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Large celestine orebodies formed by early-diagenetic replacement of gypsified stromatolites (Upper Miocene, Montevive–Escúzar deposit, Granada Basin, Spain)

Javier García-Veigas [a,*], Laura Rosell [b], Dioni I. Cendón [c,d], Luis Gibert [b], José M. Martín [e], José Torres-Ruiz [f], Federico Ortí [b]

[a] CCiTUB Scientific and Technological Centers, Universitat de Barcelona, 08028 Barcelona, Spain
[b] Departament de Geoquímica, Petrologia i Prospecció Geològica, Universitat de Barcelona, 08028 Barcelona, Spain
[c] Australian Nuclear Science and Technology Organization, Kirrawee DC, NSW 2322, Australia
[d] Connected Waters Initiative, School of BEES, UNSW, Sydney, NSW 2052, Australia
[e] Departamento de Estratigrafía y Paleontología, Universidad de Granada, 18071 Granada, Spain
[f] Departamento de Mineralogía y Petrología, Universidad de Granada, 18071 Granada, Spain

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ABSTRACT

The Montevive and the Escúzar stratabound celestine orebodies in the Upper Miocene evaporite succession of the intramontane Granada Basin (Spain) constitute one of the largest strontium deposits in the world. Celestine occurs within a gypsum/anhydrite–halite evaporite sequence where it replaces gypsum and gypsified stromatolites preserving carbonate peloids. ^{87}Sr/^{86}Sr and δ^{34}S values in the Montevive celestine deposit are close to those reported for the saline unit (Chimeneas Halite; marine to nonmarine) but higher than those of the overlying gypsum unit (Agrón Gypsum; nonmarine). ^{87}Sr/^{86}Sr and δ^{34}S isotope values in the Escúzar celestine deposit match the nonmarine values recorded in the upper part of the Agrón Gypsum. The similarity in isotope values between celestine and the corresponding gypsum host in the Escúzar deposit points to early-diagenetic mineralization. According to that, both orebodies are diachronous. Gypsum pseudomorphs and molds, intraformational breccias and karst structures in these celestine deposits point to dissolved gypsum as the main sulfate source. Diagenetic–hydrothermal CaCl$_2$ brines are interpreted to be the main strontium source. The spatial relationship between gypsified stromatolites and the ore deposits suggests the existence of coeval thermal springs related to fractures, bordering the saline lake. The proposed model envisages gypsum dissolution by SO$_4^{2-}$-poor and Sr^{2+}-rich, CaCl$_2$ diagenetic–hydrothermal water discharging in coastal ponds at times of dry periods and low meteoric water inflow. The increase in SO$_4^{2-}$ concentration by gypsum dissolution and the low solubility of SrSO$_4$ would lead to celestine precipitation replacing gypsum and gypsified stromatolites.

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1. Introduction

Celestine (SrSO$_4$) is a common minor mineral in modern and ancient marine sediments and in some lacustrine evaporites. There are even marine planktonic protozoan organisms (the *Acantharia*) that precipitate celestine shells biogenically (Bernstein et al., 1987; Deckker, 2004). The limited amount of celestine in marine sediments agrees with the low concentration of Sr^{2+} in modern seawater due to the low solubility of strontium sulfate. Although celestine is expected to precipitate during evaporation of seawater (Braitsch, 1971; Zherebstova and Volkova, 1966) it never forms significant accumulations. However, the largest known celestine orebodies are hosted in shallow-water carbonates and evaporites, commonly interfingering with clastic sediments (Hanor, 2004). Based on their relationships with associated sedimentary successions and their stable isotope geochemistry, two principal mechanisms for the formation of massive celestine ore deposits have been proposed (Hanor, 2000, 2004): 1) a syngenetic mechanism with primary precipitates derived from evaporated seawater, and 2) a diagenetic (epigenetic) replacement of carbonates and sulfate evaporites.

All large celestine orebodies are related to evaporite deposits: the Upper Permian of East Greenland (Scholle et al., 1990), the Lower Cretaceous deposits in Argentina's Neuquen Basin (Brodtkorb et al., 1982), and in the Sabinas Basin of Mexico (González-Sánchez et al.,

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[*] Corresponding author. Tel.: +34 934021701; fax: +34 934021398.
E-mail address: garcia_veigas@ub.edu (J. García-Veigas).

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2009; Kesler and Jones, 1981), and the Cenozoic Ulas-Sivas Basin deposits of Central-Eastern Turkey (Tekin et al., 2001, 2002). Smaller replacements of Ca-sulfate evaporites by celestine in non-economic deposits have been described elsewhere (Carlson, 1987; Dill et al., 2009; Olaussen, 1981; Taberner et al., 2002; West, 1960; Wood and Shaw, 1976).

The Miocene Montevive–Escúzar deposit (Granada, Spain), with an annual production up to 200,000 tons of almost pure celestine, is the second largest known strontium deposit in the world after the Sabinas deposit of Mexico. The Montevive–Escúzar deposit is characterized by: 1) stratabound orebodies hosted by gypsum evaporites; 2) evidence of subaerial exposure (intraclastic breccias and karstic cavity fillings); 3) location in specific sites of the basin, generally along the margins and in local shoals; and 4) celestine formation followed by precipitation of calcite cement (Martín et al., 1984).

Taking into account the poor efficiency of $SrSO_4$-transport in solution, the understanding of the build-up of these large celestine deposits, particularly in a sedimentary context as occurs in the Granada Basin, requires the integrated study of the orebodies and the host sedimentary succession. The aim of this work is to propose a genetic model for the Montevive–Escúzar celestine deposit which could be applicable to other similar ore deposits.

2. Geological setting

The Betic Chain (southern Spain) and the Rif Mountains (in northern Africa) constitute the western portion of the Alpine peri-Mediterranean Orogenic belt, which formed as a result of the closure of the Tethys Ocean during Africa–Eurasia plate convergence. From the Late Miocene onward, an extensional regime was imposed, resulting in a group of postorogenic intramontane basins, referred to as 'Neogene Basins'. The Granada Basin (Fig. 1), situated in the center of the Betic Chain, at the western foot of the Sierra Nevada, is filled with Neogene and Pleistocene sediments unconformably overlying fault-controlled basement rocks. The basement consists of Paleozoic metamorphic rocks and Triassic carbonates in the southeastern half of the basin (Betic Internal Zone) and Mesozoic sedimentary rocks in the northwestern half (Betic External Zone). The main E–W directed fault-system in the basin (Rodríguez-Fernández and Sanz de Galdeano, 2006) is related to the major crustal Cádiz–Alicante Fault oriented NE–SW (Sanz de Galdeano, 2008) which affects the whole of the Betic Chain. A second NW–SE directed fault system cuts and displaces the previous one and defines the main areas of present-day basin subsidence.

The Neogene infilling of the Granada Basin (Braga et al., 1990, 2003; Corbí et al., 2012; Dabrio et al., 1982; Martín et al., 1984;

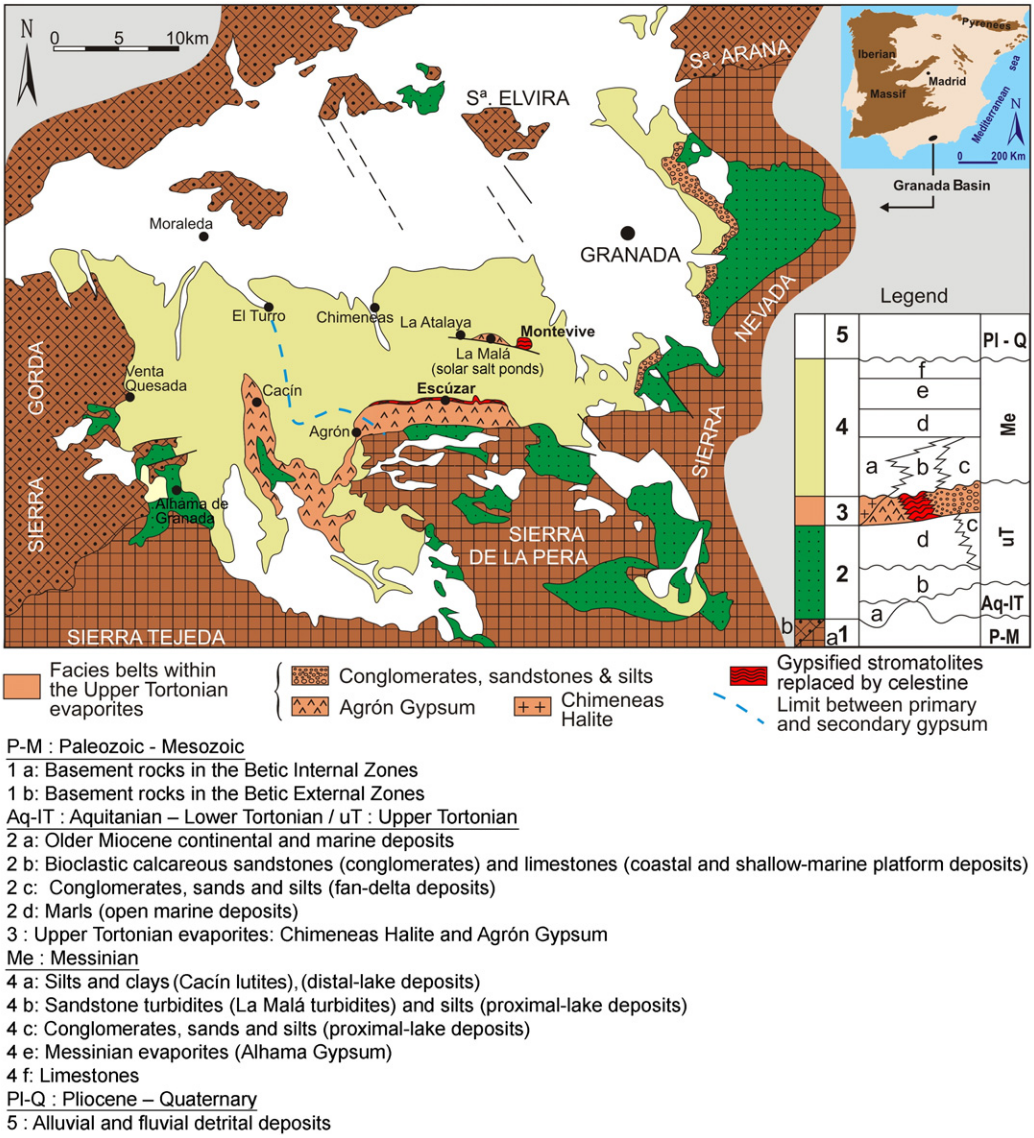

Fig. 1. Simplified geological map of the Granada Basin (modified after Martín et al., 1984, and after Dabrio et al., 1982).

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