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Paleozoic bedded barite deposits from Sonora (NW Mexico): Evidence for a hydrocarbon seep environment of formation

Carles Canet [a,b,*], Pere Anadón [c], Eduardo González-Partida [d], Pura Alfonso [e], Abdorrahman Rajabi [f], Efrén Pérez-Segura [g], Leticia A. Alba-Aldave [b]

[a] Instituto de Geofísica, Universidad Nacional Autónoma de México, Del. Coyoacán, 04510 México, D.F., Mexico
[b] Instituto de Geología, Universidad Nacional Autónoma de México, Del. Coyoacán, 04510 México, D.F., Mexico
[c] Institut de Ciències de la Terra Jaume Almera CSIC, Lluís Solé i Sabarís s.n., 08028 Barcelona, Spain
[d] Centro de Geociencias, Universidad Nacional Autónoma de México, Campus Juriquilla, 76230 Santiago de Querétaro, Mexico
[e] Departament d'Enginyeria Minera i Recursos Naturals, Universitat Politècnica de Catalunya, Av. Bases de Manresa 61-73, 08242 Manresa, Spain
[f] Department of Geology, Faculty of Basic Sciences, University of Birjand, Birjand, Iran
[g] Departamento de Geología, Universidad de Sonora, Rosales y Boulevard Luis Encinas s/n, 83000 Hermosillo, Sonora, Mexico

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A B S T R A C T

The Mazatán barite deposits, Sonora, NW Mexico, represent an outstanding example of Paleozoic bedded barite, a poorly understood type of mineral deposit of major economic interest. The deposits of this type commonly occur hosted by shales and are characterized by the lack of base-metal sulfide mineralization, in contrast to classic sedimentary-exhalative (or SEDEX) deposits. A throughout study of the Mazatán barite deposits, based on petrography, fluid inclusions analyses and isotope geochemistry, confirmed the link between bedded barite and fossil hydrocarbon seeps, thereby leaving hydrothermal vent-related processes ruled out. Hence, modern cold seeps in continental margins would account for the geological setting and genetic aspects of this type of deposit.

The largest barite bodies of Mazatán are hosted within an Upper Carboniferous flysch succession, which formed part of an accretionary wedge related to the subduction of the Rheic Ocean beneath Gondwana. As well, a few barite occurrences are hosted in Upper Devonian, pre-orogenic turbidites. A variety of mineralized structures is displayed by barite, including: septaria nodules, enterolitic structures, rosettes and debris-flow conglomerates. Barite is accompanied by chalcedony, pyrite (framboids) and berthierine. Gas-rich fluid inclusions in barite were analyzed by micro-Raman spectroscopy and methane was identified, suggesting the occurrence of light hydrocarbons in the environment within which barite precipitated. ^{13}C-depleted carbonates ($\delta^{13}C$: −24.3 to −18.7‰) were found in the barite deposits; they likely formed through anaerobic oxidation of methane coupled to sulfate reduction. Besides, these carbonates yield negative $\delta^{18}O$ values (−11.9 to −5.2‰) reflecting the isotopic composition of Devonian–Carboniferous seawater; alternatively, this ^{18}O-depletion could reflect late diagenetic processes. Methane-derived carbonates occur at modern hydrocarbon seeps and have been reported from Mesozoic, Cenozoic and even Paleozoic seep sediments, but they have never before been described in Paleozoic bedded barite deposits. $\delta^{34}S$ values of barite vary from +17.6 to +64.1‰, with the lowest values overlapping the range for coeval seawater sulfate; this distribution indicates a process of sulfate reduction. Barite precipitation can be explained by mixing methane- and barium-rich fluids with pore-water (seawater) containing sulfate residual from microbial reduction. Two analyses from barite gave an $^{87}Sr/^{86}Sr$ within and slightly above the range for seawater at the time of deposition, with 0.708130 and 0.708588, which would preclude the involvement of hydrothermal fluids in the mineralization process.

1. Introduction

Sediment-hosted, stratiform barite deposits —also known as bedded barite deposits (Orris, 1986) — account for the largest global barite resources (Jewell, 2000). Although they have been described in sedimentary sequences from Archean to Jurassic (Johnson et al., 2009 and references therein), the volumetrically most important are by far those of Paleozoic age (Jewell, 2000). Prominent examples of this type of deposit occur in south China (Early Cambrian) and in Nevada (Ordovician–Upper Devonian), the latter with total reserves of ~90 Mt (Jewell, 2000). Although smaller, those of Mazatán, in the northern state of Sonora (Fig. 1), contain the largest resources of barite of Mexico, exceeding 13 Mt of ore with a specific gravity of 3.6–3.8 g cm^{-3}. The largest barite

* Corresponding author at: Instituto de Geofísica, Universidad Nacional Autónoma de México, Del. Coyoacán, 04510 México, D.F., Mexico. Tel.: +52 55 56224133; fax: +52 55 55502486.
E-mail address: ccanet@geofisica.unam.mx (C. Canet).

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bodies of Mazatán are hosted within an Upper Carboniferous flysch succession, which formed part of an accretionary wedge related to the subduction of the Rheic Ocean beneath Gondwana (Poole et al., 2005). However, few barite occurrences are hosted in Upper Devonian pre-orogenic turbidites (Fig. 1).

An outstanding feature of all deposits cited above, categorized as the "continental margin type" by Maynard and Okita (1991), is the lack of base-metal sulfide mineralization that is commonly associated to classic sedimentary-exhalative (or SEDEX) deposits (*cf.* Goodfellow et al., 1993; Large, 1981; Leach et al., 2010; Rajabi et al., 2012).

Contrasting hypotheses have been proposed for the origin of bedded barite, which has given rise to controversy (Emsbo and Johnson, 2004 and Torres et al., 2003). Most of the early work (*e.g.* Dubé, 1988; Maynard and Okita, 1991; Poole et al., 1991) considered that these deposits formed at the seafloor from low-temperature (~100–200 °C) hydrothermal solutions, without clearly addressing the lack of Pb–Zn mineralization. It should be noted, however, that Howard and Hanor (1987) had suggested that barite from Carboniferous bedded deposits of Arkansas might form from "subsurface formation fluids" enriched in Ba, Sr and Ca. Alternatively, it has also been proposed a biogenic origin for these deposits; so that, barite would precipitate biogenically from high productivity, sulfate-deficient open ocean water and then would accumulate to the seafloor (*e.g.* Jewell, 2000). However, it seems unlikely that this process by itself has originated deposits with the shape, tonnage and grades as those of Paleozoic age; hence, Clark et al. (2004) proposed that these deposits formed as a result of a combination of hydrothermal and biogenic processes.

Becoming an important focus of research, cold seeps in continental margins provided new clues for the origin and geologic significance of bedded barite deposits (Torres et al., 2003). Authigenic barite has been reported at many modern cold seeps, associated with methane-derived carbonates, forming chimneys, massive bodies

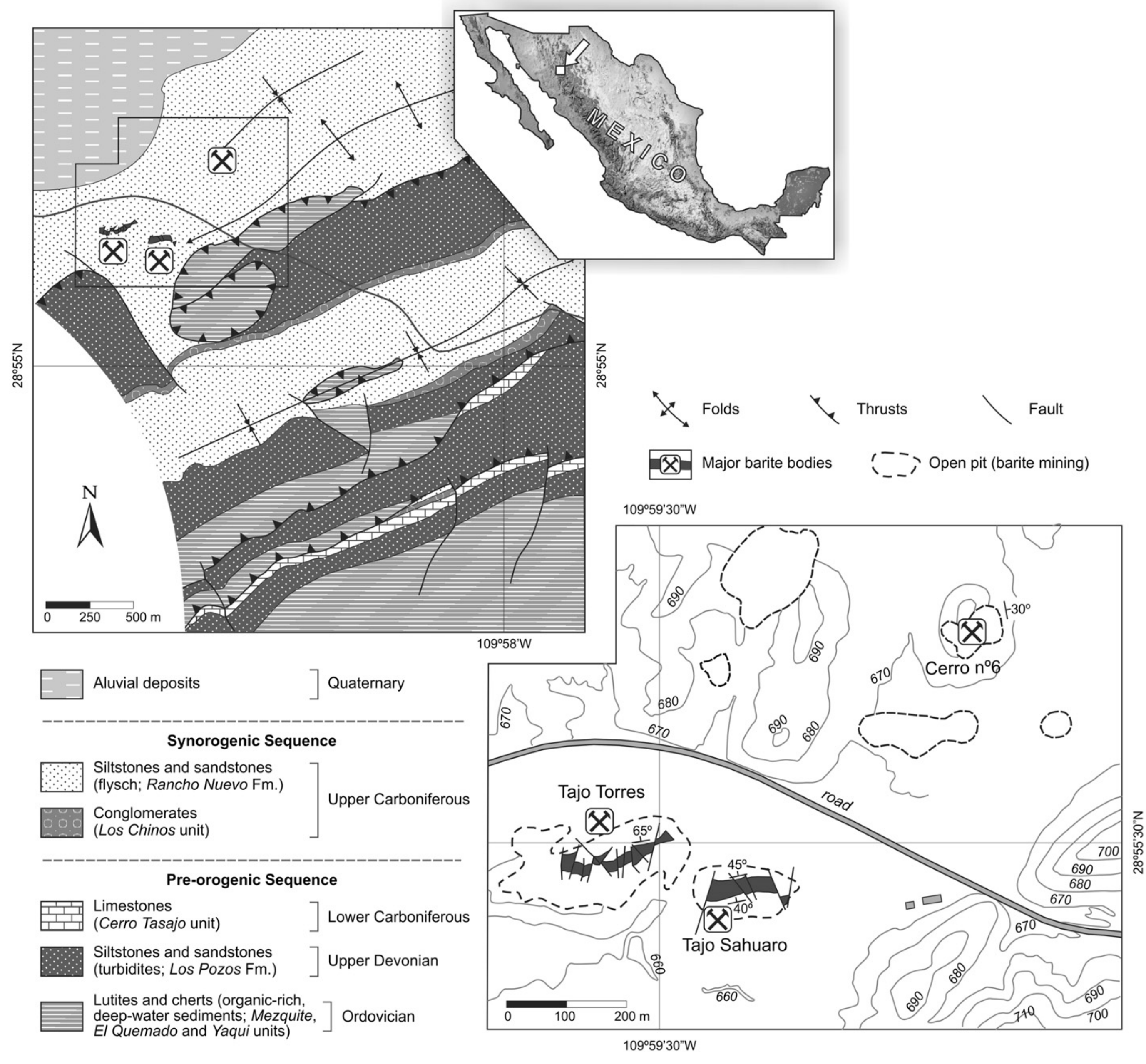

Fig. 1. Geologic map of the Mazatán barite mining district in Sonora, northwest Mexico (after Poole et al., 2005); and topographic map (bottom right) showing the main open pits (contour lines in meters).