## Preliminary analysis of fluid inclusions in Messinian Halite of Volterra basin and Crotone basin (Italy)

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Typical neogenic sedimentary succession of Mediterranean Area comprises a thick evaporitic sequence of Messinian age, deposited during the "salinity crisis" between ≈6 and 5.33 Ma (Rouchy & Caruso, 2006), including thick Halite deposits.

To obtain information both on temperature at salt deposition time and on subsequent diagenetic transformation of Halite deposits, fluid inclusions analysis is a fundamental instrument.

We focused our attention on two areas of Italian peninsula: the Volterra basin (Tuscany) and the Crotone basin (Calabria) (Fig. 1). Both are filled by neogenic sedimentary sequences of Miocene to Pleistocene, including Messinian evaporites and Halite (Roda, 1964; Testa & Lugli, 2000).

In the Crotone area samples were collected directly from salt diapirs outcropping in the Vitravo river valley. Samples from Volterra basin come from cores from S1113 borehole made by Solvay Company for salt exploitation in the area.

Salt blocks were first cut using a diamond saw, then manually reduced to a thickness of about 500µm and manually polished using routine types of grinding papers. We watched out for samples temperature to not exceed roughly 25 °C.

Halite from Vitravo river is constituted by large, irregular crystals, up to 4-5cm, with portions of "clear" salt and portions of primary "cloudy" salt (chevrons, cubes and hoppers) (Hardie et al, 1983). These crystals contain many primary fluid inclusions, all liquid with cubic shape, often organized in typical growth bands (Fig. 2) (Counter Benison & Goldstein, 1999). Few inclusions contain daughter crystals which have been identified as gypsum and polyhalite by SEM investigations (Salvi & William-Jones, 1990).

Volterra samples consist of smaller (<1cm) crystals than Vitravo halite, with irregular shape. Cloudy halite, made up of countless minute inclusions, often take up the central area of the crystals, surrounded by clear halite. We recognized at least two generations of fluid inclusions (Goldstein, 2001; Kerkhof & Hein, 2001). Primary fluid inclusions, all liquid with cubic shape, are located at the edges of cloudy areas or isolated. Secondary fluid inclusions occur as planes or rows of more or less rounded inclusions, both liquid-rich and vapour-rich, clearly located into healed fractures. Large networks of tubular inclusions are also present

During the microthermometric runs (Linkam stage model THMSG 600), samples were first cooled until -25/-30 °C in order to avoid stretching and reaction with inclusion walls. For this reason no measures of fluid salinity could be possible. Samples were held at this temperature for about 30 minutes. In general, on cooling, vapour bubbles do not appear before  $\cong$  0 °C.



Fig. 1. Map showing distribution and extent of the Messinian evaporites in the Mediterranean area and location of samples (A: Volterra basin; B: Crotone basin). Modified from Rouchy & Caruso, 2006.



Fig. 2. Photomicrograph of fluid inclusions in halite from Vitravo 1 diapir (Crotone).

In general, bubbles appear earlier (i.e. at higher temperature) in Crotone inclusions than in Volterra ones, and usually earlier in larger inclusions than in smaller ones. The gas-to-liquid ratio appear constant within inclusions of the same generation. Then samples were heated at variable rate between 1 and 5 °C/min until  $T_h$  are reached.

 $T_h$  data vary between 12 and 42 °C (Fig. 3), in good agreement with previous works on primary fluid inclusions in Halite (Roberts & Spencer, 1995; Counter Benison & Goldstein, 1999). However,  $T_h$  data fall mostly in the range between 15 – 22 °C, a quite lower temperatures compared to those in Permian Halite as reported in Counter Benison & Goldstein, 1999. These data fit well with climatic conditions at salt deposition time, a glacial stage (TG 20 e TG 22 peaks) that, during Messinian salinity crisis, concurred in establishing evaporative conditions in the Mediterranean area (Rouchy & Caruso, 2006).

Furthermore, it can be noticed that Volterra samples exhibit Th slightly higher than Crotone samples. This can be due to local conditions at salt deposition time or to possible subsequent modification. In fact, during burial history of Volterra basin a high heat flow affected the area in Pliocene and Pleistocene, due to the emplacement of crustal and subcrustal magmatic bodies (Testa & Lugli, 2000).

We can conclude that  $T_h$  data from primary fluid inclusions are consistent with growth of halite crystals under evaporative conditions reported in Mediterranean area during Messinian (Rouchy & Caruso, 2006). Moreover we outline the fluid inclusion differences between Crotone and Volterra samples due to local conditions both at deposition time or during sin-depositional and postdepositional history. Observed differences can offer an important indication in order to explain different bulk properties of same rocks.

Analysis of secondary inclusions and samples from other rock salt mines (Sicily) are still in progress.



Fig. 3. Histogram of homogenization temperatures  $(T_h)$  of Volterra and Crotone halite primary fluid inclusions. Total number of measurements: 79 (Crotone 58; Volterra 21).

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