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Hydrothermal quartz and calcite in gypsum pseudomorphs: Tera Group, Tithonian-Berriasian, Cameros Basin.

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This study is focused on Tithonian-Berriasian fluvial and lacustrine-palustrine deposits in a rift basin located in Northern Spain. Analysis of the lacustrine deposits reveals an evolution from (1) shallow carbonate ramps in lakes, to (2) shallow alkaline ephemeral lakes, and then (3) carbonate lakes rich in organic matter. This evolution in facies indicates that these lakes evolved from open to more closed hydrologic conditions. The cause may be a tectonic one, with progressive rift development and faulting leading to progressive isolation. Limestones and dolostones formed in the alkaline lakes contain abundant lenticularly shaped gypsum pseudomorphs. Lenticular gypsum is considered to form early and displacively in association with evaporative conditions in the lake system. They are replaced by quartz and non-ferroan calcite (Ca-2, Fig. 1-3). The corrosion of the quartz by Ca-2 indicates that Ca-2 postdates quartz. Quartz contains solid inclusions of a former phase of non-ferroan calcite (Ca-1) anhydrite and less commonly celestine (Figs 2-3). Where Ca-2 is a replacement phase, it also contains solid inclusions of anhydrite and in a few examples celestine (Fig. 1-3). Solid inclusions are typically oriented, 40-80 µm-size, rectangular in shape, and preserving some crystal faces. Small pyrite crystals (10-100 µm) are commonly observed in the limestone host rock and in the inner boundaries of the pseudomorphs, probably indicating they predate both quartz and Ca-2. The solid inclusions in quartz and Ca-2 are probably relicts of earlier diagenetic processes. This suggests that gypsum was converted to anhydrite during burial.

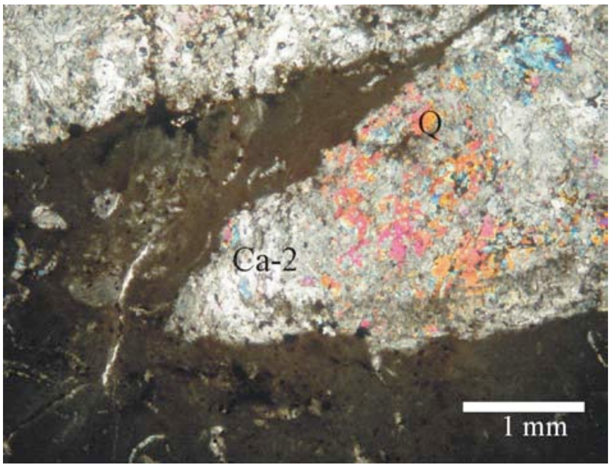

Fig. 1. Gypsum pseudomorph replaced by quartz (Q) which has subsequently been replaced by non ferroan calcite (Ca-2). (crossed polarized light)

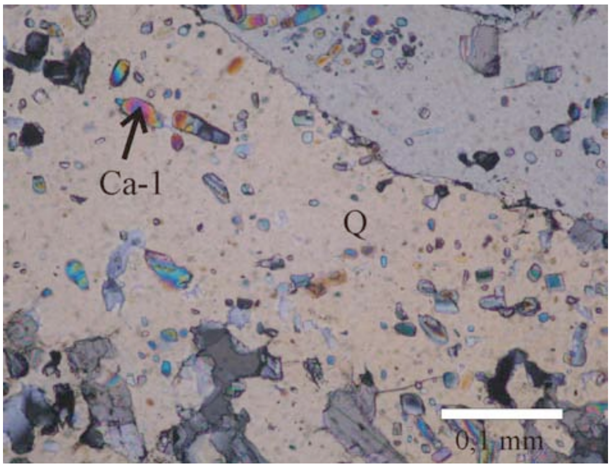

Fig. 2. Gypsum pseudomorph replaced by quartz with abundant solid inclusions of calcite (Ca-1), anhydrite and celestine. (crossed polarized light)

The quartz contains biphasic fluid inclusion assemblages (FIAs) of secondary origin with inclusion sizes ranging between 2-14 µm. No petrographically paired vapour-rich and vapourpoor inclusions were observed, indicating that there is no evidence for necking down after a phase change. In addition, no vapour-dominant inclusions were found, evidence against heterogeneous entrapment (e.g. Goldstein and Reynolds 1994). In FIA's, inclusions have highly variable liquid to vapour volume ratios. Homogenization temperatures (T_h) measured in these FIA's are inconsistent and range from 147 to 351 ºC, with higher T_h in the deeper samples. Final melting of ice measurements, T_m(ice), are between -4.9 and -1.6 ºC. Final melting temperatures of clathrate are typically between 5 and 10ºC

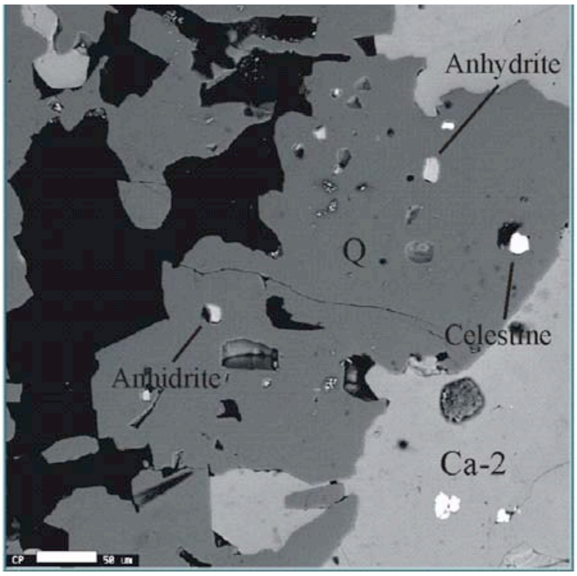

Fig. 3. Gypsum pseudomorph replaced by quartz (Q) with solid inclusions of anhydrite and celestine. Notice the corrosion of quartz by Ca-2 (BSE image).

Ca2 contains FIA's with all-liquid fluid inclusions of secondary origin. They have very irregular shapes and variable sizes (1-16 µm), and are probably related to uplift and unroofing. In addition, secondary biphasic FIA's have fluid inclusions with small size (typically 2-6 µm) and highly variable liquid to vapour volume ratios. Again, no petrographic pairing or vapour-dominant inclusions were found. T_h measured in these FIA's range from 108-352 ºC with T_m(ice) of -0.1 ºC.

As demonstrated by the high T_h values and the inconsistency of FIA's measured in secondary fluid inclusions in quartz (147-351 ºC) and calcite (108-352 ºC), both minerals experienced high temperatures after their formation and after entrapment of originally lower temperature FIAs. The temperatures are in the same range as other re-equilibrated fluid inclusions measured in thick quartz veins in the same area, related to a Cretaceous hydrothermal process that affected this part of basin (Barrenechea et al., 2001; González-Acebrón et al., 2010). The observations indicate early gypsum precipitation associated with an evaporitic depositional environment. This was followed by anhydrite replacement, likely during burial heating. Later, the anhydrite was partially replaced by Ca-1 in associated with a burial thermal regime and intermediate temperatures. It is possible that intermediate temperature thermochemical sulphate reduction led to pyrite precipitation as well. After all of these intermediate-temperature processes, both anhydrite and Ca-1 were partially replaced by quartz and this by Ca-2 during higher temperature hydrothermal processes in association with a CO_2-H_2O fluid. Progressive heating and different heat fluid flow pulses produce the re-equilibration of the FIAs. This was followed by uplift and cooling.

Despite the secondary nature of the fluid inclusions, and their thermal re-equilibration, these data contribute significantly to understand the geologic history of this system.

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