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Carbonate deposition and diagenesis in evaporitic environments: The evaporative and sulphur-bearing limestones during the settlement of the Messinian Salinity Crisis in Sicily and Calabria

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ABSTRACT

The depositional and diagenetic processes involved in the formation of carbonates in the evaporitic environment of the Messinian Salinity Crisis are investigated in Southern Italy (Sicily and Calabria). Strong differences are observed between the studied sections that reflect specific depositional and diagenetic evolution in the interconnected sub-basins resulting from the syn-sedimentary tectonic fragmentation of the Central Sicilian and Calabrian domains. These carbonates formed diachronously in restricted perched sub-basins between the Tripoli Formation and the hypersaline settings of the MSC. The Calcare di Base (CdB) that can be interbedded with gypsum layers occurs rhythmically at the transition between the upper part of the Tripoli Formation and the massive gypsum, and at places synchronously with the deposition of the Lower Gypsum unit. It deposited initially as primary peloidal and microbial limestones, but their original structure and mineral composition were modified by the superimposition of early to late diagenetic processes. The first diagenetic step was the development of interstitially grown gypsum and halite crystals from trapped saturated brines that locally led to the formation of salt beds. The Sulphur Limestone (SL) resulted from the activity of sulphate reducing bacteria that occurred locally in the deeper parts of the various basins where anoxic bottom waters favoured microbial processes fuelled by biogenic methane and crude oil, and caused the carbonate replacement of gypsum and the formation of native sulphur. The migration of hydrocarbon and H_2S-rich fluids caused the epigenetic dissemination of sulphur and a late diagenetic carbonate replacement of the gypsum. Later influxes of continental fresh waters were responsible for the dissolution of the halite crystals and their replacement by sparry calcite. The vugs, formed during both the gypsum/calcite conversion and the halite dissolution, either remained empty or were filled with calcite, celestine, fibrous silica, anhydrite, secondary gypsum, and native sulphur. The initial accumulation of fine-grained carbonate and gypsum sediments was strongly destabilised by volumetric changes resulting from mineral replacements and fluidisation processes. Their superimposition explains the vuggy and boxwork-like textures, in situ brecciation and lateral displacement, which are responsible for the chaotic organisation without necessarily involving basin-scale re-sedimentation in the form of debris flows.

1. Introduction

Various types of carbonate deposits formed in the Mediterranean Basin, before, during and near the end of the Messinian Salinity Crisis (MSC). They mostly correspond to carbonate platforms and coral reef complexes that were widely distributed along the margins of the Mediterranean Basin before the onset of the MSC, as well as to stromatolitic and ooid-bearing carbonates belonging to the Terminal Carbonate Complex unit (Rouchy and Saint-Martin, 1992; Esteban, 1996; Bourillot et al., 2010). This paper deals with completely different types of carbonate deposits, which are directly linked to the environmental conditions of the salinity crisis itself. Their formation results from primary carbonate and evaporite precipitation in hypersaline conditions that have been affected by a multistaged set of diagenetic and epigenetic transformations controlled by bio-geochemical processes. The best occurrences can be observed in Sicily and Calabria where these carbonates are classically distinguished into two major groups, i.e. the "Calcare di Base" (CdB) and the Sulfifera Limestone (SL), although these groups may be often closely interrelated in some sedimentary successions.

The CdB from Sicily and Calabria constitutes a complex carbonate unit up to 50 m thick, which is irregularly interbedded between the pre-evaporitic diatomite-bearing unit (Tripoli Fm) and the Gypsum

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formations. The first petrographic description of the CdB was provided by Ogniben (1957) who interpreted these deposits as being the result of chemical precipitation during the first stages of increasing salinity. Many authors (Decima and Wezel, 1973; Richter-Bernburg, 1973; Pierre, 1974, 1982, 1988; Schreiber, 1976, 1988; Schreiber et al., 1976; Rouchy, 1982; McKenzie, 1985; Decima et al., 1988; Bellanca et al., 2001; Rouchy and Caruso, 2006; Ziegenbalg et al., 2010, 2012) have acknowledged, although with some disagreements, the evaporitic origin of these carbonates ("evaporative limestone") taking into consideration both the abundance of evaporite mineral ghosts and the stable isotope composition of the carbonates.

The SL consists of native sulphur-rich carbonate deposits that are common in Sicily where it was intensely worked for sulphur extraction until the 1970's in a great number of mines including those of Trabonella, Cozzo Disi, and Capodarso. Like the typical CdB, the sulphur-rich limestones are usually intercalated between the Tripoli and Gypsum formations and are sometimes directly intercalated within the Lower Gypsum unit. Locally, their close imbrication with the CdB makes it difficult to differentiate these two groups of carbonates from each other to the point that Decima et al. (1988) have even assimilated the SL to a subfacies of the CdB. From a very detailed isotopic study, Dessau et al. (1959, 1962) linked the sulphur ore formation to the process of bacterial sulphate reduction that also caused the carbonate replacement of calcium sulphate.

Until the 2000's it was accepted that most of the CdB was an evaporative limestone that was contemporary with the local onset of the MSC. The common vuggy and brecciated structures were attributed to processes of in situ transformation (auto-brecciation) caused by either variations of the depositional and diagenetic conditions (Caruso and Rouchy, in Roveri et al., 2006b: Rouchy and Caruso, 2006) or to dissolution, karstification and pedogenetic alteration when sediments were subaerially exposed during sea-level lowstands (Pedley and Grasso, 1993; Butler et al., 1995; Pedley and Maniscalco, 1999). In these two kinds of processes, the hypersaline conditions and the early precipitation of evaporite minerals (gypsum, anhydrite, halite) during the deposition of these carbonates played a major role. The formation of the SL involved mechanisms of bacterial sulphate reduction (Dessau et al., 1959, 1962; Pierre, 1974, 1982; McKenzie, 1985; Decima et al., 1988; Rouchy and Caruso, 2006; Ziegenbalg et al., 2010, 2012) as observed in the Messinian Lorca Basin (Spain) (Rouchy et al., 1998; Taberner et al., 1998) and in the Middle Miocene of the Red Sea and Gulf of Suez (Pierre and Rouchy, 1988; Aref, 1998; Aloisi et al., 2013). Decima et al. (1988) provided the most comprehensive geochemical analysis of the CdB by mapping the stable isotope composition of these carbonates at the basin scale. They characterized the main depositional and diagenetic steps comprising the former sedimentation in hypersaline and locally anoxic settings where bacterial sulphate reduction was active. This latter was locally coupled with anaerobic methane oxidation as indicated by the very low $\delta^{13}C$ values down to −50‰ (Decima et al., 1988; Ziegenbalg et al., 2010) and lipid biomarkers (Ziegenbalg et al., 2012). The Calcare di base and Sulphur Limestones are described separately as they are differentiated by petrographic characters, but the presence of scattered sulphur nodules in typical CdB, the close regional relations between outcropping CdB and sulphur-mines, and the number of mining works in the CdB indicate that these diagenetic processes were under the control of local palaeoenvironmental changes, with no need to separate them into too much formal types.

Recently, Manzi et al. (2011) distinguished three types of CdB by applying the conceptual model of re-sedimentation defined for the Lower Gypsum unit by Roveri et al. (2006b, 2008). Types 1 and 2 correspond respectively to sulphur-rich deposits involving process of bacterial sulphate reduction, and primary dolomitic limestone considered as formed in situ. In contrast, type 3 is represented by brecciated limestones that would have resulted from gravity flow redeposition occurring coevally of the Lower Gypsum unit interpreted as resedimented deposits. This model implies a major erosional surface between types 1–2 and type 3. For Caruso (1999) and Caruso and Rouchy (in Roveri et al., 2006b) the passage between type 2 and the overlying brecciated unit, in the studied sections, occurs transitionally without any erosional discontinuity as also pointed out by Guido et al. (2007) and Iadanza (2011). Moreover, the rhythmic pattern of the underlying Tripoli Fm may be followed through the CdB from which it differs by progressive changes of lithology.

Based on sedimentological and geochemical analyses, especially lipid biomarkers, Guido et al. (2007) considered that the CdB from the Rossano Basin in Calabria deposited in normal marine conditions with no evaporitic influences. From the analyses of archeal biomarkers of CdB samples from Sicily, Birgel et al. (2014) confirmed that the deposition took place in hypersaline conditions. Iadanza (2011) and Iadanza et al. (2013) proposed an alternative hypothesis to explain the formation of the CdB from Sicily and Calabria and of the post-evaporitic carbonates from the Maiella area (central Apennines), whose brecciation and fluidisation features would be the result of processes of active methane seeping that took place with the destabilisation of gas hydrates during the Messinian sea level fall.

Besides these two main types of carbonates, carbonate deposits are rhythmically interlayered within the Lower Gypsum unit as a discrete matrix cementing the gypsum crystals, carbonate partings between gypsum crystals and discontinuous carbonate beds containing scattered crystals or clusters of gypsum crystals. Although the stratigraphic distribution of these carbonates differs from the typical CdB, their composition and structure display similar features. In fact these carbonates are present in the central area of the basin where the Lower Gypsum unit reaches its maximum thickness while the typical CdB disappears. It must be noted that CdB and SL layers themselves may locally extend within the Lower Gypsum unit or be interbedded with gypsum. These carbonates have never been described in detail.

This short review of the various diverging and controversial interpretations shows the difficulty of unravelling the complex mechanisms involved in the formation of those carbonates directly linked to the MSC. This is mainly due to the fact that the reconstruction of the primary depositional signal has been hampered by a succession of diagenetic, biodiagenetic and epigenetic overprints caused by the rapid changes of palaeoenvironmental conditions (marine, hypersaline and freshwater, anoxic or oxygenated) that were constrained by the local palaeogeography, the climate fluctuations and the syn- to post-depositional structural deformation including the impact of salt tectonics and collapse.

In the present study, we present new sedimentological and stable isotope data on the CdB, the SL and the carbonates intercalated in the Lower Gypsum unit. This study differs from previous works by its approach based on the study of several continuous field sections of the CdB from Sicily and Calabria. It should be noted that in the Sicilian sections the underlying Tripoli unit has already been investigated at a high resolution providing then a continuous record of the succession of depositional changes up to the base of the CdB (Caruso, 1999; Bellanca et al., 2001; Blanc-Valleron et al., 2002). Additional samples were also collected in several CdB outcrops. Because the SL is dispersed within the CdB and the Lower Gypsum unit, samples have also been collected both specifically in the mining area as well as in their surrounding area. Finally it has been decided to study the carbonates interbedded within the Lower Gypsum unit as they represent the record of the carbonate sedimentation in the central trough of the Caltanissetta basin where the typical CdB is absent or poorly represented. A continuous section has been studied at Santa Elisabetta and an additional sampling was done in various outcrops from both the Caltanissetta Basin and the northern Gibellina Basin. This new approach leads to better constrain depositional conditions and brought to light a new palaeogeographical pattern characterized by separated sub-basins whose sedimentological and biogeochemical parameters introduced a different and diachronous response to the global constraints of the MSC.