FLUIDS AND CEMENTS IN THE LOWER DEVONIAN LA VID GROUP, CANTABRIAN MOUNTAINS (NW-SPAIN)

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Cements in the different carbonate units from the Lower Devonian La Vid Group record various fluid events, which penetrated the rocks during the burial history of that succession. After sedimentation this succession was buried by about 2700 m of sediments until the orogenic movements of Variscan and later Alpine age set in where these deposits were faulted and tilted. Several fluids were active during these processes and precipitated different kinds of cements. Fluid inclusions in these cements provide substantial information of the chemical and physical conditions of these processes. The succession is composed at the base by transitional sandstones, which merge into dolostone, and different types of limestones. The top of the carbonates is constituted by cinoidal grainstones interlayering with shales, which build up the upper part of the La Vid Group.

Cement Sequence

Petrographic studies reveal several cement generations, which are put in a relative temporal diagenetic sequence, based on geometrical relations. During basin stage a first calcite cement (Cal 1) crystallised at the inner rim of open cavities, fossil fragments and vein walls. This was followed by precipitation of minor amounts of barite (Bar), restricted to veins in only a small limestone unit of the succession. Subsequently, ferroan carbonate cements exert a major impact on the carbonates: siderite, ferroan saddle dolomite (iS-Dol) and ankerite precipitated in the remaining open spaces in veins and fossil fragments, and replaced mimetically aragonite and high-Mg shells. The second saddle dolomite (S-Dol) without a significant Fe component has a cloudy appearance and occurs only in irregular veins and on fault planes of the transitional sandstones and dolostones. After a brecciation event, a clearer type of saddle dolomite (cS-Dol) and minor amounts of quartz (Qtz) precipitated in veins and open cavities of dolostones. However, there are no obvious genetic relations to subsequent cement generations. A late tectonic event is indicated by the crosscutting of fractures filled with fibrous calcites (Cal 2 and Cal 3), which is associated with layer-parallel shortening stylolites and brecciated fragments of formerly mineralised cements. Significantly later a blocky calcite occurs together with celestite (Cel) and kaolinite in reactivated thrust faults and their vicinity. Goethite and hematite occur as oxidation/weathering products of the iron-rich carbonatic cements, e.g. iS-Dol.

Fluid Inclusions and Organic Matter

Fluid inclusions have been characterised by microthermometry, Raman spectroscopy and UV-Fluorescence in Cal 1, Bar, iS-Dol, cS-Dol, Qtz and Cal 3 as well as in Cel. Inclusions in the other cements were either absent or too small for optical analysis.

Stage 1 : Burial diagenesis

Cal 1 contains trails of secondary petroleum inclusions, which have a blue fluorescence. Homogenisation temperatures of the petroleum and CH_4-rich phases in these inclusions vary from 32 to 63 °C (disappearance of vapour bubble). These trails can not be traced in the overgrowing iS-Dol. The barite contains many primary petroleum inclusions, which also have a blue fluorescence with an average wavelength of 452 nm. Homogenisation behaviour is similar to Cal 1 and occurs around 45 °C. Locally, primary petroleum inclusions are also found in iS-Dol, which have also a blue fluorescence (average wavelength of 441 nm). Primary aqueous inclusion defining growth zones are also found in iS-Dol. Total homogenisation of these inclusions occurs around 114 °C in the liquid phase.

The iS-dol in dolostones may also contain solid inclusions of organic matter. Micro-Raman spectra of these inclusions are characteristic for first and second order graphite peaks, indicating a thermal maturity below 1.4% R_0 (Spötl et al., 1998). The surrounding host rock contains grey bituminite in cavities of microfossils and irregular shaped cavities, which can be categorised after Jacob (1989) as epi-impsonite. Bituminite reflection values can be transformed after Baker and Pawlewicz (1994) to temperatures of 154°C. The preserved fluorescence wavelength of petroleum in iS-Dol corresponds with this temperature and can be correlated with an API gravity of 43° after Allan & Wiggins (1993) classifying the petroleum as condensate. The thermal overprint for the petroleum inclusions in barite is less, as indicated by a longer wavelength. This oil has a lower maturity (c.f. Hagemann & Hollerbach 1986).

Stage 2 : Syn-Variscan

Qtz and cS-Dol have similar primary fluid inclusions that occur in growthzones as illustrated by cathodoluminescence. Two types of aqueous inclusions are present:

(1) low salinity. The inclusions have a size up to 20 μm with maximally 10 vol.% CH_4 vapour bubble. Homogenisation temperatures vary between 73 to 200 °C (in the liquid phase). The relative low density of the vapour bubble is indicated by melting of a clathrate phase before ice.

(2) high salinity. The formation of salt hydrates during freezing experiments indicates the presence of NaCl and $MgCl_2$ in the entrapped aqueous solution.

Stage 3 : Post-Variscan

The Cel contains a high amount of primary and secondary fluid inclusions, which mainly have a low salinity aqueous character, with a varying filling degree (from all-vapour to all-liquid). Homogenisation temperatures of liquid-rich inclusions vary between 197 and 211 °C. Melting temperatures of ice are about -0.1 °C. Furthermore, Cel may contain some petroleum inclusions with a CH_4 vapour bubble, and solid inclusions, like anhydrite and organic matter. Micro-Raman investigations of the organic matter indicate graphitisation at low temperatures, below 2% R_0.

These high homogenisation temperatures in Cel, which occurs cogenetic with Cal 3, are in contrast to the all-liquid aqueous inclusions in this cement indicating temperatures below 50°C (Goldstein & Reynolds, 1994). The kaolinite mineralisation correspond to these low temperatures conditions

Conclusions

Three major fluid events had a major impact on the Lower Devonian La Vid Group. After an initial calcite precipitation, Fe-enriched fluids coexistent with petroleum fluids were associated with an early dolomitisation. The Fe-source originated probably in the underlying San Pedro Fm. (Silurian). During the Variscan orogeny (including brecciation), dolomitisation continued without the Fe-component in the fluid system, and clear saddle dolomite and quartz were precipitated out of both highly saline and low saline fluids. In a post-Variscan stage, celestite and calcite precipitated out of a low salinity aqueous fluid at low temperature-pressure conditions.

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