  
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53 181 dipping towards the ESE, are related to a sinistral restraining bend that favoured the uplift of the  
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55 182 Sierra Almagrera mountain ranges located to the East of the zone (Booth-Rea *et al.*, 2004). In the  
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1  
2 183 studied area, small bodies of high-K calc-alkaline to shoshonitic rhyodacites (Lopez Ruiz &  
3  
4 184 Rodriguez Badiola, 1980, Benito *et al.*, 1999) are encountered along the transcurrent fault system.  
5  
6 185 Regional ages determined on this volcanic suite are between 11.9 and 6.2 Ma (Duggen *et al.*, 2004).  
7  
8 186 Less abundant lamproites from the ultrapotassic series (Lopez Ruiz & Rodriguez Badiola, 1980),  
9  
10 187 dated at between 8.4 and 6.4 Ma (Prelevic *et al.*, 2008), crop out within the Vera basin to the south  
11  
12 188 of Sierra Almagrera (Figure 1-b).

13  
14  
15 189 Mineralizations in the Sierra Almagrera are found in veins within the metamorphic rocks of  
16  
17 190 the currently uplifted metamorphic range (Figure 1-b). In the present study, this formerly exploited  
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19 191 area is referred to as the Sierra Almagrera mining district. While some mineralised veins are  
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21 192 exposed at outcrop in the Sierra, the sulphides are frequently oxidized. Non-altered veins can still  
22  
23 193 be sampled along the E-W striking horizontal gallery at El Arteal. Subvertical fractures filled by  
24  
25 194 siderite, barite, hematite and ore minerals crosscut the metamorphic fabric of graphitic schists and  
26  
27 195 quartz veins transposed or partly transposed within the main rock foliation. Our study shows that  
28  
29 196 the mineralised fractures are arranged in two main clusters striking N160°-N180° and N120°-N130°  
30  
31 197 (Figure 1-c).

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34  
35 198 The area located within the Palomares Fault Zone (hanging-wall) is referred to here as “the  
36  
37 199 subsident area”. Locally, mineralizations can be found within the Messinian sediments (Las  
38  
39 200 Herrerias). The ore consists of barite veins, with native Ag and base-metal sulphides in very small  
40  
41 201 amounts (Alvado, 1986, Martínez-Frías, 1998, Carrillo-Rosúa *et al.*, 2002, 2003).

## 42 43 44 202 **3. Methods**

### 45 46 47 203 **3.1. Fluid inclusion investigations**

#### 48 49 50 204 **3.1.1 Fluid inclusion petrography**

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52  
53 205 Double-polished 150-200- $\mu\text{m}$ -thick sections were prepared for microscopic and  
54  
55 206 microthermometric observations of mineralized veins of quartz, siderite, barite and calcite. The  
56  
57 207 sections were oriented (using azimuth convention) to determine present-day strike and dip of fluid  
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1  
2 208 inclusion planes. Isolated fluid inclusions or clusters are interpreted as primary. Intragranular fluid  
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4 209 inclusion planes are found within single grains in microcracks that do not cross-cut grain boundaries  
5  
6 210 (Van Den Kerkhof & Hein, 2001). Transgranular fluid inclusion planes result from healing of  
7  
8 211 former open cracks (Krantz, 1983, Boullier, 1999, Lespinasse, 1999, Lespinasse *et al.*, 2005) as  
9  
10 212 rocks undergo brittle deformation. Systematic measurements of the fluid inclusion planes were  
11  
12 213 carried out on each section using an ANIMA interactive videographic image analyzer (Lespinasse  
13  
14 214 *et al.*, 2005). The plunge and dip directions of the fluid inclusion planes are represented on equal-  
15  
16 215 area lower-hemisphere stereograms using Stereonet® software.

### 20 216 **3.1.2 Microthermometry**

21  
22 217 The phase transitions of the fluid inclusions were characterised between  $-170\text{ }^{\circ}\text{C}$  and  $+600\text{ }^{\circ}\text{C}$   
23  
24 218 using a LINKAM MDS 600 heating-freezing stage mounted on an Olympus microscope, calibrated  
25  
26 219 using  $\text{CO}_2$  and  $\text{H}_2\text{O}$  synthetic and natural alpine fluid inclusions. The accuracy of measurements  
27  
28 220 varies from  $\pm 0.2\text{ }^{\circ}\text{C}$  at low temperature (experiments at  $0.5\text{-}1\text{ }^{\circ}\text{C}/\text{min}$ ) to  $\pm 2\text{ }^{\circ}\text{C}$  at high temperature  
29  
30 221 (experiments at  $1\text{-}5\text{ }^{\circ}\text{C}/\text{min}$ ). Table 1 reports the abbreviations of terms and the phase transition  
31  
32 222 temperatures observed during microthermometric experiments. For barite and calcite, the high-  
33  
34 223 temperature transitions were studied first to prevent leakage of fluid inclusions during ice formation  
35  
36 224 on cooling. Photographs of fluid inclusions after each measurement were compared with the  
37  
38 225 original picture to evaluate any leakage.

### 43 226 **3.1.3 Raman microspectroscopy**

44  
45 227 Raman analysis of fluid inclusions was performed with a LabRAM microspectrometer  
46  
47 228 (Horiba Jobin Yvon, at GeoRessources, Vandœuvre-lès-Nancy, France) equipped with a  $1800$   
48  
49 229  $\text{gr. mm}^{-1}$  grating and a  $\times 80$  Olympus objective. The exciting radiation was provided by the  $514.5\text{ nm}$   
50  
51 230 line of an  $\text{Ar}^+$  laser (Stabilite 2017, Newport Corp., Spectra Physics) at a power of  $400\text{ mW}$ . The  
52  
53 231 signal-to-noise ratio was optimized by adjusting acquisition time and accumulation number. The  
54  
55 232 quantitative analysis of the gas phase was performed using a specific calibration of the laboratory.  
56  
57 233 Results are given as mol% relative to the volatile phase.  
58  
59  
60

#### 234 **3.1.4 *P-V-T-X calculation of fluid inclusions***

235 In this study, we use microthermometric data associated with mole fractions of the different  
236 gas species obtained by Raman spectroscopy to reconstruct the *P-V-T-X* evolution of fluid  
237 inclusions. The salinities of aqueous fluid are calculated using the final melting temperature of ice  
238 when gases are not present in sufficient amounts to form gas hydrates (Bodnar, 2003). In this case,  
239 the isochore is a function of the homogenization temperature at a given salinity, and the empirical  
240 equation of state of Zhang and Frantz (1987) is used within a *P-T* domain of validity of *T*: 180-700  
241 °C and *P*: 0.1-300 MPa.

242 The salinities of aqueous carbonic fluids and molar volumes ( $V_m$ ) of the volatile phase are  
243 calculated using the program ICE and the dissociation temperature of clathrate (Bakker, 1997,  
244 2003) when gases are present in significant amounts to allow the formation of gas hydrates. The  
245 isochores are calculated using the program ISOC (Bakker, 1997, 2003) and the equation of state  
246 (Bowers & Helgeson, 1983) revised by Bakker (1999) for the system H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub>-NaCl, with  
247 a *P-T* domain of validity of *T*: 350-600 °C and *P*: 50-200 MPa.

#### 248 **3.1.5 *Crush-leach analysis for halogen chemistry***

249 Because the halogens display a conservative behaviour in solution, and remain relatively  
250 unaffected by fluid-rock interactions (Banks *et al.*, 1991), the signature of the elements Cl and Br in  
251 a fluid can be used to characterize its source (Böhlke & Irwin, 1992).

252 Bulk crush-leach analyses were performed to extract and analyse fluids hosted in quartz,  
253 barite and siderite. Samples were prepared according to the methodology of Bottrell *et al.* (1988).  
254 The amount of sample crushed was between 0.5 and 1.0 g. Analysis of the anions F, Cl, Br, I and  
255 SO<sub>4</sub> was performed by ion chromatography using a ICS 3000 Dionex system with a AS20 column  
256 at the LIEC laboratory (Nancy, France). Br was also analysed by LA-ICPMS in a series of  
257 representative fluid inclusions using the procedure described by Leisen *et al.* (2012a).

#### 258 **3.1.6 *Laser Ablation ICP-MS***

1  
2 259 This technique allows direct ablation of individual fluid inclusions within the host mineral,  
3  
4 260 represented in the present study by quartz, siderite and barite. The LA-ICP-MS instrument  
5  
6 261 (GeoRessources laboratory, Vandœuvre-lès-Nancy, France) comprises a GeoLas excimer laser  
7  
8 262 (ArF, 193 nm, Microlas, Göttingen Germany) and an Agilent 7500c quadrupole ICP-MS equipped  
9  
10 263 with an octopole reaction-cell using H<sub>2</sub> gas, and a collision-cell using He gas. The laser beam is  
11  
12 264 focused onto the sample within an ablation cell with a Schwarzschild objective (magnification x25)  
13  
14 265 linked with a CCD camera. Synthetic glass provided by the National Institute of Standards and  
15  
16 266 Technology (NIST) is used for calibration of the different analysed elements and respective masses  
17  
18 267 (200 pulses at 5 Hz). The design as an optical imaging system allows the use of different crater  
19  
20 268 diameters (24, 32 or 60 µm) at constant energy density on the sample, by adjusting an aperture in  
21  
22 269 the laser beam path. Na, K, Mg, Ba, Sr, Mn, Li, Fe, Cu and Zn are analysed here. Concentrations  
23  
24 270 are calculated according to Leisen *et al.* (2012b).

### 271 **3.2. Raman spectroscopy of carbonaceous materials**

272 The Raman Spectrum of Carbonaceous Material (RSCM) has been calibrated as a  
273 geothermometer in the range 330-640 °C (Beyssac *et al.*, (2002, 2004)). The RSCM displays one  
274 graphite band (G band) and several defect-activated bands (D1 and D2 bands) between 1100 and  
275 1800 cm<sup>-1</sup> (Beyssac & Lazzeri, 2012), whose intensities decrease with increasing metamorphic  
276 grade. Raman analysis of graphite-bearing schists was performed on thin sections oriented  
277 perpendicular to the foliation and parallel to the lineation by focusing the laser beam beneath a  
278 transparent crystal to avoid the effect of amorphization due to polishing. The Raman spectrometer  
279 used in this study is a LabRAM HR instrument (Horiba Jobin Yvon) (GeoRessources, Vandœuvre-  
280 lès-Nancy, France) equipped with a 600 gr.mm<sup>-1</sup> grating and a ×100 objective (Olympus). The  
281 excitation beam is provided by an Ar<sup>+</sup> laser (Stabilite 2017, Newport Corp., Spectra Physics) at  
282 457.9 nm. Laser power is reduced to avoid heating the samples, using optical filters of various  
283 optical densities, and was always lower than 5 mW. The acquisition time is 15 seconds, with each  
284 measurement repeated 6 times. 10 to 15 spectra are recorded for each sample for statistical

1  
2 285 purposes. Peak fitting is performed using the Peak Analyser of the OriginPro 8.5.1 software. The  
3  
4 286 following expression (Beysac *et al.*, 2002) is used to derive peak temperature conditions:  $T(^{\circ}\text{C}) = -$   
5  
6 287  $445R_2 + 641$ , with  $R_2$  (peak area ratio) =  $(D_1/(G+D_1+D_2))$ .  
7

### 8 9 288 **3.3. Stable isotopes**

#### 10 11 289 **3.3.1 $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of siderite**

12  
13  
14 290 15 to 20 mg of siderite were reacted at 70 °C with  $\text{H}_3\text{PO}_4$  for 15 days (Scheppard &  
15  
16 291 Schwarcz, 1970). Isotopic ratios were measured using a modified VG 602D mass spectrometer at  
17  
18 292 the CRPG laboratory (Vandœuvre-lès-Nancy, France), and the results are reported using  
19  
20 293 conventional  $\delta^{18}\text{O}$  (V-SMOW) and  $\delta^{13}\text{C}$  (V-PDB) notations. The analytical reproducibility is  $\pm 0.1$   
21  
22 294 ‰ for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$ .  
23  
24

#### 25 26 295 **3.3.2 $\delta^{18}\text{O}$ of quartz**

27  
28 296 6.5 to 7.5 mg of quartz (same grains as those used for fluid inclusion analyses) were analysed  
29  
30 297 using the conventional fluorination method (Clayton & Mayeda, (1963). The measurements were  
31  
32 298 carried out with a VG SIRA 10 triple-collector instrument at the University of Rennes 1 (France).  
33  
34 299 The analytical reproducibility (estimated from duplicates performed on different Ni fluorination  
35  
36 300 tubes) is  $\pm 0.2\%$ .  
37  
38  
39

#### 40 41 301 **3.3.3 $\delta^{34}\text{S}$ of sulphides and sulphates**

42  
43 302 Sulphur isotope compositions were measured following the method of Giesemann *et al.*  
44  
45 303 (1994) at the CRPG laboratory (Vandœuvre-lès-Nancy, France) by EA-IRMS (Elemental Analyser-  
46  
47 304 Isotopic Ratio Mass Spectrometer).  $\delta^{34}\text{S}$  was measured with a GV Instruments Isoprime mass  
48  
49 305 spectrometer coupled in continuous-flow mode to a EuroVector elemental analyser. Results are  
50  
51 306 reported using conventional  $\delta^{34}\text{S}$  (CDT). No inter-sample memory effect was observed. Linearity of  
52  
53 307 the mass spectrometer and reproducibility of the analysis were checked using CRPG internal  
54  
55 308 reference materials. The analytical reproducibility obtained on the barium sulphate reference  
56  
57 309 material used at CRPG is lower than 0.3 ‰.  
58  
59  
60

1  
2 310 **3.3.4  $\delta D$  of white micas**

3  
4 311 2 to 3 mg of powdered host-rock were analysed for the isotopic composition of hydrogen-  
5  
6 312 bearing minerals, mainly phengite.  $\delta D$  was measured with a GV Instruments Isoprime mass  
7  
8 313 spectrometer coupled in continuous-flow mode to a EuroVector elemental analyser. No inter-  
9  
10 314 sample memory effect can be observed. Linearity of the mass spectrometer and reproducibility of  
11  
12 315 the analysis were checked using CRPG internal reference materials with an analytical  
13  
14 316 reproducibility lower than 0.3‰.

17  
18 317 **3.3.5  $\delta D$  of fluid inclusions**

19  
20 318 Fluids trapped in quartz, barite and siderite crystals were extracted for isotopic analyses by  
21  
22 319 crushing under vacuum. Aliquots of 1.0 to 5.1 g of mm-sized grains were loaded into steel tubes and  
23  
24 320 degassed overnight at 120 °C under vacuum to release any water adsorbed at the mineral surface  
25  
26 321 (Dublyansky & Spötl, 2009). Preliminary tests conducted under the microthermometric heating  
27  
28 322 stage showed no decrepitation or stretching of the studied fluid inclusions at temperatures below  
29  
30 323 200 °C. H<sub>2</sub>O was separated cryogenically from other gases and reduced to H<sub>2</sub> in a uranium reactor  
31  
32 324 at 800 °C. D/H ratio of H<sub>2</sub> was determined using a dual-inlet VG Micromass 602D mass  
33  
34 325 spectrometer at the CRPG laboratory (Vandœuvre-lès-Nancy, France). External reproducibility of  
35  
36 326 D/H measurements was estimated to be lower than 3 ‰ by normalizing raw data to the V-SMOW-  
37  
38 327 SLAP scale. Two CRPG water standards were analysed along with each weekly batch of water  
39  
40 328 samples obtained from the fluid inclusions.

41  
42 329 To avoid any memory effect on D/H ratios within the uranium reactor, samples were  
43  
44 330 systematically duplicated. For each duplicate,  $\delta D$  values from the first extraction are discarded since  
45  
46 331 they could be affected by this memory effect.

47  
48 332 For quartz containing primary inclusions,  $\delta^{18}O_{\text{fluid}}$  was calculated from  $\delta^{18}O_{\text{quartz}}$  using the  
49  
50 333 quartz-water fractionation equation of Zheng (1993) at a given temperature.

51  
52 334



## 335 4. Results

### 336 4.1. Characteristics of the host-rock

337 All sampled veins are hosted in schists composed of phengite, quartz, graphite and rutile.  
338 Although not observed in this study, biotite and garnet have also been described in these rocks  
339 (Álvarez & Aldaya, 1985) as well as chloritoid (Booth-Rea *et al.*, 2004). The strike of the foliation  
340 on the western flank of Sierra Almagrera (the studied area) oscillates between N045E and N100E,  
341 with an average dip of around 25-30°SE-S that can reach up to 45°SE-S at El Arteal mine (Figure 1-  
342 b). Although stretching lineation is not always observed, deformed quartz veins (V-Qtz1) indicate a  
343 top to the West shearing (Figure 2-a).

344 The Raman study of graphitic carbon yields R2 ratios from 0.12 to 0.21 (mode: 0.18; n=8, in  
345 3 samples), corresponding to temperatures ranging between 545 and 590 °C. These results are in  
346 agreement with the temperatures of 535-550 °C determined using the same method in the Calar  
347 Alto unit from the Sierra de Los Filabres (Augier *et al.*, 2005b). Phengite shows Si contents ranging  
348 from 3.31 to 3.05 a.p.f.u (n=4, in 2 samples), corresponding to an estimated pressure ranging from  
349 2.2 kbar at 545 °C to 9.7 kbar at 590 °C (Massonne & Schreyer, 1987). These pressures are similar  
350 to those obtained in the Calar-Alto unit in the Sierra de Los Filabres (10±0.7 kbar to 3.1±0.3 kbar)  
351 (Augier *et al.*, 2005b).

### 352 4.2. Vein and fluid inclusion petrography

353 According to their geometry, petrography and position relative to the host rock foliation, five  
354 types of veins can be defined (Table 2). Table 3 summarizes the characteristics of the fluid  
355 inclusions observed within each vein.

#### 356 4.2.1 V-Qtz1, quartz veins parallel to host-rock foliation

357 V-Qtz1 veins (thickness less than 30 cm) may be found in both structural blocks (Figure 2-a).  
358 These quartz veins are characterised by high-temperature recrystallization mechanisms with  
359 granoblastic euhedral texture, with grains of about 200 µm showing triple points with an angle of



1  
2 360 120° (Figure 2-b) or lobate grain boundaries interpreted as due to grain boundary migration (Jessell,  
3  
4 361 1987, Passchier & Trouw, 2005, Stipp & Kunze, 2008) (Figure 2-c). No primary inclusions are  
5  
6 362 observed in Qtz1 grains, and transgranular fluid inclusion planes are only observed in the Sierra  
7  
8 363 Almagrera mining district. Relative chronology criteria indicate that Qtz1-tg1 predates Qtz1-tg2.  
9  
10 364 Each set of plane displays a distinct orientation (Figure 2-d-e-f; Table 3).

#### 13 365 **4.2.2 V-Qtz2, quartz veins parallel to or oblique to host-rock foliation**

16 366 V-Qtz2 (thickness of about 10 cm) are oblique to the rock foliation along certain sections of  
17  
18 367 the vein, while other parts are parallel (Figure 3-a). Since V-Qtz2 partly crosscuts the rock foliation,  
19  
20 368 they are considered as postdating V-Qtz1, which is parallel to the foliation. V-Qtz2 are  
21  
22 369 characterized by anhedral quartz grains of about 3-5 mm, showing undulose extinction. These  
23  
24 370 grains are characterized by wave-shaped grain-boundaries and subgrain boundaries. Subgrain  
25  
26 371 rotation and bulging recrystallization processes can be distinguished (Figure 3-b). Microstructures  
27  
28 372 indicate dynamic recrystallization processes at slightly lower temperatures than V-Qtz1 (Figure 3-b;  
29  
30 373 Passchier & Trouw, (2005)). Fluid inclusions in V-Qtz2 are found within intragranular (Qtz2-ig)  
31  
32 374 (Figure 3-b-c) or transgranular planes (Qtz2-tg) (Figure 4-a-b-e). The direction and dip of Qtz2-ig  
33  
34 375 fluid inclusion planes are randomly distributed (Figure 3-e) throughout the vein, but are parallel to  
35  
36 376 each other within a single grain. This suggests that these veins are related to crystallographic  
37  
38 377 directions reactivated during crystal plastic deformation rather than tectonic fracturing. Qtz2-tg  
39  
40 378 veins are parallel to each other and to the walls of V-Qtz2 (Figure 4-b-e). They were likely  
41  
42 379 produced by crack-and-seal deformation.

#### 47 380 **4.2.3 V-Qtz3, oblique veins from the mining district**

50 381 V-Qtz3 are composed of euhedral quartz associated with hematite, developed in veins  
51  
52 382 (thickness < 5 cm) oblique to the host-rock foliation or in voids. Although euhedral Qtz3 overgrows  
53  
54 383 Qtz2 (Figure 4-b), it is never intersected by Qtz2-tg. Isolated primary fluid inclusions are  
55  
56 384 interpreted as contemporaneous to crystal growth (Qtz3-p; Figure 4-f). Hematite is found within  
57  
58 385 microfissures extending from the wall rock to Qtz2 (Figure 4-b-d) and in voids between euhedral  
59  
60

1  
2 386 Qtz3 (Figure 4-a-b). The lack of microfractures affecting Qtz3 and the almost systematic  
3  
4 387 association of Qtz3 with hematite minerals suggest that both minerals grew during the same  
5  
6 388 mineralization event.  
7

#### 8 9 389 **4.2.4 V-ore, oblique mineralised veins from the mining district**

10  
11 390 An extensive study of ore mineralogy in the mining district (Morales Ruano, 1994) shows the  
12  
13 391 occurrence of abundant siderite, barite, pyrite, marcasite, galena, chalcopryrite, sphalerite,  
14  
15 392 tetrahedrite-tennantite, veenite, gersdorffite and bournonite and trace amounts of pyrrhothite,  
16  
17 393 bismuthinite, arsenopyrite and bravoite. Our sampled veins (V-ore) show only part of this  
18  
19 394 paragenesis.  
20

21  
22 395 V-ore veins crosscut V-Qtz1 (Figure 5-a), V-Qtz2 and V-Qtz3 (Figure 4-a). The thickness of  
23  
24 396 the sampled V-ore veins can reach several dm. They are distributed in two main clusters striking  
25  
26 397 N000-160E and N120-130E. Micro-euhedral quartz (0.5-1.0 mm) is observed on the walls of V-ore  
27  
28 398 (Figure 5-a) predating siderite formation. Pyrite is included in siderite (Figure 5-c). Galena occurs at  
29  
30 399 the contact between siderite and barite (Figure 5-b). The mineral sequence can be summarized as  
31  
32 400 follows: micro-euhedral quartz-siderite-pyrite-galena-barite (Figure 5-c).  
33

34  
35 401 Qtz-ore-tg inclusions are parallel to the wall rock and crosscut several micro-euhedral quartz  
36  
37 402 grains. Fluid inclusions in siderite and barite are observed along cleavage planes and interpreted as  
38  
39 403 primary (Figure 5-d-e).  
40  
41

#### 42 43 404 **4.2.5 V-Cal, oblique calcite veins from the subsident area**

44  
45 405 These lenticular tension gashes crosscut V-Qtz2 and attain a length of several cm with an  
46  
47 406 opening of a few mm (Figure 6-a). Fluid inclusions are found as clusters and are interpreted as  
48  
49 407 primary (Figure 6-b-c).  
50  
51

### 52 53 408 **4.3. Microthermometry and Raman results**

54  
55 409 Table 3 presents data concerning the size, shape and filling of the fluid inclusions. The  
56  
57 410 characteristic phase-transition temperatures and calculated compositions of fluid inclusions are  
58  
59  
60

1  
2 411 reported in Table 4 and Figure 7. Aqueous carbonic fluid inclusions are recorded in quartz veins  
3  
4 412 (Qtz1-tg1, tg2, Qtz2-ig, Qtz2-tg and Qtz3-tg), whereas aqueous fluid inclusions are recorded in ore  
5  
6 413 veins.

#### 9 414 **4.3.1 Fluid inclusions in Qtz1**

10  
11 415 The salinity of Qtz1-tg1 ranges between 9.7 and 22.6 mass% NaCl<sub>eq.</sub>, with  $T_h$  (L) between  
12  
13 416 319 and 350 °C. The volatile phase is predominantly CO<sub>2</sub> (70-85 vol%), with minor amounts of  
14  
15 417 CH<sub>4</sub> (10-17 vol %) and N<sub>2</sub> (0-18 vol%).

16  
17  
18 418 The salinity of Qtz1-tg2 ranges between 21.6 and 23.8 mass% NaCl<sub>eq.</sub>, with  $T_h$  (L) between  
19  
20 419 305 and 344 °C. The volatile phase is predominantly CO<sub>2</sub> (89-97 vol %), with minor amounts of  
21  
22 420 CH<sub>4</sub> (0-8 vol%) and N<sub>2</sub> (0-7 vol%).

#### 23 421 **4.3.2 Fluid inclusions in Qtz2**

24  
25  
26  
27  
28 422 The salinity of Qtz2-ig ranges between 11.9 and 20.6 mass% NaCl<sub>eq.</sub>, with  $T_h$  (L) between 220  
29  
30 423 and 400 °C. This broad scatter of homogenization temperatures is attributed to volume modification  
31  
32 424 of fluid inclusions during high-temperature deformation (Vityk *et al.*, 1995, Bodnar, 2003,  
33  
34 425 Diamond *et al.*, 2010). Therefore, we only consider  $T_h$  of intact inclusions with the smallest gas  
35  
36 426 bubbles (flw > 65 vol %), resulting in a range from 220 to 355 °C. The volatile phase is dominated  
37  
38 427 by CO<sub>2</sub> (87-98 vol %), with minor amounts of CH<sub>4</sub> (1-8 vol %) and N<sub>2</sub> (1-7 vol %).

39  
40  
41 428 The salinity of Qtz2-tg ranges between 0.1 and 2.4 mass% NaCl<sub>eq.</sub>, with  $T_h$  (L) between 290  
42  
43 429 and 330 °C. Raman spectroscopy shows that the volatile phase is predominantly CO<sub>2</sub> (57-85 vol %),  
44  
45 430 with presence of CH<sub>4</sub> (5-30 vol %), N<sub>2</sub> (7-12 vol %) and H<sub>2</sub>S (1-5 vol %).

#### 46 47 48 431 **4.3.3 Fluid inclusions in Qtz3**

49  
50  
51 432 The salinity of Qtz3-p ranges between 12.7 and 20.9 mass% NaCl<sub>eq.</sub>, with  $T_h$  (L) between 235  
52  
53 433 and 310 °C. The volatile phase is predominantly CO<sub>2</sub> (91-99 vol %), with minor amounts of CH<sub>4</sub> (1-  
54  
55 434 7 vol %) and N<sub>2</sub> (0-5 vol %).

56  
57  
58 435

#### 4.3.4 *Fluid inclusions in Qtz, Sd and Brt from V-ore veins*

The salinity of Qtz-ore-tg ranges between 18.4 and 25.0 mass% NaCl<sub>eq.</sub>. Methane (traces) is the only volatile present.  $T_h(L)$  ranges between 150 and 248 °C.

The salinity of Sd-p ranges between 15.4 and 24.6 mass% NaCl<sub>eq.</sub>. Because no hydrohalite melting or clathrate dissociation temperature could be observed, our calculation is based on the final ice melting only and does not take into account the complexity of the fluid system. Therefore, some data yield salinity higher than halite saturation in the H<sub>2</sub>O-NaCl system.  $T_h(L)$  is observed between 110 and 222 °C. Such a large variation is likely related to leakage within this highly cleavable mineral (Bodnar, 2003). Raman spectroscopy shows that CH<sub>4</sub> is the only volatile in the gas phase.

The salinity of Brt-p ranges between 20.7 and 25.8 mass% NaCl<sub>eq.</sub>. Again, because hydrohalite is never observed, our calculations only take account of  $T_m(\text{ice})$  and the complexity of the system is not fully expressed. Therefore, some of our data show salinities higher than NaCl saturation in the H<sub>2</sub>O-NaCl system.  $T_h(L)$  is observed between 237 and 335 °C. Although the inclusions were carefully checked before and after measurements, leakage before microthermometric experiments cannot be excluded (Ulrich & Bodnar, 1988, Bodnar, 2003), so these values in barite should be considered very carefully. Raman spectroscopy shows that the volatile phase is predominantly composed of CO<sub>2</sub> (45-93 vol %) (although present in small amount) and N<sub>2</sub> (5-52 vol %) with minor CH<sub>4</sub> (0-5 vol %).

#### 4.3.5 *Fluid inclusions in calcite from V-Cal*

The salinity of Cal-p ranges between 11.8 and 18.4 mass% NaCl<sub>eq.</sub>, with  $T_h(L)$  between 67 and 87 °C (Figure 7). Raman spectroscopy does not allow us to identify the nature of the gas phase.

### 4.4. Halogen chemistry

For V-Qtz1, a Cl/Br molar ratio of 1000 is obtained by crush-leach analysis and LA-ICPMS for a chlorinity of 4200 mmol/kg solution (Figure 8). The crushing experiments release fluids derived from Qtz1-tg1 and Qtz1-tg2 as well as the fluid contained at grain boundaries.

1 461 Sd-p and Brt-p yield a Cl/Br ratio of between 3 500 and 10 000 for a chlorinity between 4 200  
2  
3  
4 462 and 5 400 mmol/kg solution, respectively. The Cl/Br ratio of Brt-p obtained with LA-ICP-MS is  
5  
6 463 between 1 200 and 4 500 (Figure 8). The other populations of fluid did not give an interpretable  
7  
8 464 signal.

#### 11 465 **4.5. Major and trace element chemistry**

14 466 In both types of fluids (Qtz1-tg1 (n=8), Qtz2-tg (n=2), Qtz3-p (n=4) and Brt-p (n=9))  
15  
16 467 inclusions major (Na, K, Mg) and trace elements (Li, Mn, Fe, Cu, Zn, Sr and Ba) have been  
17  
18 468 measured (Table 5, Figure 9). The other generations of fluids do not give any interpretable signals.

20 469 In Qtz1-tg1 high salinity fluid, Na content ranges from 27000 to 122 000 ppm, K from 2000  
21  
22 470 to 7600 ppm, yielding Na/K ratio ranging from 10 to 30. Mg content is relatively variable (100-  
23  
24 471 1600ppm). Li content is relatively high (200 to 1000 ppm). Mn, Fe, Ba and Sr display noticeable  
25  
26 472 concentration (Table 5, Figure 9).

29 473 On the contrary, Qtz2-tg having very low salinity show lower cation content and Na/K ratio is  
30  
31 474 ranging from 1 to 6. Due to the low salinity fluid, few data could be obtained.

34 475 Qtz3-p fluids displayed similar values as for Qtz1-tg1 (Na around 70 000 ppm). However K  
35  
36 476 content is lower (1500 ppm) and consequently Na/K ratio is higher (around 50). Mg, Sr, and Mn  
37  
38 477 content are the highest (Table 5, Figure 9).

40 478 In Brt-p fluids, Ba and Sr content could not be measured due to matrix contamination. Na  
41  
42 479 content is slightly lower than those of Qtz1-tg1 (20000 and 65000 ppm) whereas K content is  
43  
44 480 ranging from 2600 and 9500 ppm (Na/K: 4 to 10). It can be notice that Zn content could reach 4700  
45  
46 481 ppm. However, we cannot exclude a contribution of the barite crystal (Table 5, Figure 9).

#### 50 482 **4.6. Stable isotopes**

52 483  $\delta^{13}\text{C}$  in siderite ranges between  $-9.5$  and  $-10.9$  ‰<sub>V-PDB</sub> (n=4), while  $\delta^{18}\text{O}$  ranges between  
53  
54 484  $20.6$  and  $22.5$  ‰<sub>V-SMOW</sub> (Table 6).  $\delta^{18}\text{O}$  in barite ranges from  $13.0$  to  $13.2$  ‰<sub>V-SMOW</sub> (n=2), and  
55  
56 485  $\delta^{34}\text{S}$  (n=4) from  $19.4$  to  $23.1$ ‰<sub>V-CDT</sub>. Pyrite (n=3) yields  $\delta^{34}\text{S}$  between  $5.4$  and  $6.4$  ‰<sub>V-CDT</sub> and  
57  
58 486 galena (n=3) yields  $\delta^{34}\text{S}$  between  $-2.4$  and  $8.3$  ‰<sub>V-CDT</sub>.

1  
2 487 Table 6 reports the  $\delta^{18}\text{O}$  values of minerals containing fluid inclusions. White micas from the  
3  
4 488 host-rock yield  $\delta\text{D}$  values of  $-52 \pm 1$  ‰  $\text{V-SMOW}$ .  $\delta\text{D}_{\text{fluid}}$  values from Qtz1 sampled in the subsident  
5  
6 489 area (recrystallised quartz devoid of visible inclusions) range between  $-33$  and  $-36$  ‰  $\text{V-SMOW}$ .  
7  
8 490 Former trapped fluid inclusions appear to have been transported to the grain boundaries during  
9  
10 491 hydrolytic weakening (e.g. (Kerrick, 1976, Wilkins & Barkas, 1978, Johnson & Hollister, 1995,  
11  
12 492 Hollister, 1990, Bakker & Jansen, 1990, 1994), so it is likely that remnants of this fluid were  
13  
14 493 measured. In the mining district, V-Qtz1 veins host Qtz1-tg1 and Qtz1-tg2 type inclusions. The  
15  
16 494 transgranular fluid inclusion planes show  $\delta\text{D}$  values between  $-28$  and  $-32$  ‰  $\text{V-SMOW}$ , possibly  
17  
18 495 reflecting the influence of  $\delta\text{D}$  inherited from earlier fluids displaced to grain boundaries during  
19  
20 496 quartz recrystallization.  
21

22  
23  
24 497  $\delta\text{D}_{\text{fluid}}$  from Qtz2-ig and Qtz3-p inclusions cover a similar range between  $-23$  and  $-36$  ‰  $\text{V-SMOW}$   
25  
26 498 (Table 6, Figure 10).  $\delta\text{D}_{\text{fluid}}$  from Qtz2-tg (selected section with dominant Qtz2-tg inclusions  
27  
28 499 in the quartz grains) display a larger range of values between  $-17$  and  $-48$  ‰  $\text{V-SMOW}$  (Table 6,  
29  
30 500 Figure 10).  
31

32  
33 501 V-ore veins are significantly more D-depleted.  $\delta\text{D}_{\text{fluid}}$  of Sd-p range between  $-65$  and  $-80$  ‰  
34  
35 502  $\text{V-SMOW}$ .  $\delta\text{D}_{\text{fluid}}$  of Brt-p ranges between  $-53$  and  $-69$  ‰  $\text{V-SMOW}$  (Table 6, Figure 10).  
36

## 37 503 **5. Discussion**

### 38 504 **5.1. Key criteria to reconstruct the fluid sequence**

39  
40  
41 505 Early fluid stage: Ductile deformation affecting V-Qtz1 and V-Qtz2 in the Sierra Almagrera  
42  
43 506 is compatible with top-to-the-W / top-to-the-SW extensional shearing similar to that observed in the  
44  
45 507 Sierra de los Filabres (Augier *et al.*, 2005c) (Figure 1). This deformation is not dated in the Sierra  
46  
47 508 Almagrera. The only known age constraint is given by the youngest ductile extensional stages  
48  
49 509 recognized within the Betics metamorphic pile, which are dated around the Langhian-Serravalian  
50  
51 510 boundary at 14 Ma (Gomez-Pugnaire *et al.*, 2004, Platt *et al.*, 2006, Gomez-Pugnaire *et al.*, 2012).  
52

53  
54  
55 511 Although no fluid inclusions are observed in V-Qtz1 veins sampled from the subsident area,  
56  
57 512 crushing techniques allowed us to extract a fluid, which could then be analysed for its  $\delta\text{D}$ . This  
58  
59  
60

1  
2 513 suggests that fluid inclusions trapped prior to plastic deformation are displaced towards grain  
3  
4 514 boundaries during recrystallization processes (Kerrick, 1976, Wilkins & Barkas, 1978, Johnson &  
5  
6 515 Hollister, 1995) and are then partly preserved. The calculated equilibrium temperature between this  
7  
8 516 fluid and host-rock, based on hydrogen isotope fractionation, is comprised between 488 and 520 °C  
9  
10 517 (Table 6), which is in agreement with ductile conditions. Plastically deformed or dismembered  
11  
12 518 inclusions are found within intragranular planes of V-Qtz2 (Qtz2-ig), while non-deformed  
13  
14 519 inclusions are found within transgranular planes affecting V-Qtz1 in the mining district where V-  
15  
16 520 ore barite veins are also frequently present. Transgranular planes result from the healing of former  
17  
18 521 open cracks (Lespinasse, 1999, Lespinasse et al., 2005), and thus more brittle conditions are  
19  
20 522 required than for intragranular planes. As a consequence, Qtz2-ig likely formed at conditions more  
21  
22 523 ductile than Qtz1-tg1, 2.

24  
25  
26 524 Similar microthermometric phase transitions are observed for Qtz2-ig and Qtz1-tg1, 2  
27  
28 525 (average  $T_h$  around 340 °C and with comparable maximum salinity). Relative chronology criteria  
29  
30 526 indicate that Qtz1-tg1 predates Qtz1-tg2, but no other direct data allow us to constrain the  
31  
32 527 chronological position of Qtz1-tg (1, 2) in the general fluid history. Two interpretations can be  
33  
34 528 proposed. The dominant NW-SE strike of Qtz1-tg1 may be consistent with late Tortonian  
35  
36 529 shortening directions associated with strike-slip tectonics (Montenat & Ott D'estevou, 1990). This  
37  
38 530 deformation occurred prior to the Messinian N-S to NNE-SSW shortening that could correspond to  
39  
40 531 the subsequent Qtz1-tg2 fluid inclusion planes. In such a scenario, the transgranular fluid inclusions  
41  
42 532 could be coeval with V-ore mineralizing events displaying similar tectonic directions, and thus  
43  
44 533 would not correspond to an early fluid trapped during the brittle-ductile transition.

45  
46  
47  
48 534 An alternative explanation would be that both kinds of microcracks are related to brittle  
49  
50 535 extensional fracturing, implying that the tectonic regime previously expressed by ductile  
51  
52 536 deformation belongs to an earlier stage of exhumation. In such a case, the brittle deformation would  
53  
54 537 predate the onset of a Late Miocene transcurrent regime related to the mineralizing events.  
55  
56 538 Therefore,  $\sigma_3$  measured normal to the microcracks would be similar for both the extensional and  
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59  
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1  
2 539 transcurrent regimes, with the result that this question cannot be resolved solely on the basis of  
3  
4 540 structural criteria. If fluids were trapped soon after the ductile-brittle transition for quartz, this  
5  
6 541 would explain certain similarities of the microthermometry and salinity data with Qtz2-ig fluid  
7  
8 542 inclusions trapped during this transition.  
9

10 543 Intermediate fluid stage: Qtz2-tg fluids are characterised by a much lower salinity than  
11  
12 544 observed in the other types of fluid inclusions. Since Qtz2-tg never affects V-Qtz3 nor V-Cal, this  
13  
14 545 suggests an episodic arrival of low-salinity fluid after the formation of V-Qtz2 but prior to V-Qtz3  
15  
16 546 and V-Cal. Considering the youngest ages inferred for ductile deformation in the eastern Betics  
17  
18 547 (around the Langhian-Serravalian boundary), the exhumation of this part of the Sierra Almagrera  
19  
20 548 within the brittle domain probably occurred during Langhian to Serravalian times. Only marine  
21  
22 549 sediments of Serravalian age are preserved further north in the Aguilas block (Griveaud *et al.*,  
23  
24 550 1990). Younger sediments of Late Serravalian – Early Tortonian age recognized further west in the  
25  
26 551 Huerca Overa Basin (Pedrera *et al.*, 2010) are represented by alluvial fan deposits reflecting the  
27  
28 552 uplift of mountain ranges prior to the return of marine conditions in the Vera Basin from Late  
29  
30 553 Tortonian times onwards (Figure 1). The uplift of the Sierra de los Filabres bordering the Huerca  
31  
32 554 Overa Basin has been linked to a local N-S extension (Augier *et al.*, 2005a) or the onset of  
33  
34 555 transcurrent tectonics (Montenat & Ott D'estevou, 1990). Regardless of the associated tectonic  
35  
36 556 regime at this time, the paleogeography suggests that hydrogeological conditions within the brittle  
37  
38 557 crust favoured the input of meteoric water from the uplifted ranges into the upper reservoir, but  
39  
40 558 prior to the Late Tortonian return to marine conditions.  
41  
42  
43  
44

45 559 Pre-ore fluid stage: The obliquity with respect to the host-rock foliation and the lack of  
46  
47 560 undulose extinction in the euhedral quartz shows that V-Qtz3 formed within the brittle domain.  
48  
49 561 Euhedral Qtz3 formed during the same event that led to the formation of hematite. The input of Fe  
50  
51 562 in the fluid is related here to an increase of salinity. Although oxidizing conditions prevailed at a  
52  
53 563 certain stage of the fluid evolution, it is possible that early siderite was subsequently oxidized.  
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1  
2 564 Ore fluid stage: V-ore veins crosscut V-Qtz3 (Figure 4-a). The maximum salinities are  
3  
4 565 observed either in fluid inclusions from transgranular planes within early micro-euhedral quartz on  
5  
6 566 the wall-rock (Qtz-ore-tg), or in primary fluid inclusions from siderite and barite (Sd-p and Brt-p).  
7  
8 567 The formation of siderite postdating V-Qtz3-hematite veins not only indicates the ongoing input of  
9  
10 568 Fe in the fluid, but also a shift towards reducing conditions. Quartz and siderite trapped fluids at  
11  
12 569 lower temperatures ( $T_h$  of Sd-p around 190 °C) compared with the pre-ore fluid stage ( $T_h$  of Qtz3-p  
13  
14 570 around 265 °C). V-ore vein sets have two main strike directions: N000E-N340E and N120E-  
15  
16 571 N130E. The N-S trend is coherent with the Messinian direction of horizontal shortening and E-W  
17  
18 572 extension, being related to the major transcurrent activity of the Palomares Fault Zone. The  
19  
20 573 interpretation of fluid inclusions in barite is more problematic. The data appears to indicate an  
21  
22 574 increase of  $T_h$  compared to the estimated conditions of siderite formation (Figure 7), but  $T_h$   
23  
24 575 obtained from this kind of mineral are usually considered to be overestimated (Ulrich & Bodnar,  
25  
26 576 1988). This raises the question of the chronological position of N-S to NNE-SSW-striking fluid  
27  
28 577 inclusion planes belonging to Qtz1-tg2, since both Brt-p and Qtz1-tg2 show closely similar  $T_h$   
29  
30 578 values and high salinities (Figure 7). It is possible that this similarity is just a coincidence or maybe  
31  
32 579 Qtz1-tg2 inclusions in quartz reflect a thermal pulse that leads to values typical of Brt-p.  
33  
34  
35  
36

37 580 Late fluid stage: Inclusions in calcite record lower  $T_h$  around 80 °C, suggesting formation at a  
38  
39 581 more superficial position. The relative chronology of this late stage in the fluid sequence could be  
40  
41 582 debated since the calcite veins were not sampled in the same structural block as V-ore veins. The  
42  
43 583 only chronological criterion is the crosscutting geometry with V-Qtz2.  
44  
45

## 46 584 **5.2. P-V-T-X evolution**

47  
48  
49 585 The Raman spectrometry study of graphitic schists constrains the maximum temperature  
50  
51 586 attained by the host-rock to 545-587 °C. These results are in agreement with metamorphic peak  
52  
53 587 temperatures of the Nevado-Filábride complex obtained in other parts of the orogen (De Jong, 2003,  
54  
55 588 Augier *et al.*, 2005b).  
56  
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1  
2 589 The  $P$ - $T$  ranges of fluid inclusion entrapment are constrained by the isochores and geothermal  
3  
4 590 gradients (Figure 11). For the Sierra Almagrera, geothermal gradient data are poorly documented.  
5  
6 591 The only available data comes from the Sierra Nevada located to the West of Sierra Almagrera,  
7  
8 592 where a gradient of 60 °C/km under lithostatic conditions is indicated for the final stages during  
9  
10 593 ductile deformation (Gomez-Pugnaire & Fernandez-Soler, 1987, Bakker *et al.*, 1989, Jabaloy *et al.*,  
11  
12 594 1993, Augier *et al.*, 2005b). A gradient of 30 °C/km is arbitrarily taken as an upper limit,  
13  
14 595 corresponding to the European average anorogenic gradient.

15  
16  
17 596 In the absence of other metamorphic constraints, hydrogen isotopes can be used to assess the  
18  
19 597 temperature of equilibrium between fluid inclusions and mica-rich host-rock (Tarantola *et al.*,  
20  
21 598 2007). In the case of isotopic equilibrium,  $P$ -  $T$  boxes are also constrained by the minimum and  
22  
23 599 maximum values of hydrogen equilibrium temperatures (Table 6 and Figure 11).

24  
25  
26 600 Early fluid stage: Qtz2-ig inclusion shapes range from euhedral to dismembered (Tarantola *et*  
27  
28 601 *al.*, 2010 and 2012), with large variations of the gas filling ratio. This is indicative of plastic  
29  
30 602 deformation and would thus be related to lithostatic pressure conditions. The box shown in Figure  
31  
32 603 11 is also constrained by minimum and maximum hydrogen equilibrium temperatures since the  
33  
34 604 calculated temperatures are of the order of 400-520 °C (Table 6).

35  
36  
37 605 Transgranular fluid inclusion planes Qtz1-tg1 and Qtz1-tg2 indicate brittle behaviour within  
38  
39 606 the quartz vein, but the mica-rich host-rock may still have been affected by ductile deformation.  
40  
41 607 Fluids may have been trapped during the brittle-ductile transition of mica-rich lithologies within a  
42  
43 608 temperature and pressure range already corresponding to brittle rheology for the quartz. In such a  
44  
45 609 case, both Qtz1-tg1 and Qtz1-tg2 possibly formed under a lithostatic regime. As an alternative  
46  
47 610 hypothesis, these microcracks may be indicative of a hydrostatic regime due to late Miocene  
48  
49 611 transcurrent tectonics that formed V-ore veins in the brittle domain. In fact, Qtz1-tg1/Qtz1-tg2  
50  
51 612 fluids seem to be in equilibrium with the host-rock (Table 6), but in strong disequilibrium with  
52  
53 613 respect to V-ore veins. In addition, the gas contents of Qtz1-tg1 and Qtz1-tg2 are more closely  
54  
55 614 similar than those of Sd-p and Brt-p fluid inclusions (Table 4). All these data suggest a resident

1  
2 615 fluid derived from the lower reservoir rather than the presence of fluids of external origin in the  
3  
4 616 upper reservoir. Finally, this explains why Qtz1-tg1 and Qtz1-tg2 could be related to the early fluid  
5  
6 617 stage in the selected scenario (Figure 11). Thus, the rather large  $T$  and  $P$  range reflects the trapping  
7  
8 618 conditions of inclusions related to this stage between Qtz2-ig (400-520 °C and 270-380 MPa) and  
9  
10 619 Qtz1-tg1, 2 (440-480 °C and 110-230 MPa) (Figure 11).

12  
13 620 Intermediate fluid stage: There is no evidence of whether transgranular Qtz2-tg planes formed  
14  
15 621 under a lithostatic or a hydrostatic fluid regime. From this intermediate stage of fluid evolution until  
16  
17 622 the final stages of fluid trapping, the hydrogen isotope fractionation seems to be no longer in  
18  
19 623 equilibrium between the fluid inclusions and the mica-rich host-rock (Table 6). Hydrogen  
20  
21 624 equilibrium temperature constraints do not allow us to define the  $P$ - $V$ - $T$ - $X$  boxes. The decrease of  
22  
23 625 salinity related to an input of surficial fluids rather suggests an opening of the system under  
24  
25 626 hydrostatic conditions. The trapping conditions for these fluid inclusions are in the range 300-450  
26  
27 627 °C and 40-140 MPa (Figure 11).

28  
29  
30 628 Pre-ore fluid stage: Since the euhedral quartz Qtz3 veins were no longer affected by ductile  
31  
32 629 deformation and recrystallization processes, it is considered that they crystallized in the brittle  
33  
34 630 domain under hydrostatic pressure, within the  $P$ - $T$  range: 250-380 °C and 40-120 MPa (Figure 11).

35  
36  
37 631 Ore fluid stage: Crystallization of quartz, siderite and barite occurred in an open system.  
38  
39 632 Hydrostatic conditions allow us to constrain the  $P$ - $T$  range of entrapment for fluid inclusions at 160-  
40  
41 633 300 °C and 30-90 MPa in Qtz-ore-tg and at 120-260 °C and 20-80 MPa in Sd-p (Figure 11).  
42  
43 634 Unfortunately, the confidence on microthermometric data obtained on barite is low (Ulrich &  
44  
45 635 Bodnar, 1988). The observed homogenization temperatures would imply a significant increase of  
46  
47 636 the trapping temperature to 280-440 °C at 40-130 MPa. This could be explained by a magmatic  
48  
49 637 input from contemporaneous active volcanism, but it could also be related to an overestimation due  
50  
51 638 to stretched inclusions in barite.  $T_h$  and salinity of Brt-p are similar to Qtz1-tg2 inclusions, while  
52  
53 639 strike directions of barite V-ore veins are more or less parallel to Qtz1-tg2 fluid inclusion planes.  
54  
55 640 These inclusions in quartz support the hypothesis of a thermal pulse defined by inclusions in barite.  
56  
57  
58  
59  
60

1  
2 641 In fact,  $P$ - $V$ - $T$ - $X$  data from Qtz1-tg2 (Figure 11) seem to indicate a significant increase of pressure  
3  
4 642 compared to Sd-p fluid trapping conditions, which is apparently incompatible with an ongoing  
5  
6 643 exhumation of the Sierra Almagrera. Hydrogen isotopic fractionation indicates a strong  
7  
8 644 disequilibrium between primary fluid inclusions from V-ore veins and the host-rock. On the  
9  
10 645 contrary, hydrogen isotope data for Qtz1-tg2 indicate a fluid in equilibrium, rather suggesting its  
11  
12 646 formation during an early fluid stage. This interpretation does not support the existence of a thermal  
13  
14 647 pulse.

15  
16  
17 648 Late fluid stage: The calcite stage is characterized by lower homogenization temperatures,  
18  
19 649 suggesting a cooling of the system down to 70-110 °C at 10-30 MPa hydrostatic pressure (Figure  
20  
21 650 11).

### 22 651 **5.3. Source of fluids**

23  
24  
25  
26  
27 652 Early fluid stage: Hydrogen isotope fractionation data showing equilibrium between fluid  
28  
29 653 inclusions and mica-rich host-rock suggest a resident fluid in the lower reservoir. The  $\delta D_{\text{fluid}}$  values  
30  
31 654 obtained from Qtz1 (early fluids displaced towards grain boundaries during recrystallization  
32  
33 655 processes) and Qtz2-ig ranging between  $-23$  and  $-36$  ‰  $V$ -SMOW (Table 6, Figure 10) are compatible  
34  
35 656 with a fluid of metamorphic origin.

36  
37  
38 657 V-Qtz1 quartz grains also containing Qtz1-tg1 and Qtz1-tg2 fluids yield similar  $\delta D$  values ( $-$   
39  
40 658  $28$  to  $-30$  ‰  $V$ -SMOW). Their halogen signatures plot along the seawater evaporation trend in  
41  
42 659 agreement with halite evaporation (Figure 8). At first sight, this would indicate a primary brine.  
43  
44 660 Two brine sources can be considered according to the geological history: Triassic and Messinian. It  
45  
46 661 is very unlikely that primary brines could have been preserved since Triassic times, considering the  
47  
48 662 metamorphic processes affecting the rocks in the lower reservoir. The other hypothesis would be to  
49  
50 663 explain Qtz1-tg1 and Qtz1-tg2 signatures as representing surficial brines coming from Messinian  
51  
52 664 pre-crisis evaporitic basins. This interpretation revives the hypothesis linking Qtz1-tg2 and Brt-p  
53  
54 665 inclusions during mineralization events. However, stable isotope results and  $P$ - $V$ - $T$ - $X$  data rather  
55  
56 666 identify fluids trapped in Qtz1-tg1 and Qtz1-tg2 microcracks as resident fluids that have undergone  
57  
58  
59  
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1  
2 667 long-time fluid-rock exchange with the mica-rich host-rock. The interaction of fluids with black  
3  
4 668 graphite schists may have led to a Br enrichment (Yardley, 2005) of secondary brines derived from  
5  
6 669 the dissolution of Triassic evaporites, which could explain the position of the data points on the  
7  
8 670 seawater evaporation curve (Figure 8).

9  
10 671 The variability observed in the salinity of both Qtz2-ig and Qtz1-tg1/Qtz1-tg2 fluids might  
11  
12 672 either reflect i) an original heterogeneity related to discontinuous interaction with Permo-Triassic  
13  
14 673 evaporites, ii) the effect of plastic deformation for Qtz2-ig (Diamond *et al.*, 2010), or iii) a mixing  
15  
16 674 between deep high-salinity and a low-salinity fluid end-members.

17  
18  
19 675 Intermediate fluid stage: Fluid isotope values obtained on Qtz2 grains containing Qtz2-tg also  
20  
21 676 incorporate the signature of fluids from the early stage displaced to grain boundaries during  
22  
23 677 recrystallization processes.  $\delta D_{\text{fluid}}$  values ranging from  $-17$  to  $-48$  ‰<sub>v-SMOW</sub> are generally lower  
24  
25 678 than values obtained for the early fluid stage.  $\delta D$  values of the dilute fluid are thus D-depleted  
26  
27 679 compared to those of the early stage, with values that are unlikely to be buffered by the host-rock  
28  
29 680 (Table 6). This suggests the input of an external low-salinity fluid from the upper reservoir, which  
30  
31 681 did not interact with evaporites/metaevaporites (i.e. Permo-Triassic).

32  
33  
34  
35 682 It is possible that the volume of low-salinity fluids was sufficient to dilute high-salinity fluids  
36  
37 683 from the early stage, or more likely, the lower ductile and the upper brittle reservoirs were not  
38  
39 684 connected during exhumation and thus behaved independently. The penetration of low-salinity  
40  
41 685 fluids is likely associated with the uplift of mountain ranges during the Serravalian and Early  
42  
43 686 Tortonian (Martínez-Martínez & Azañón, 2002, Platt, 2007) (Figure 12). However, in the absence  
44  
45 687 of  $\delta^{18}\text{O}$  values and interpretable LA-ICP-MS data, it cannot be concluded whether this fluid is of  
46  
47 688 meteoric or basinal origin.

48  
49  
50 689 Pre-ore fluid stage: Hydrogen isotopic composition is not buffered by the host-rock (Table 6).  
51  
52 690 The enrichment of iron in the fluid led also to the formation of hematite in the voids between Qtz3  
53  
54 691 crystals (Figure 4-b and Figure 12). This stage corresponds to tectonic conditions in the brittle  
55  
56 692 domain.

1  
2 693 The salinity is comparable to that in the early fluid stage.  $\delta^{18}\text{O}_{\text{quartz}}$  is lower than for the early  
3  
4 694 fluid stage, and trapping temperatures define a  $\delta\text{D}/\delta^{18}\text{O}_{\text{fluid}}$  signature shifted towards  
5  
6 695 basinal/meteoric water compositions. The major and trace elements (Na/K ratio around 50, Sr/Ba  
7  
8 696 ratio around 20 and Sr, Mg content, Table 5) of this fluid reflect a basinal origin (Yardley, 2005).  
9  
10 697 These data are coherent with mixing between low-salinity basinal/meteoric fluids and with an  
11  
12 698 upward migration of high-salinity fluids coming from the lower reservoir. This may reflect the  
13  
14 699 onset of transcurrent tectonics during this period, and a structural connection between the two  
15  
16 700 reservoirs through the brittle ductile transition zone (Figure 12).

17  
18  
19 701 Ore fluid stage: Although siderite from El Arteal in the mining district yields slightly lower  
20  
21 702  $\delta^{13}\text{C}$  (about 2 ‰, with values of  $-9.5$  and  $-10.9$  ‰  $\text{V-PDB}$ ) and slightly higher  $\delta^{18}\text{O}$  (about 1 ‰  $\text{V-}$   
22  
23 703  $\text{SMOW}$ ), it can be compared with the siderite from Jaroso Ravine (Figure 1-b). The results from this  
24  
25 704 latter locality have been interpreted as indicative of meteoric water and low-temperature  
26  
27 705 hydrothermal conditions (Martinez-Frias *et al.*, 2007). However,  $\delta^{13}\text{C}$  may also be buffered by the  
28  
29 706 metasedimentary sequence during fluid interaction, whatever the origin of the fluids.

30  
31  
32 707 The combination of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values suggests a fluid with a magmatic or metamorphic  
33  
34 708 signature (Field & Fifarek, 1985). As well as having a high salinity, the fluids do not fit the  
35  
36 709 meteoric water line (Figure 10), thus contradicting the conclusions of Martinez-Frias *et al.* (2007).  
37  
38 710 Since  $\delta\text{D}_{\text{fluid}}$  is strongly in disequilibrium with the host-rock, this implies an external source for the  
39  
40 711 ore fluid, so it cannot be of meteoric origin.

41  
42  
43 712 Fluids in siderite were trapped at lower temperatures than the previous fluid stages, and thus  
44  
45 713 at shallower depths (Figure 12). The fluid inclusions in siderite show higher values of salinity than  
46  
47 714 obtained for the earlier stages, reaching up to 25 mass%  $\text{NaCl}_{\text{eq}}$ . (Figure 7, Table 4). Cl/Br data  
48  
49 715 show that the fluid is Br-depleted and far from the seawater evaporation trend. As Br is not easily  
50  
51 716 incorporated in halite, dissolution of halite would yield this type of fluid. Cl/Br ratios thus indicate  
52  
53 717 signatures that could be compared to secondary brines (Banks *et al.*, 2000) resulting from  
54  
55 718 dissolution of evaporites (Figure 8).

1 719 The strong salinity increase might result from a combination of volcanism in the Palomares  
2  
3 720 Fault Zone, as suggested by  $\delta D$  and  $\delta^{18}O$  values (Figure 10), and dissolution of evaporites as  
4  
5  
6 721 suggested by their halogen signatures (Figure 8). The strike direction of the veins is coherent with  
7  
8 722 the Messinian strike-slip regime related to major activity of the Palomares Fault Zone (Montenat *et*  
9  
10 723 *al.*, 1987, Booth-Rea *et al.*, 2004). Of major interest here is the  $\delta^{34}S$  composition of barite, which is  
11  
12 724 more closely comparable to Miocene sea water (Claypool *et al.*, 1980, Morales Ruano *et al.*, 1995)  
13  
14 725 than Triassic values. Therefore, the increase of salinity in the ore fluid stage compared to previous  
15  
16 726 stages could also be related to secondary brines linked to the dissolution of Messinian evaporites  
17  
18 727 rather than exclusively of Triassic evaporites. Dissolution of Messinian marginal evaporites  
19  
20 728 (deposited from 5.96 to 5.67 Ma ago in the Sorbas basin) (Clauzon *et al.*, 1996, Bourillot *et al.*,  
21  
22 729 2009) is a possible scenario (Figure 12). These Messinian evaporites preceded the main sea-level  
23  
24 730 drop related to the peak of the salinity crisis (5.60-5.46 Ma). Pre-incision Messinian evaporitic  
25  
26 731 deposits were available, as revealed by the “Formation à blocs” in the Vera basin, which reworked  
27  
28 732 Messinian early gypsum during the main incision event (Figure 12) (Clauzon, 1980, Clauzon *et al.*,  
29  
30 733 1996). Messinian sediments from Las Herrerias (Figure 1) were mineralised prior to the main  
31  
32 734 Messinian incision (Alvado, 1986, Fortuin *et al.*, 1995, Booth-Rea *et al.*, 2004), and such a scenario  
33  
34 735 would provide a relatively accurate dating of the mineralizing event around 5.65 Ma (Figure 12).  
35  
36  
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38

39 736 A thermal pulse at constant salinity is suspected because the fluid trapping conditions in barite  
40  
41 737 exceed 400 °C, but this result should rather be considered as an artefact arising from this particular  
42  
43 738 mineral (Figure 12). If the high-K calc-alkaline, shoshonitic and ultrapotassic magmatism were  
44  
45 739 related to mineralization during the ore-fluid stage, this could represent a possible metal source. The  
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47 740 high contents of K or metals such Zn or Cu in fluid inclusions (Table 5, Figure 9) tend to support  
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49 741 this hypothesis, but a leaching of basement rocks could also be an alternative explanation.  
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52 742 Late fluid stage: Homogenization temperatures of fluid inclusions within calcite around 80 °C  
53  
54 743 suggest deep burial or a shallow expression of hot fluids. The salinity of these fluids may be  
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56 744 compared to the salinity of early and pre-ore stages. Calcite veins may correspond to a shallow  
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2 745 expression of deeper fluid flows, recorded as veins currently cropping out in the uplifted block  
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4 746 represented by the mining district (Figure 12). In such a case, the superficial equivalent of rocks in  
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6 747 the central block may have been eroded during the subsequent uplift, but preserved in the subsident  
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8 748 block to the West. A second hypothesis is that these calcite veins only developed during a later  
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10 749 stage at lower temperature.

11  
12 750 Fluids trapped as fluid inclusion planes during the early stage are characterized by a rather  
13  
14 751 low density of the CO<sub>2</sub>-rich volatile phase. The significant presence of CH<sub>4</sub> (around 20% of the  
15  
16 752 volatile molar composition) is not strictly expected in the case of water-graphite equilibrium  
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18 753 (Dubessy, 1984, Huizenga, 2001, 2011). Such a distribution of volatiles is fairly common in  
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20 754 metamorphic environments at around 350-450 °C, where local equilibrium is reached between  
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22 755 water and graphite. Through mixing with other fluids, this contributes to the common metamorphic  
23  
24 756 signature found in most retrograde fluids during exhumation (Cathelineau *et al.*, 1993, Boiron *et al.*,  
25  
26 757 2003). At lower temperatures, in the presence of graphite, CH<sub>4</sub> is expected to be the dominant  
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28 758 species if redox conditions are moderately reducing. This applies in the case of a predominance of  
29  
30 759 CH<sub>4</sub> in fluid inclusions during the precipitation of siderite at the beginning of the Ore stage, which  
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32 760 occurred with a  $T_h$  around 190 °C. The precipitation of siderite from Fe<sup>2+</sup>-rich solutions requires a  
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34 761 significantly low  $fO_2$  and an increase in  $fCO_2$ .

## 35 36 37 38 39 40 762 **6. Conclusions**

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43 763 Fluid circulation events are recorded within the studied veins at different positions of the  
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45 764 Sierra Almagrera metamorphic belt during its exhumation. The general  $P$ - $T$  path is characterized by  
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47 765 an evolution from lithostatic to hydrostatic conditions. Despite the rather exceptional constant fluid  
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49 766 composition throughout exhumation, different geological contexts associated with fluid circulation  
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51 767 can be considered: i) a first stage during which the host-rock passed through the brittle-ductile  
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53 768 transition and the quartz trapped metamorphic fluids, ii) a second stage when the host-rock  
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55 769 definitively entered the brittle domain and predominantly collected shallower fluids from the upper  
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57 770 reservoir and, iii) a final stage, related to ore formation and possibly magmatism as well, resulting  
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2 771 in a marked tectonic change that modified the relative hydrogeologic independence between the  
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4 772 deeper and upper reservoirs.

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6 773 More generally, the tectonic and paleotopographic evolution of the Sierra Almagrera leads us  
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8 774 to consider two stages in the fluid circulation history. Prior to the transcurrent tectonic regime, the  
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10 775 metamorphic rocks of the Sierra Almagrera were exhumed as a whole, and V-Qtz1 and V-Qtz2  
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12 776 veins were developed throughout the studied area. The onset of transcurrent tectonics had two  
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14 777 consequences: i) it localized the deformation and associated fluid pathways within the brittle crust  
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16 778 and, ii) it generated local transtension and transpression leading to final exhumation of the central  
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18 779 area corresponding to the mining district where V-Qtz3 and V-ore veins are found.

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21 780 The first record of exhumation is characterized by ductile-brittle deformation related to  
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23 781 extensional tectonics. We propose that, during this early stage, metamorphic brines resulted from  
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25 782 the dissolution of Triassic evaporites. Low-salinity fluids were then recorded as the structural unit  
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27 783 progressively entered the brittle domain. These low-salinity fluids are likely related to the  
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29 784 penetration of basinal or meteoric waters from the surface, favoured by a hydraulic gradient related  
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31 785 to the uplift of mountain ranges during late Serravalian to early Tortonian times.

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34 786 The upper fluids could have retained their specific characteristics until the present-day, but  
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36 787 the geodynamic changes related to the onset of Trans-Alboran tectono-volcanism modified the  
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38 788 hydrogeological decoupling between the lower and upper reservoirs. The pre-ore stage is  
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40 789 characterized by the occurrence of brittle quartz veins related to intermediate salinity and  
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42 790 homogenization temperatures indicative of mixing between meteoric or basinal fluids and the  
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44 791 upward migration of high-salinity fluids coming from the lower reservoir. These fluids are similar  
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46 792 to those from the early fluid stage. They have a volatile phase dominated by CO<sub>2</sub> but devoid of CH<sub>4</sub>,  
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48 793 being associated with Fe which is expressed by the formation of hematite under oxidizing  
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50 794 conditions, but possibly after the crystallization of primary siderite. This pre-ore stage can be  
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52 795 interpreted as the first evidence of the influence of volcanism.

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2 796 Reducing conditions prevailed at a later stage of Fe-rich fluid migration. This is reflected by  
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4 797 the formation of siderite and Fe sulphides in the mining district, and is related to the activity of the  
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6 798 Palomares sinistral fault zone during the Messinian. An evolution towards more oxidizing  
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8 799 conditions led to the formation of galena and barite, whose  $\delta^{34}\text{S}$  signatures indicate the involvement  
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10 800 of Miocene sulphate. This suggests the involvement of a second type of secondary brines (Ore  
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12 801 stage) which may have dissolved Messinian evaporites from the Vera Basin. Since the marginal  
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14 802 evaporitic basins in the Betics are dated at around 5.96 to 5.67 Ma (Sorbas basin; Bourillot *et al.*  
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16 (2009)), and since the Las Herrerias stratabound ore-deposits were incised during the main  
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18 803 Messinian salinity crisis and sea-level fall in the Mediterranean domain (5.6-5.46 Ma), this scenario  
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20 804 would provide an accurate constraint on the age of the mineralization stage around 5.65 Ma  
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24 806 The overall evolution of fluid migration in this part of the Betic Cordillera points out the role  
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26 807 of three main driving forces: i) an exhumation path related to an overall cooling, ii) a drastic change  
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28 808 to transcurrent tectonics associated with hydrogeological connections at depth favouring the ascent  
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30 809 of hot hydrothermal fluids and, iii) the involvement of two types of secondary brines, an input from  
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32 810 the deep reservoir involving Triassic evaporites and a more recent input from the Messinian at the  
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34 811 surface, which might have caused the migration and concentration of elements of economic interest.  
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36 812 The interference between these factors influenced the redox conditions within the upper brittle  
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38 813 reservoir, leading to an alternation of oxidizing and reducing conditions that controlled the  
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40 814 formation of Fe-rich minerals ((siderite?) hematite, then siderite-pyrite). The deep penetration of  
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42 815 late-stage oxidizing Messinian secondary brines is related to the crystallization of barite. This  
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44 816 process reflects the existence of large convection cells extending from the surface to deep aquifers,  
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46 817 associated with transtensional tectonics and local heat flow, which are presumed to be related to  
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48 818 Miocene magmatism at depth.  
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21 1206  
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25 1208 Figure 1: a) Geological context of the Eastern Betics and location of the Sierra Almagrera (modified after Augier  
26 1209 (2004)). b) Geological map of the Sierra Almagrera, Vera basin and Palomares fault zone (modified after Booth-Rea  
27 1210 (2004) and Montenat & Ott D'estevou (1990), and location of sampling areas. c) Poles of mineralized V-ore veins  
28 1211 (barite and siderite) in El Arteal tunnel represented on lower-hemisphere stereogram.

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30 1212  
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32 1213 Figure 2: a) V-Qtz1 quartz vein parallel to the rock foliation. b) Optical microphotograph under cross-polarized light  
33 1214 (XPL) showing petrography of Qtz1: static recrystallization (120° angles) and grain boundary migration  
34 1215 recrystallization. c) Qtz1: recrystallised quartz with transgranular FIP. d) Qtz1-tg1 FIP. e) Qtz1-tg2 FIP. f) Pole  
35 1216 projections of Qtz1-tg1 and Qtz1-tg2 fluid inclusion planes represented on lower hemisphere stereogram. Arrows  
36 1217 indicate the directions of opening. L for liquid, V for vapour and S for solid.

37 1218  
38 1219 Figure 3: a) V-Qtz2 quartz vein locally parallel to the foliation (upper part), while the main section is discordant to the  
39 1220 foliation (central part). b) Relationship between petrography of recrystallised quartz (subgrain rotation and bulging) and  
40 1221 fluid inclusions. c) Optical microphotographs under plane-polarized light showing intragranular Qtz2-ig. d) Deformed  
41 1222 fluid inclusion Qtz2-ig. e) Pole projections of Qtz2-ig fluid inclusion planes represented on lower-hemisphere  
42 1223 stereogram.

43 1224  
44  
45 1225 Figure 4: a) N10E V-Qtz2 discordant to the foliation reopened as V-Qtz3, intersected by V-ore discordant vein. Optical  
46 1226 microphotographs under natural light: b) Contact between Qtz2 and Qtz3. Qtz2 grains still showing undulose extinction  
47 1227 and affected by Qtz2-tg. Qtz3 euhedral quartz containing only Qtz3-p primary fluid inclusions. Hematite microfissures  
48 1228 affecting Qtz2. Hematite also filling open spaces between Qtz3 crystals. c) Zoom of zone localized in b). d) Hematite in  
49 1229 reflected light. e) Qtz2-tg. f) Qtz3-p.

50 1230  
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52 1231 Figure 5: Optical microphotographs of V-ore and related minerals, in plane-polarized light (PPL), cross-polarized light  
53 1232 (XPL) and reflected light (RL). a) Vein of siderite and micro-euhedral quartz (XPL). b) Sequence of siderite, galena and  
54 1233 barite (PPL+ RL). c) Schematic representation of chloritoid-schist breccia cemented by various minerals (V-ore). d) Sd-  
55 1234 p primary fluid inclusion in siderite. e) Brt-p in barite.

56 1235  
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58 1236 Figure 6: a) V-Qtz2 oblique quartz vein intersected by V-Cal oblique calcite vein. b) Relationships between V-Qtz2  
59 1237 grains, Qtz2-tg and calcite vein containing Cal-p. c) Detail of Cal-p.

1 1238 Figure 7: Microthermometry and salinity data for all types of fluid inclusions from the Sierra Almagrera.

2 1239

3 1240 Figure 8: Cl/Br molar ratio vs. Cl concentration for fluid inclusions analysed both by LA-ICP-MS (empty symbols) and  
 4 1241 crush-leach methods (CL, full symbols) (samples from the mining district). The seawater evaporation trend is indicated  
 5 1242 (Fontes & Matray, 1993) as SW: Seawater, G: Gypsum, H: Halite, E: Epsomite, S: Sylvite, C: Carnallite, B: Bischofite.  
 6 1243 Comparison data (crush-leach analysis) in boxes 1 to 4: 1—Variscan fluids equilibrated with host rocks (granite and  
 7 1244 metamorphic rocks), (Boiron *et al.*, 2003), 2—Primary brines derived from Triassic evaporites in the Pyrenees (Mccaig  
 8 1245 *et al.*, 2000), 3—Primary brines from Ag deposits in Morocco (Essarraaj *et al.*, 2005), 4—Secondary brines associated  
 9 1246 with emerald mineralization in Columbia (Banks *et al.*, 2000).

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11 1248 Figure 9: Box-and-whisker plots showing the concentrations of various elements concentrations (in ppm) in fluid  
 12 1249 inclusions Qtz1-tg1, Qtz2-tg, Qtz3-p and Brt-p obtained by LA-ICP-MS method (other FI did provide significant  
 13 1250 signal). Sr and Ba concentrations are not significant for Brt-p because of the presence of the element in the ablated  
 14 1251 mineral matrix. Lower whiskers, bottoms of boxes, red central lines, tops of boxes and upper whiskers represent 10th,  
 15 1252 25th, 50th, 75th and 90th percentiles respectively. n, number of fluid inclusions analysed, it is identical for all the  
 16 1253 elements.

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18 1255 Figure 10:  $\delta^{18}\text{O}_{\text{fluid}} \text{‰ V-SMOW}$  vs.  $\delta\text{D}_{\text{fluid}} \text{‰ V-SMOW}$  for Qtz2-ig, Qtz3-p and Sd-p fluids. Fields of some representative  
 19 1256 fluids from the literature: basinal fluids (Sheppard (1986): GC = Gulf Coast; C = California; M= Michigan).  
 20 1257 Metamorphic and magmatic fluids boxes are plotted from Field and Fifarek (1985).

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22 1259 Figure 11:  $P$  (MPa) vs.  $T$  ( $^{\circ}\text{C}$ ) of fluid inclusion stages in the Sierra Almagrera. l.p.: geothermal gradient at lithostatic  
 23 1260 pressure; h.p.: geothermal gradient at hydrostatic pressure.

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25 1262 Figure 12: Exhumation of the Sierra Almagrera with associated tectonic regime, paleo-orographic evolution and  
 26 1263 paleofluid sequence

27 1264

28 1265 Table 1: Abbreviations referring to microthermometric experiments.

29 1266

30 1267 Table 2: Nomenclature, location and description of sampled veins

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32 1269 Table 3: Nomenclature, chronology and characteristics of fluid inclusions. Abbreviations: -tg stands for transgranular, -  
 33 1270 ig for intragranular and -p for primary, L: liquid, V: vapour, acc.: accidentally trapped mineral, Sd: siderite, Brt: barite,  
 34 1271 Cal: calcite.

35 1272

36 1273 Table 4: Microthermometric and compositional data for all generations of fluid inclusions from the Sierra Almagrera  
 37 1274 (values of mode in italics). - : not determined

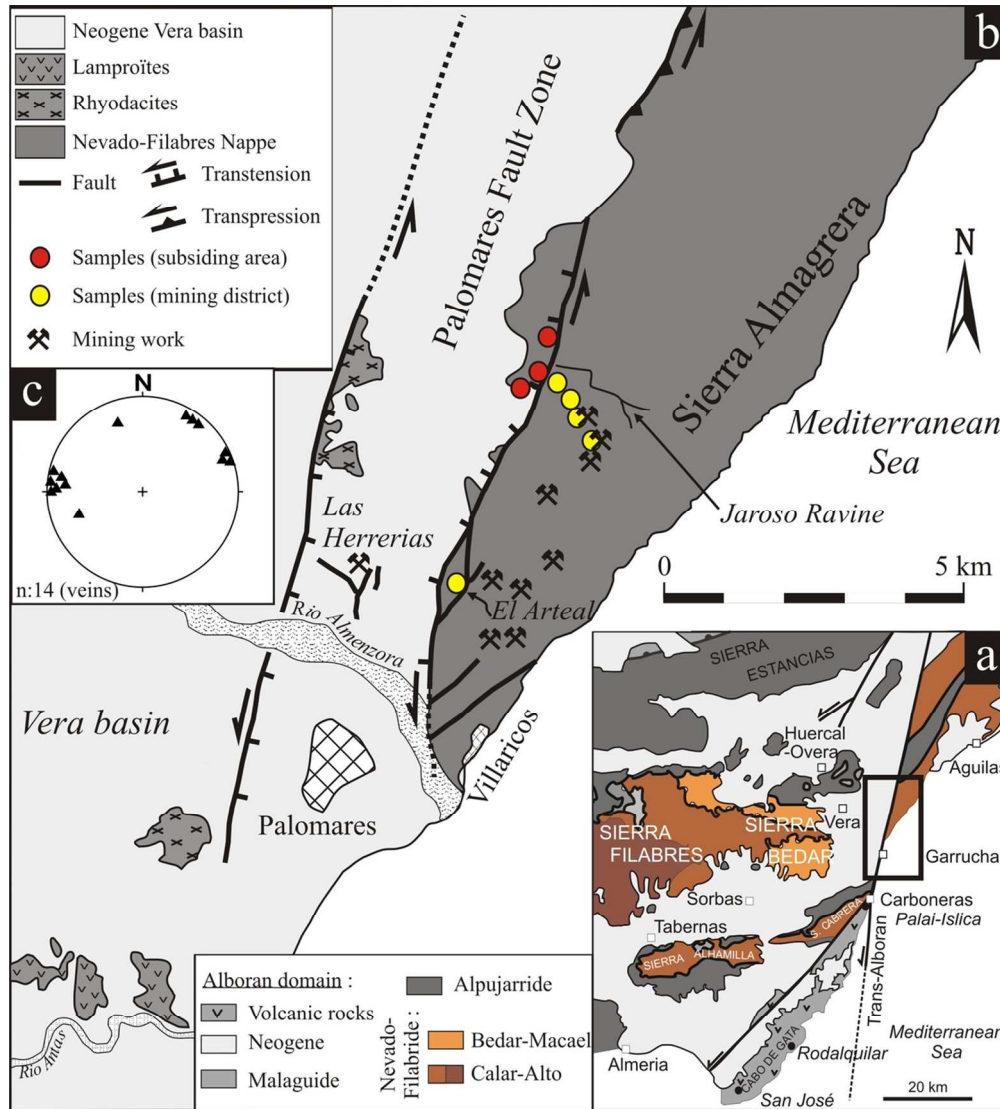
38 1275

39 1276 Table 5: LA-ICP-MS data for four generations of fluid inclusions from the Sierra Almagrera. Concentrations are given  
 40 1277 in ppm and Na/K are mass ratios. - : not determined

41 1278 Table 6: Isotopic data for various stages of fluid inclusions from the Sierra Almagrera, - : not determined.

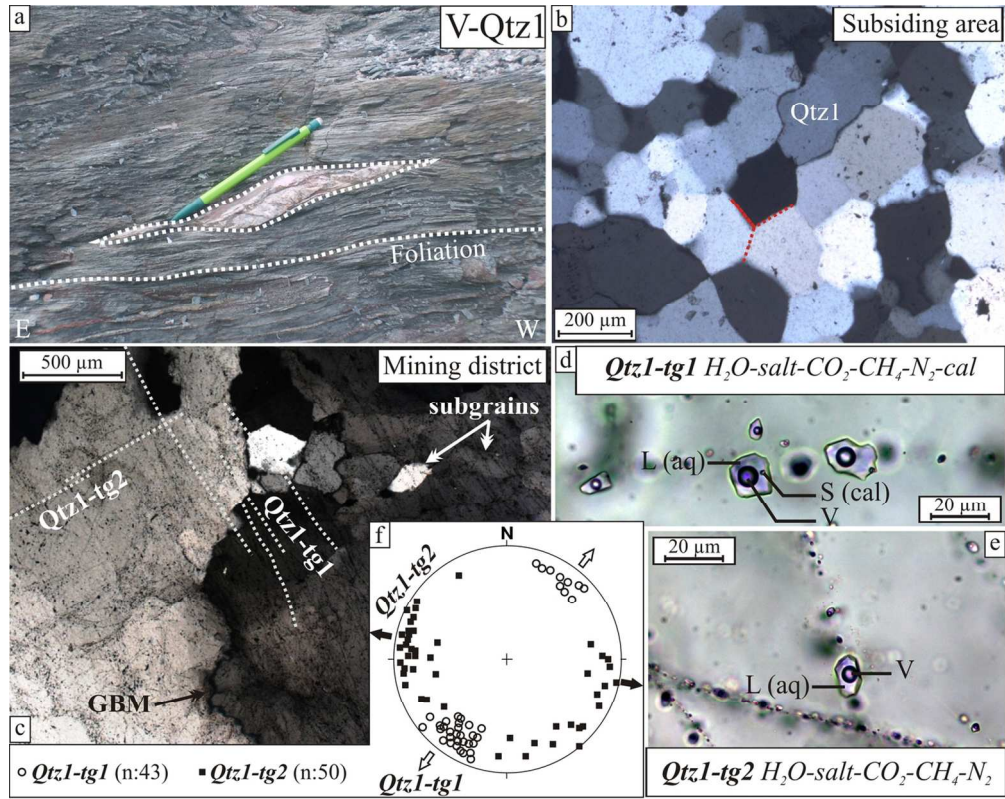
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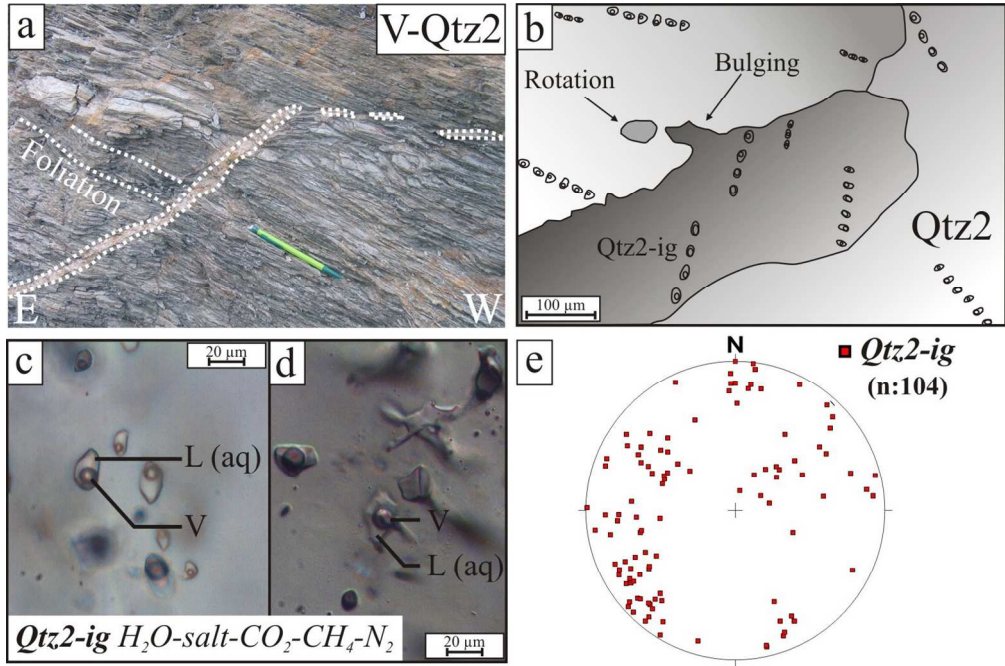
a) Geological context of the Eastern Betics and location of the Sierra Almagrera (modified after Augier (2004)). b) Geological map of the Sierra Almagrera, Vera basin and Palomares fault zone (modified after Booth-Rea (2004) and Montenat & Ott D'estevou (1990)), and location of sampling areas. c) Poles of mineralized V-ore veins (barite and siderite) in El Arteal tunnel represented on lower-hemisphere stereogram.

109x121mm (300 x 300 DPI)



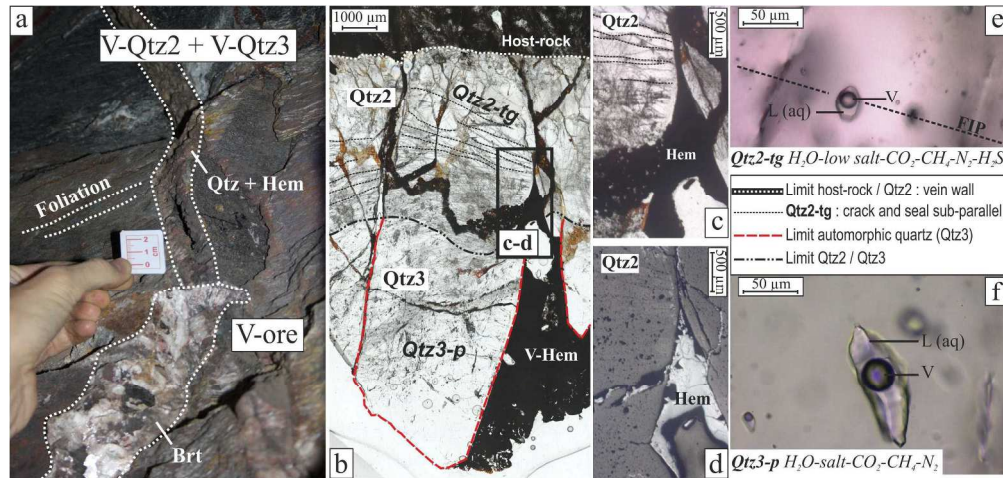
a) V-Qtz1 quartz vein parallel to the rock foliation. b) Optical microphotograph under cross-polarized light (XPL) showing petrography of Qtz1: static recrystallization (120° angles) and grain boundary migration recrystallization. c) Qtz1: recrystallised quartz with transgranular FIP. d) Qtz1-tg1 FIP. e) Qtz1-tg2 FIP. f) Pole projections of Qtz1-tg1 and Qtz1-tg2 fluid inclusion planes represented on lower hemisphere stereogram. Arrows indicate the directions of opening. L for liquid, V for vapour and S for solid.  
126x100mm (300 x 300 DPI)

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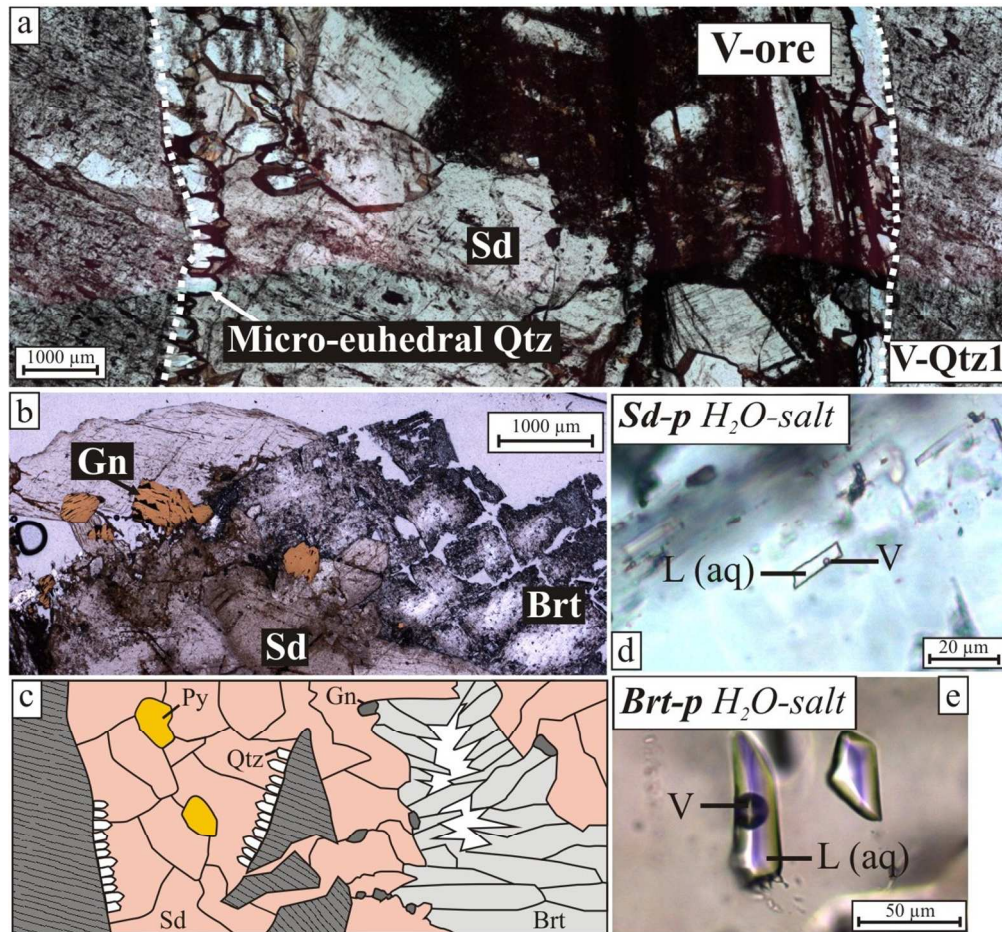


a) V-Qtz2 quartz vein locally parallel to the foliation (upper part), while the main section is discordant to the foliation (central part). b) Relationship between petrography of recrystallised quartz (subgrain rotation and bulging) and fluid inclusions. c) Optical microphotographs under plane-polarized light showing intragranular Qtz2-ig. d) Deformed fluid inclusion Qtz2-ig. e) Pole projections of Qtz2-ig fluid inclusion planes represented on lower-hemisphere stereogram.  
133x88mm (300 x 300 DPI)





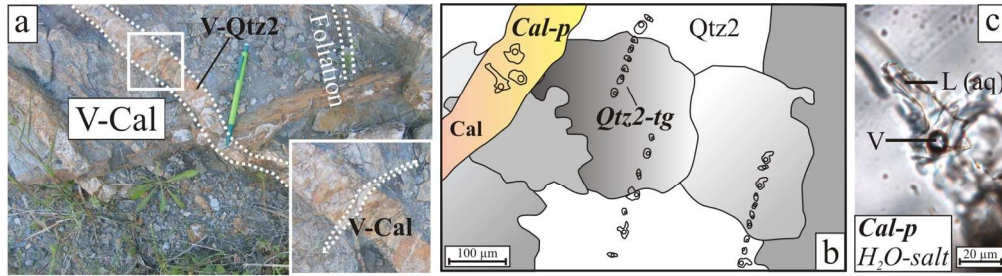
a) N10E V-Qtz2 discordant to the foliation reopened as V-Qtz3, intersected by V-ore discordant vein. Optical microphotographs under natural light: b) Contact between Qtz2 and Qtz3. Qtz2 grains still showing undulose extinction and affected by Qtz2-tg. Qtz3 euhedral quartz containing only Qtz3-p primary fluid inclusions. Hematite microfissures affecting Qtz2. Hematite also filling open spaces between Qtz3 crystals. c) Zoom of zone localized in b). d) Hematite in reflected light. e) Qtz2-tg. f) Qtz3-p.  
 239x113mm (300 x 300 DPI)



Optical microphotographs of V-ore and related minerals, in plane-polarized light (PPL), cross-polarized light (XPL) and reflected light (RL). a) Vein of siderite and micro-euhedral quartz (XPL). b) Sequence of siderite, galena and barite (PPL+ RL). c) Schematic representation of chloritoid-schist breccia cemented by various minerals (V-ore). d) Sd-p primary fluid inclusion in siderite. e) Brt-p in barite.

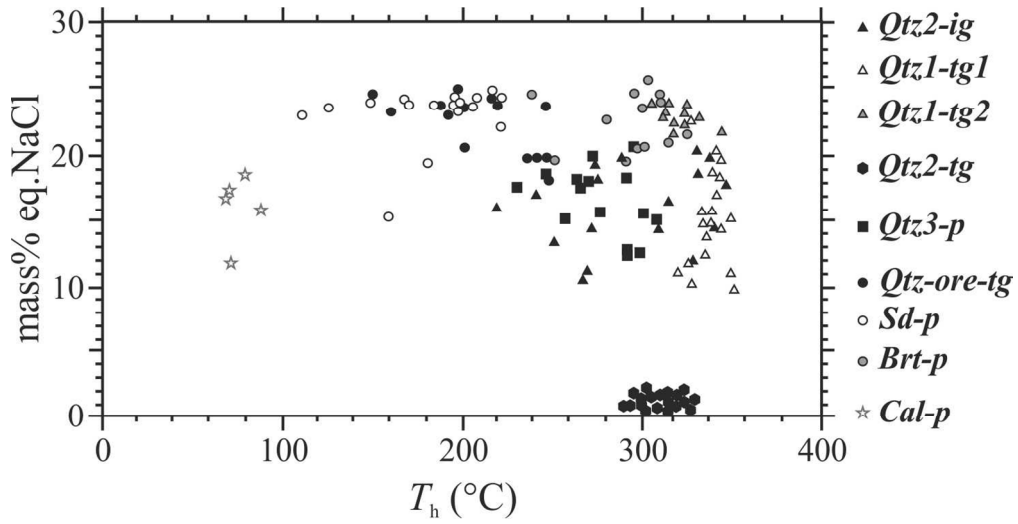
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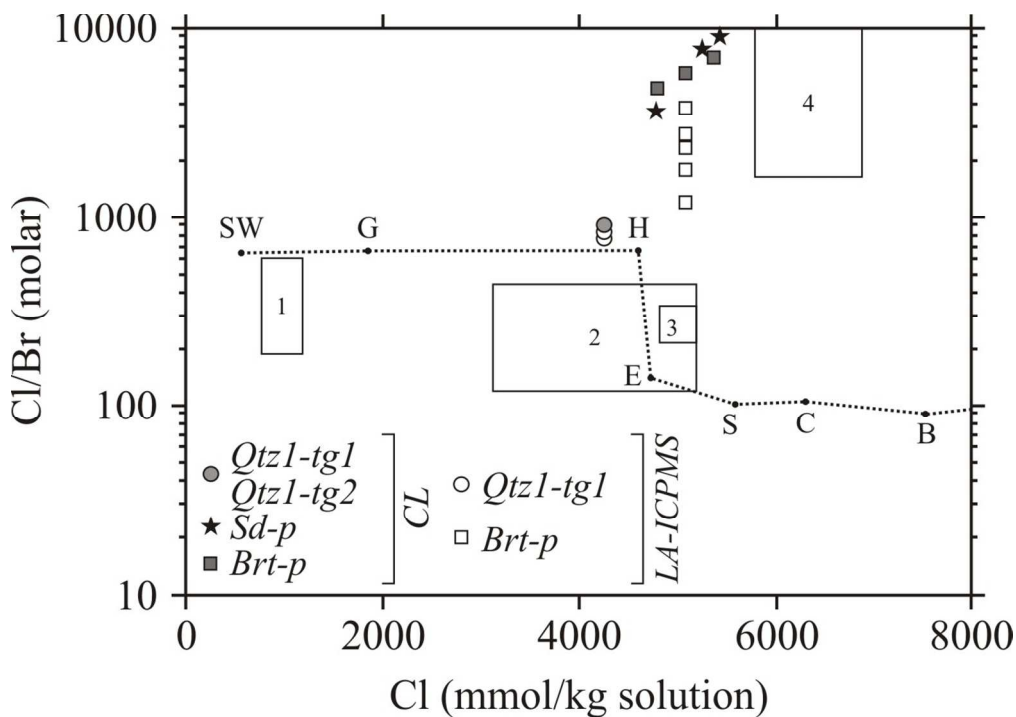


a) V-Qtz2 oblique quartz vein intersected by V-Cal oblique calcite vein. b) Relationships between V-Qtz2 grains, Qtz2-tg and calcite vein containing Cal-p. c) Detail of Cal-p.  
161x44mm (300 x 300 DPI)

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Microthermometry and salinity data for all types of fluid inclusions from the Sierra Almagrera.  
124x63mm (300 x 300 DPI)

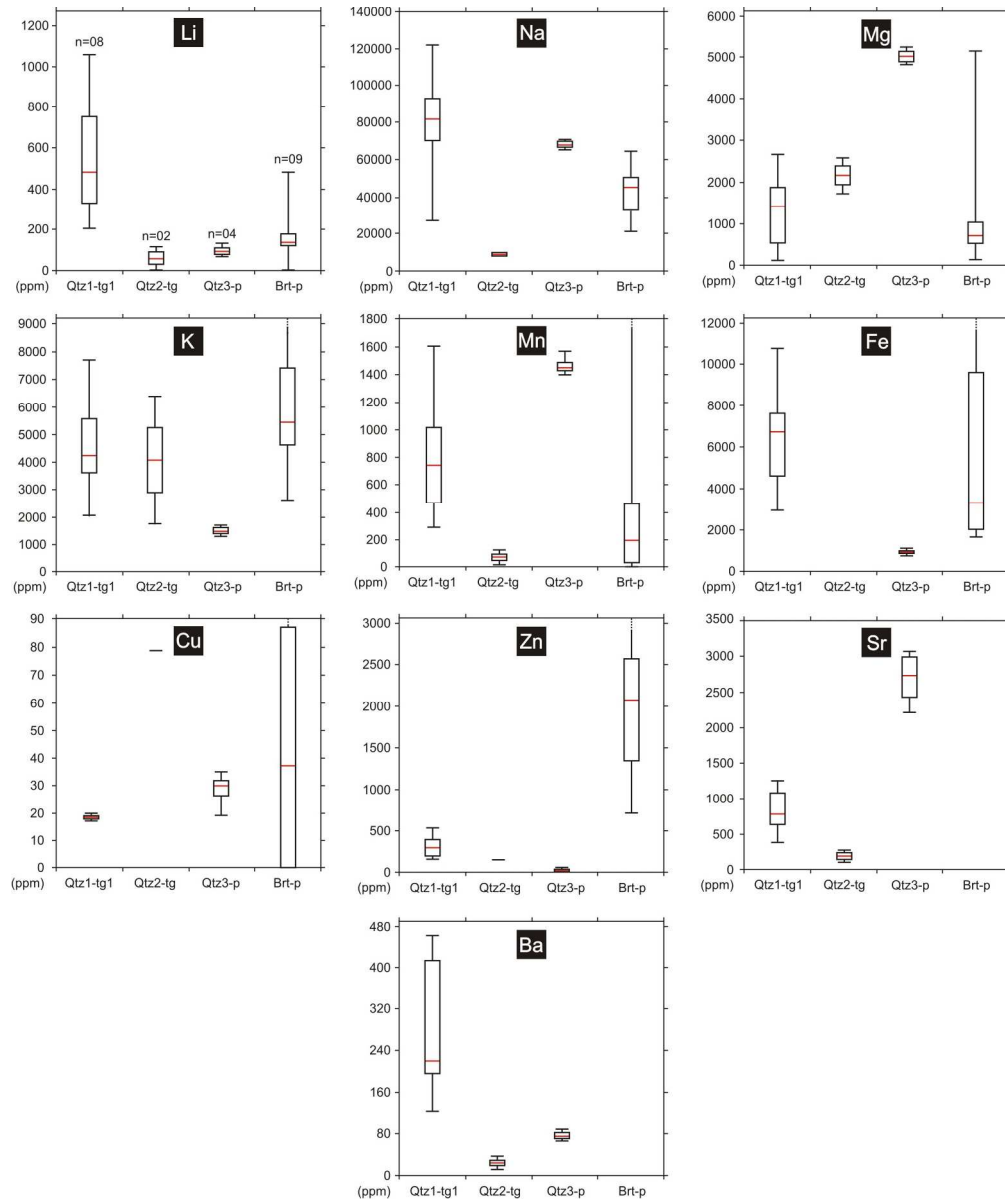


Cl/Br molar ratio vs. Cl concentration for fluid inclusions analysed both by LA-ICP-MS (empty symbols) and crush-leach methods (CL, full symbols) (samples from the mining district). The seawater evaporation trend is indicated (Fontes & Matray, 1993) as SW: Seawater, G: Gypsum, H: Halite, E: Epsomite, S: Sylvite, C: Carnallite, B: Bischofite. Comparison data (crush-leach analysis) in boxes 1 to 4: 1—Variscan fluids

equilibrated with host rocks (granite and metamorphic rocks), (Boiron et al., 2003), 2—Primary brines derived from Triassic evaporites in the Pyrenees (Mccaig et al., 2000), 3—Primary brines from Ag deposits in Morocco (Essarraj et al., 2005), 4—Secondary brines associated with emerald mineralization in Columbia (Banks et al., 2000).

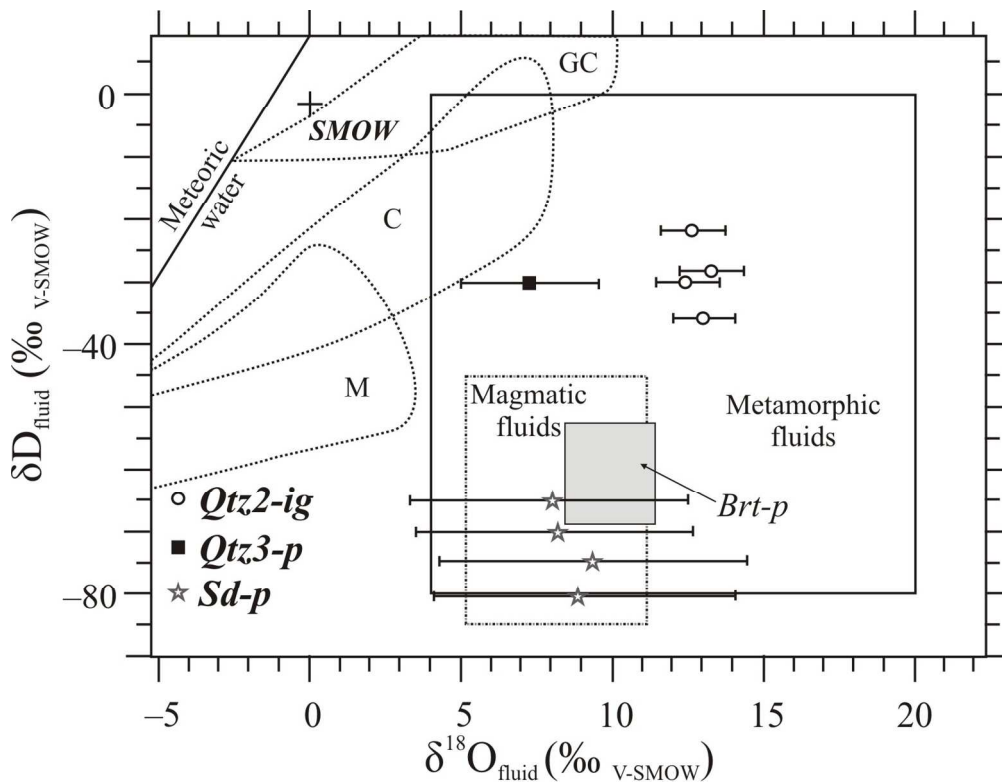
116x82mm (300 x 300 DPI)





Box-and-whisker plots showing the concentrations of various elements concentrations (in ppm) in fluid inclusions Qtz1-tg1, Qtz2-tg, Qtz3-p and Brt-p obtained by LA-ICP-MS method (other FI did provide significant signal). Sr and Ba concentrations are not significant for Brt-p because of the presence of the element in the ablated mineral matrix. Lower whiskers, bottoms of boxes, red central lines, tops of boxes and upper whiskers represent 10th, 25th, 50th, 75th and 90th percentiles respectively. n, number of fluid inclusions analysed, it is identical for all the elements.

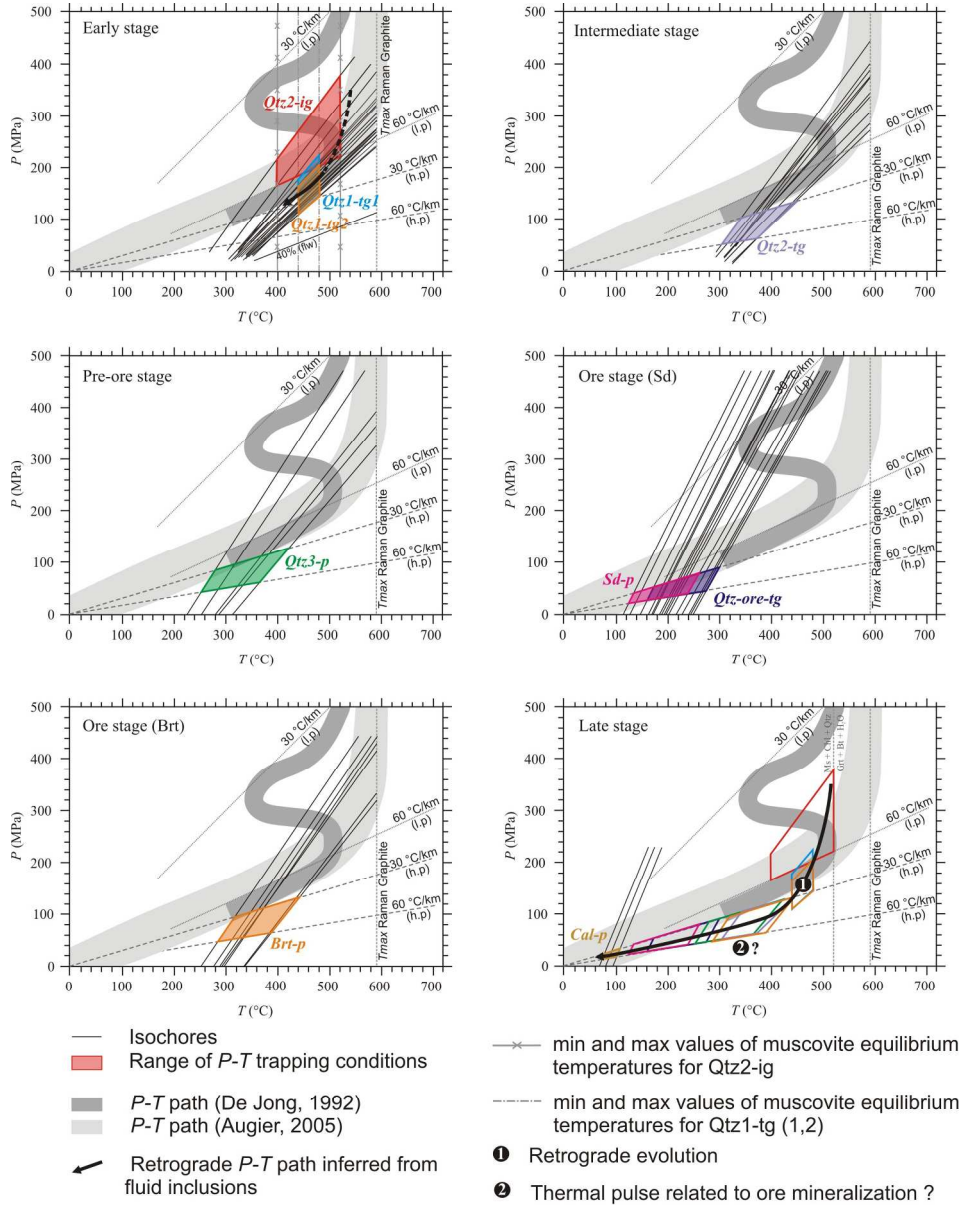
194x231mm (300 x 300 DPI)



$\delta^{18}\text{O}_{\text{fluid}} \text{‰ V-SMOW}$  vs.  $\delta\text{D}_{\text{fluid}} \text{‰ V-SMOW}$  for Qtz2-ig, Qtz3-p and Sd-p fluids. Fields of some representative fluids from the literature: basinal fluids (Sheppard (1986): GC = Gulf Coast; C = California; M= Michigan). Metamorphic and magmatic fluids boxes are plotted from Field and Fifarek (1985).  
 146x113mm (300 x 300 DPI)

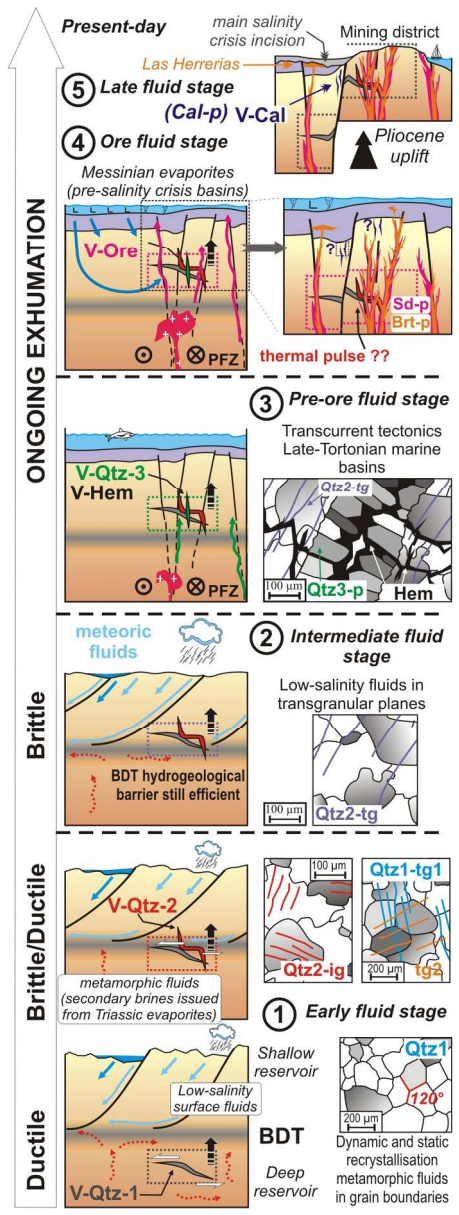


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P (MPa) vs. T (°C) of fluid inclusion stages in the Sierra Almagrera. l.p.: geothermal gradient at lithostatic pressure; h.p.: geothermal gradient at hydrostatic pressure.  
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Exhumation of the Sierra Almagrera with associated tectonic regime, paleo-orographic evolution and paleofluid sequence  
77x208mm (300 x 300 DPI)

Abbreviation	Observation
-p	Primary fluid inclusion
-ig	Intragranular fluid inclusion plane
-tg	Transgranular fluid inclusion plane
L	Liquid
V	Vapour
S	Solid
flw	Volume fraction of aqueous liquid
$T_e$	Eutectic or apparent eutectic temperature. First formation of visible liquid of solid aqueous phase on heating
$T_m(\text{ice})$	Final melting temperature of solid aqueous phase
$T_m(\text{cla})$	Dissociation temperature of clathrate
$T_h(\text{L})$	Bulk homogenization temperature via bubble-point transition ( $L+V=L$ )
$T_h(\text{V})$	Bulk homogenization temperature via dew-point transition ( $L+V=V$ )

1 Table: Abbreviations referring to microthermometric experiments. .

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Vein type and chronology	Location	Vein / rock foliation relationships	Vein mineralogy (this study)
V-Qtz1	Subsident area	Parallel to the rock foliation	Quartz (Qtz1)
	Mining district	Parallel	Quartz (Qtz1)
V-Qtz2	Subsident area	Parallel to oblique	Quartz (Qtz2)
	Mining district	Parallel to oblique	Quartz (Qtz2)
V-Qtz3	Mining district	Oblique	Quartz (Qtz3), Hematite
V-ore	Mining district	Oblique	Quartz, Siderite, Pyrite, Galena, Barite
V-Cal	Subsident area	Oblique	Calcite

1 Table: Nomenclature, location and description of sampled veins

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Vein type and chronology	Fluid inclusion petrography	Strike direction	Size (µm)	Shape	Filling	Flw (vol %)
V-Qtz1	-	Grain boundary	?		?	?
	Qtz1-tg1	N130°	~20	Equant, rounded Euhedral	L, V, acc. calcite	65-75 65-75
	Qtz1-tg2	N000° - N030°	15-25		L, V	
V-Qtz2	Qtz2-ig	Random	15-25	Euhedral to dismembered	L, V	50-80
	Qtz2-tg	N000° - N010°	10-15	Equant, rounded	L, V	70-80
V-Qtz3	Qtz3-p	Primary inclusions	>50	Elongated	L, V	70-75
V-ore	Qtz-ore-tg	N000° - N010°	5-10	Euhedral	L, V	70-90
	Sd-p	Primary (cleavage planes)	5-20	Euhedral, flat	L, V	70-90
	Brt-p	Primary (cleavage planes)	30-50	Euhedral, irregular	L or L, V	65-80
V-Cal	Cal-p	Isolated clusters	20-70	Irregular, flat	?	80-95

Table: Nomenclature, chronology and characteristics of fluid inclusions. Abbreviations: -tg stands for transgranular, -ig for intragranular and -p for primary, L: liquid, V: vapour, acc.: accidentally trapped mineral, Sd: siderite, Brt: barite, Cal: calcite.

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Fluid inclusion petrography	Fluid inclusion type	Microthermometry					Calculated composition						
		$T_e$ (°C)	$T_m(\text{Ice})$ (°C)	$T_m(\text{Cla})$ (°C)	$T_h$ (°C)	Salinity (mass% eq. NaCl)	$V_m$ (cm <sup>3</sup> /mol)	H <sub>2</sub> O (mol %)	CO <sub>2</sub> (mol %)	CH <sub>4</sub> (mol %)	N <sub>2</sub> (mol %)	H <sub>2</sub> S (mol %)	NaCl (mol %)
Qtz1-tg1	Aqueous carbonic	-48.6/-39.8 <i>-45.2</i>	-22.7/-7.7 <i>-14.5</i>	-3.8/6.5 <i>6.0</i>	319/350 <i>330</i>	9.7/22.6 <i>15.0</i>	23.1/29.2 <i>27.2</i>	85.2/88.1 <i>87.0</i>	1.9/3.6 <i>2.8</i>	0.01/0.1 <i>0.08</i>	0.01/0.05 <i>0.03</i>	-	9.5/11.3 <i>10.1</i>
Qtz1-tg2	Aqueous carbonic	-64.6/-39.8 <i>-55.1</i>	-23.1/- <i>17.6</i>	-5.7/-2.3 <i>-3.2</i>	305/344 <i>320</i>	21.6/23.8 <i>23.0</i>	22.8/25.6 <i>23.4</i>	80.7/84.2 <i>81.0</i>	2.8/5.2 <i>3.3</i>	0.01/0.3 <i>0.1</i>	0.01/0.06 <i>0.04</i>	-	12.3/16.4 <i>15.6</i>
Qtz2-ig	Aqueous carbonic	-45.7/-30.9 <i>-35.0</i>	-20.0/-8.4 <i>-16.0</i>	-2.5/-1.1 <i>-2.1</i>	220/355 <i>340</i>	11.9/20.6 <i>17.0</i>	25.3/30.0 <i>27.1</i>	82.3/89.1 <i>85.0</i>	2.4/5.6 <i>3.0</i>	0.01/0.3 <i>0.2</i>	0.01/0.07 <i>0.02</i>	-	10.1/12.8 <i>11.8</i>
Qtz2-tg	Aqueous carbonic	-	-3.0/-0.7 <i>-1.5</i>	7.3/12.3 <i>9.8</i>	290/330 <i>300</i>	0.1/2.4 <i>1.2</i>	20.5/27.0 <i>25.3</i>	92.3/96.2 <i>95.0</i>	2.5/4.1 <i>3.0</i>	0.01/0.2 <i>0.1</i>	0.05/0.3 <i>0.1</i>	0.03/0.07 <i>0.05</i>	0.1/2.5 <i>1.8</i>
Qtz3-p	Aqueous carbonic	-	-21.7/-9.0 <i>-17.3</i>	-2.7/-1.2 <i>-1.8</i>	189/308 <i>265</i>	12.7/20.9 <i>18.3</i>	20.7/23.0 <i>22.6</i>	89.2/94.1 <i>91.0</i>	1.2/3.2 <i>2.5</i>	0.01/0.1 <i>0.05</i>	0.01/0.06 <i>0.04</i>	-	5.2/8.8 <i>6.4</i>
Qtz-ore-tg	Aqueous	-49.6/-39.6 <i>-45.0</i>	-24.3/-14.7 <i>-21.2</i>	-	150/248 <i>210</i>	18.4/25 <i>23</i>	19.6/21.5 <i>20.5</i>	83.0/87.0 <i>85.0</i>	-	Trace	-	-	13.0/17.0 <i>15.0</i>
Sd-p	Aqueous	-49.0/-40.1 <i>-44.3</i>	-23.5/-11.4 <i>-23.2</i>	-	110/222 <i>190</i>	15.4/24.6 <i>24.1</i>	18.8/20.9 <i>19.4</i>	80.3/85.6 <i>83.0</i>	-	Trace	-	-	15.2/18.3 <i>17.0</i>
Brt-p	Aqueous	-59.1/-41.6 <i>-56.2</i>	-25.3/-17.7 <i>-22.4</i>	-	237/335 <i>305</i>	20.7/25.8 <i>23.0</i>	21.0/24.0 <i>23.0</i>	80.1/84.6 <i>82.0</i>	Trace	Trace	Trace	-	12.3/19.2 <i>18.0</i>
Cal-p	Aqueous	-	-15.0/-8.0 <i>-14.0</i>	-	67/87 <i>80</i>	11.8/18.4 <i>17.0</i>	18.6/18.9 <i>18.7</i>	87.2/89.1 <i>88.0</i>	-	-	-	-	10.4/13.1 <i>12.0</i>

Table: Microthermometric and compositional data for all generations of fluid inclusions from the Sierra Almagrera (values of mode in italics). - : not determined

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Fluid inclusion name	Li	Na	Mg	K	Mn	Fe	Cu	Zn	Sr	Ba	Na/K
Qtz1-tg1	1060	91098	1418	4407	1605	8376	-	523	1028	461	21
	328	69786	-	2936	400	2919	-	193	378	122	24
	543	90418	108	4994	748	5074	-	177	603	217	18
	325	70319	1444	7660	1021	6339	17	479	790	414	9
	202	27260	844	2043	285	7412	20	169	734	222	13
	750	122326	199	3847	730	7102	-	276	1217	215	32
	782	98756	2660	7222	1010	10758	-	360	1240	414	14
	569	73880	2274	3999	489	3161	-	286	641	136	18
Qtz2-tg	0	8198	1719	6347	18	-	-	-	268	13	1
	115	9551	2592	1734	122	-	80	135	104	35	6
Qtz3-p	118	69072	5173	1462	1442	953	31	21	3068	87	47
	126	68540	5236	1326	1563	1028	35	35	2958	80	52
	120	70210	4852	1652	1402	1032	19	15	2500	70	43
	145	67500	4956	1420	1453	856	29	42	2201	68	48
Brt-p	280	47306	1044	7522	310	2093	621	2075	-	-	6
	-	31792	5162	4613	10530	25082	-	4758	-	-	7
	483	63865	1379	6187	329	4438	-	1328	-	-	10
	121	64455	675	9458	842	1660	-	702	-	-	7
	176	45509	1005	4805	-	-	74	1858	-	-	9
	134	34292	511	3698	7	-	32	2124	-	-	9
	169	50607	704	5396	71	-	37	1341	-	-	9
	72	32586	444	7389	-	-	232	2688	-	-	4
125	21303	121	2629	36	-	94	2577	-	-	8	

1 Table: LA-ICP-MS data for four generations of fluid inclusions from the Sierra Almagrera. Concentrations are given in ppm and Na/K are mass ratios. - : not determined



Vein type	Fluid inclusion petrography	$\delta^{18}\text{O}_{\text{host}}$ (V-SMOW ‰) min - max ( <i>n</i> ) <i>median</i>	$T_{\text{trapping}}^{(1)}$ (°C)	$\delta^{18}\text{O}_{\text{fluid}}^{(2)}$ (V-SMOW ‰) min - max <i>median</i>	$\delta\text{D}_{\text{fluid}}$ (V-SMOW ‰) min to max ( <i>n</i> ) <i>median</i>	$T_{\text{equilibrium}}^{(3)}$ min to max (°C)
V-Qtz1	Grain boundary	16.5 - 16.7 (2) 16.6	-	-	-33 to -36 (2) -34.5	488 - 520
V-Qtz1	Qtz1-tg1+tg2	15.9 - 17.2 (2) 16.6	440 - 480	-	-28 to -30 (2) -29.0	442 - 478
V-Qtz2	Qtz2-ig	16.2 - 17.0 (4) 16.5	400 - 520	11.7 - 14.2 12.8	-23 to -36 (4) -30.0	404 - 520
V-Qtz2	Qtz2-tg	15.9 - 17.6 (7) 16.6	300 - 560	-	-17 to -48 (7) -34.0	365 - 704
V-Qtz3	Qtz3-p	14.0 - 14.5 (2) 14.3	250 - 380	5.0 - 9.6 7.4	-30 (1) -30	459
V-ore	Sd-p	20.6 - 22.5 (4) 21.5	120 - 260	3.2 - 14.5 8.8	-65 to -80 (4) -71.5	> 1630
V-ore	Brp-p	13.0 - 13.2 (2) 13.1	280 - 440	8.2 - 11.3 9.7	-53 to -69 (7) -58.0	831 - 1025

<sup>(1)</sup> Obtained from isochore intersection with PT-path

<sup>(2)</sup> Equation of Zheng (1993) for quartz-H<sub>2</sub>O fractionation; equation of Zheng (1999) for siderite-H<sub>2</sub>O and barite-H<sub>2</sub>O fractionation

<sup>(3)</sup> Equation of Suzuoki and Epstein (1976) for muscovite-H<sub>2</sub>O fractionation between  $\delta\text{D}_{\text{fluid}}$  and  $\delta\text{D}_{\text{host-rock}} = -52\text{‰}$

Table: Isotopic data for various stages of fluid inclusions from the Sierra Almagrera, - : not determined.