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Albitization evidences of Mesozoic carbonates: petrological study of authigenic albites in the northwest of the Bortziriak-Cinco Villas Massif, eastern Basque-Cantabrian Basin

Evidencias de albitización de carbonatos mesozoicos: estudio petrológico de albitas autigénicas al noroeste del Macizo Bortziriak-Cinco Villas, este de la Cuenca Vasco-Cantábrica

Martin Ladron de Guevara[1*], Arantxa Bodego[1] and Eneko Iriarte[2]

[1] Geologia Saila, Zientzia eta Teknologia Fakultatea, Euskal Herriko Unibertsitatea. Sarriena auzoa z/g, 48940 Leioa, Bizkaia.
martin.ladrondeguevara@ehu.eus ; arantxa.bodego@ehu.eus
[2] Laboratorio de Evolución Humana, Departamento de Historia, Geografía y Comunicación – Laboratorio de Isótopos Estables IsoTOPIK, Edificio de I+D+i, Universidad de Burgos, Plaza Misael Bañuelos s/n, 09001 Burgos.
eiriarte@ubu.es
*Corresponding author

ABSTRACT

The presence of authigenic Na-feldspars in sedimentary carbonate rocks is unusual and its origin is controversial in terms of genesis and timing. The use of optical microscopy, cathodoluminescence and in situ semi-quantitative EDX analysis techniques, has allowed the identification and characterization of authigenic albite crystals in the Mesozoic pre- and syn-rift carbonates of the northwestern margin of the Bortziriak-Cinco Villas Massif, in the northeastern Basque-Cantabrian Basin (western Pyrenees). The euhedral habit, crystal size, spatial distribution and crosscutting relationships, together with the pure albitic composition, suggest a relatively early replacement origin. Compaction of sediments during burial, besides possible fluid migration linked to the intense syn-rift halokinetic activity, may have been decisive for the mobilisation of cations, and hence, for the albitization of the carbonate rocks.

Key-words: *Diagenesis, albitization, Mesozoic carbonates, rifting, Basque-Cantabrian Basin.*

RESUMEN

La presencia de feldespatos sódicos autigénicos en rocas sedimentarias carbonáticas es inusual y su origen es controvertido en términos de génesis y cronología. El empleo de la microscopía óptica, catodoluminiscencia y los análisis semi-cuantitativos in situ por EDX, han permitido la identificación y caracterización de albitas autigénicas en los carbonatos pre- y sinrift del Mesozoico, en el margen noroeste del Macizo de Bortziriak-Cinco Villas, al noreste de la Cuenca Vasco-Cantábrica (Pirineos occidentales). El hábito euhédrico, el tamaño de cristal, la distribución espacial y las relaciones de corte, junto a la composición albítica, sugieren un origen relativamente temprano por remplazamiento. La compactación por enterramiento de los sedimentos además de la posible migración de fluidos relacionada con la intensa actividad halokinética syn-rift, pudo ser decisiva para la movilización de cationes, y, por lo tanto, para la albitización de las rocas carbonatadas.

Palabras clave: *Diagénesis, albitización, carbonatos mesozoicos, rifting, Cuenca Vasco-Cantábrica.*

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Introduction

Albitization is a well-known Na-metasomatic process in which usually, plagioclase feldspar or alkali feldspar is replaced completely or partially by albite. This is a very common alteration process among igneous rocks, particularly in granites, related to feldspar dissolution-precipitation processes (Pettersson and Eliasson, 1997). Albitization is also a common reaction in sandstone reservoirs at expenses of detrital feldspars (Perez and Boles, 2005). Nevertheless, Na-feldspar replacement has also been described in sedimentary carbonate rocks (*i.e.* Kastner and Siever, 1979; Spötl *et al.*, 1999). Examples of albitization processes are documented in Mesozoic carbonates of the hyperextended Arzacq-Mauléon basin, (northern Pyrenees) (Incerpi *et al.*, 2020), attributed to Cretaceous Na- and Si-rich albitizing fluids (Boulvais *et al.*, 2007).

In the Basque-Cantabrian Basin (BCB), authigenic albites have already been described and their genesis is related to diapiric processes associated with Cenozoic Mississippi Valley-type Zn-Pb deposits (Perona *et al.*, 2002; Perona, 2016). However, the occurrence of albites of authigenic origin remains poorly unknown in other parts of the BCB.

The aim of this work is twofold. Firstly, it describes for the first time the occurrence of authigenic feldspars in a Mesozoic pre- and syn-rift carbonate succession in the northeastern margin of the BCB, in the northwest of the Bortziriak-Cinco Villas massif. Secondly, this work focuses on their petrological characterization and their stratigraphical and spatial distribution in order to understand the possible origin and timing of these minerals.

Geological setting

The study area is located in the northeastern margin of the inverted, hyperextended BCB (western Pyrenees) (Roca *et al.*, 2011; Tugend *et al.*, 2014). The studied Mesozoic rift succession crops out in the northwestern margin of the Bortziriak-Cinco Villas Massif, which is composed of Carboniferous (Culm fa-

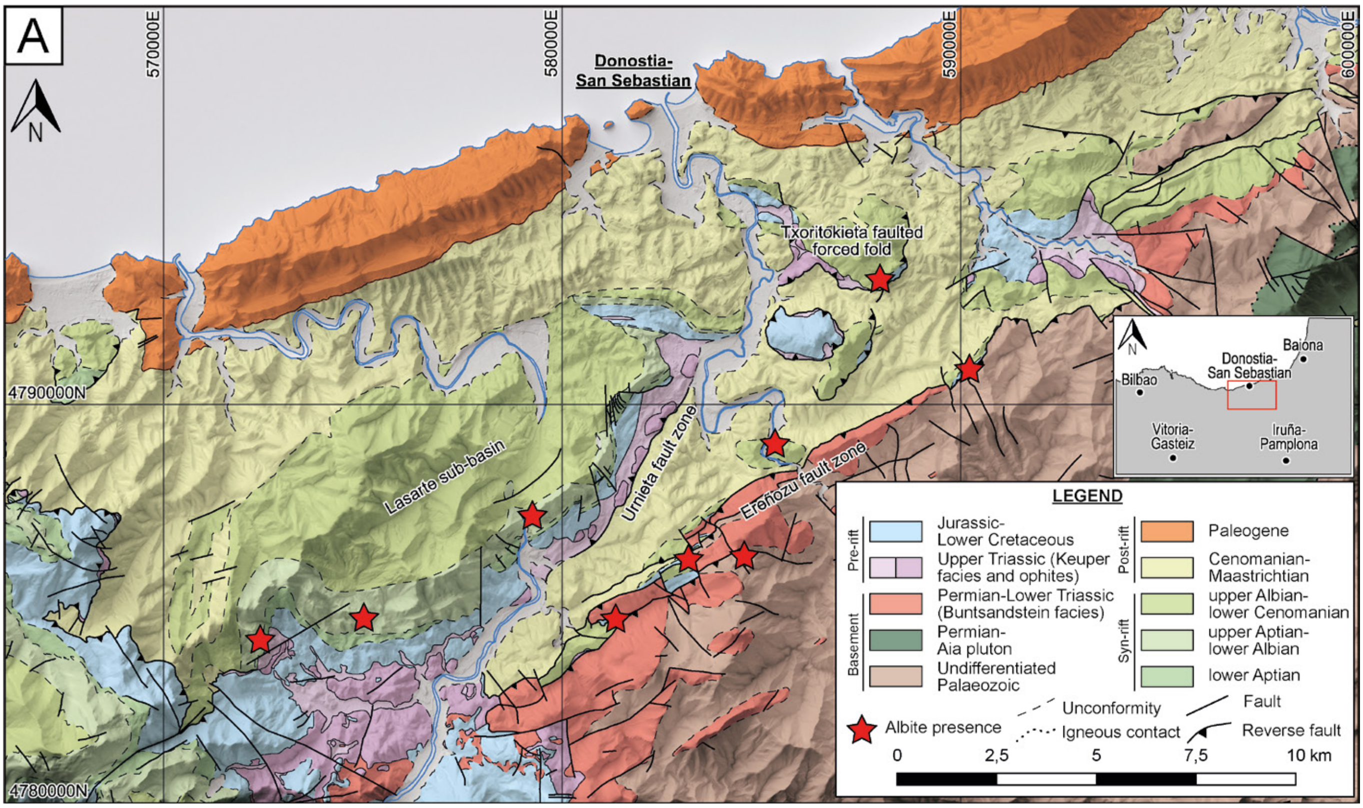

Fig. 1.- Geological map of the study area and the location of the points where albitization evidence has been found. See figure in colour in the web.

Fig. 1.- Mapa geológico de la zona de estudio y ubicación de los puntos en los que se han encontrado evidencias de albitización. Ver figura en color en la web.

cies) and Triassic (Buntsandstein and Keuper facies) rocks (Campos, 1979) (Fig. 1). These units formed the basement during the Mesozoic rifting phases. The sedimentary cover in the area is thick, particularly in the Lasarte sub-basin (Fig. 1). It consists of: Jurassic micritic limestones and marls; Lower Cretaceous siliciclastic to carbonate deposits; Aptian to Cenomanian shallow to deep-water siliciclastic and shallow-marine carbonate rocks (Campos, 1979; Bodego *et al.*, 2015 and references therein). The Meso-Cenozoic post-rift deposits are mainly composed of Upper Cretaceous deep-water alternating marls and limestones and Cenozoic turbiditic sandstones (Campos, 1979).

During the Aptian to Cenomanian rifting phase, extensional basement-involved faults (*e.g.* Ereñozu and Urnieta faults) caused the compartmentalization of the area (*i.e.* the Lasarte sub-basin) (Fig. 1). In addition, the coeval syn-extensional halokinetic movement of Keuper rocks (red clays and evaporites) conditioned the formation of syn-depositional extensional faults and forced folds (*e.g.* Txoritokieta forced fold (Fig. 1)) (Bodego and Agirrezabala, 2013; Bodego *et al.*, 2018).

Methodology

The study is based in both fieldwork and laboratory work. Fieldwork involved stratigraphic logging, detailed geological cartography and sampling, based on the lithostratigraphy and geological map of Bodego *et al.* (2015). Carbonate classification is based on Embry and Klovan (1972). Studied samples are Jurassic to lower Cenomanian mudstones, wackestones, packstones and grainstones.

The petrographic study has been carried out on polished thin sections using an Olympus BH-2 petrographic microscope attached to a Nikon Digital Sight DS – U3 camera. The cathodoluminescence study has been performed using a Technosyn Cold Cathode Luminescence 8200 MKII device coupled to the same petrographic microscope and attached to an Olympus Camedia C 7070 camera. The diameter of the electron beam used is 4.5 mm and it was accelerated with a potential of 15-17 kV at 0.5-0.6 mA. Energy Dispersion X-ray (EDX) and X-ray Diffraction (XRD) analyses were performed at the SGIKER General Services of the University of the Basque Country (UPV/EHU).

Results

Petrography

Feldspar crystals are colourless and clear under plane-polarised light (PPL) but may also show impurities such as calcite inclusions. Contrary to rounded and anhedral sand and silt size quartz grains, feldspars are euhedral, and have low surface relief and cleavage is not present (Fig. 2A). Depending on the section, they may be prismatic, tabular, or equidimensional (Figs. 2A and B). Locally, hexagonal faces are observed. Under cross-polarised light (XPL), feldspars show first order greyish interference colours, and polysynthetic and *Roc-Tourné* twinning is common (Fig. 2C). Their size is variable in the same sample, but they are usually less than 0.2 mm long. Besides, maximum crystal size is bigger among upper Albian - Cenomanian carbonates compared to older limestones. They are non-luminescent under cathodoluminescence (CL) and usually stand out in the orange dull luminescent calcareous matrix (Figs. 2D and E). Euhedral quartz, calcite, dolomite, pyrite and clay minerals complete the mineralogical paragenesis.

Feldspars are randomly oriented and

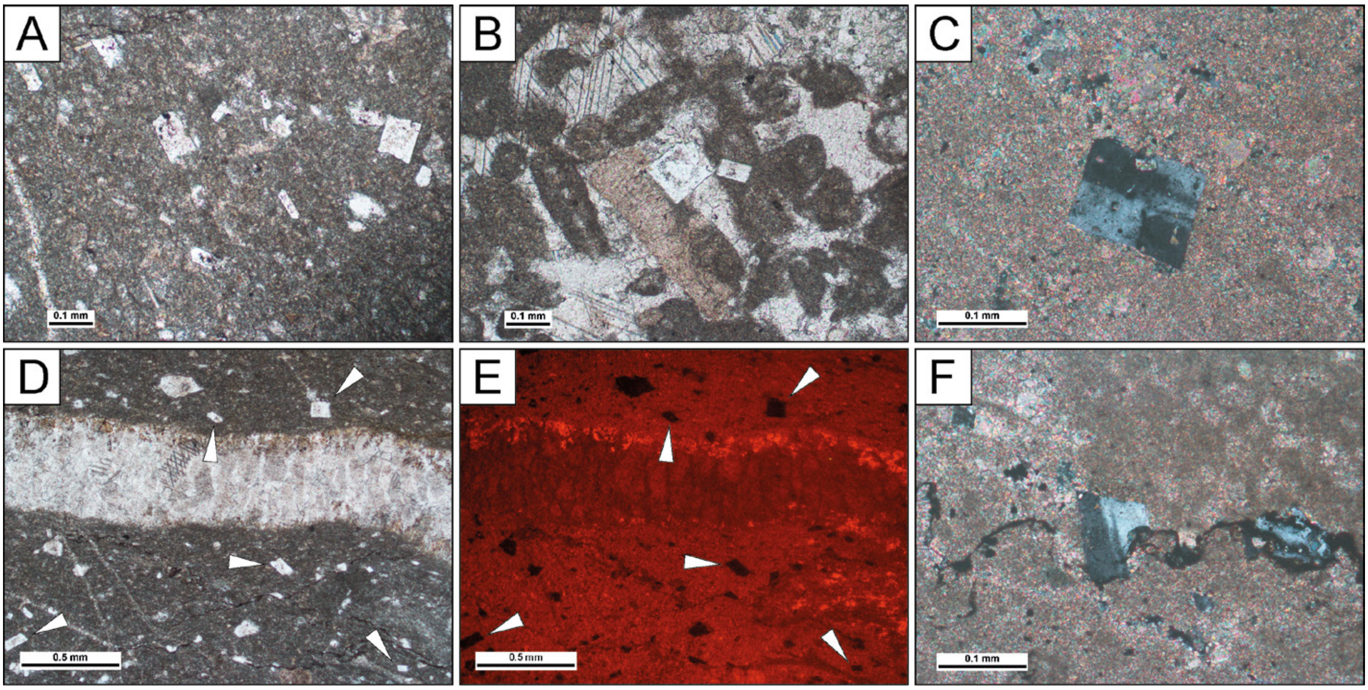

Fig. 2.- Microphotographs of: A) Tabular and prismatic euhedral crystals randomly oriented and distributed in a micrite matrix (PPL). B) Cross-cut relationship between feldspars and sedimentary allochems (PPL). C) Characteristic Roc-Tourné twinning (XPL). D) PPL and E) CL of the same visual area. Euhedral crystals are pointed out (white arrows) to differentiate them from other quartz grains. F) Crosscut relationship between a stylolite and feldspars (XPL) in which partial dissolution of the feldspars is observed. See figure in colour on the web.

Fig. 2.- Microfotografías de: A) Cristales euhédricos tabulares y prismáticos orientados al azar y distribuidos en la matriz. B) Relación de corte entre feldespatos y aloquímicos. C) Macla Roc-Tourné (polarizadores cruzados). D) Luz transmitida y E) CL, respectivamente, de la misma área. Los cristales euhédricos están resaltados (flechas blancas) para diferenciarlos de otros granos de cuarzo. F) relación de corte entre un estilolito y feldespatos en el que se observa la disolución parcial de los feldespatos (polarizadores cruzados). Ver figura en color en la web.

distributed. They crosscut primary sedimentary textures replacing completely or partially the micritic matrix (Figs. 2A and D), carbonate allochems (*e.g.* peloids and bioclasts) (Fig. 2B) and neomorphic intergranular spar calcite (Fig. 2B). On the contrary, pressure dissolution seams or stylolites crosscut the feldspars (Fig. 2F).

EDX semi-quantitative analysis

Measurements have been systematically carried out on euhedral feldspars (n=24), rounded sand and silt-sized quartz grains, carbonate matrix and on clay aggregates around stylolites (Fig. 3). Results are given in weight percentage of cations. Carbon is not considered for the semi-quantitative estimation, as it may partially or completely come from sample preparation to improve conductivity.

Analyses made on the matrix of the rocks estimates O (56%) and Ca (44%), indicating calcite as the main rock forming mineral (Fig 3). Locally, it may show other minor elements such as Fe. Euhedral crystals (Fig. 3) show the presence of O (51.10%), Na (7.97%), Al (9.45%) and Si (31.16%). Other elements such as K, Ca and Mg complete estimates. This composition corresponds to almost pure albite feldspars.

The case of quartz grains (Fig. 3), the average weight percentage for O and Si respectively are 53.49% and 46.51%. Finally, measurements on clay aggregates from stylolites show more variability detecting an array of elements comprising of O, Si, Mg, Al, K, Ca, Fe, Ti and Zr, (Fig. 3) which mainly compose quartz and clay minerals (illite and chlorite groups), apart from pyrite, rutile and zircon.

Interpretation and discussion

Authigenic nature of feldspars

On the one hand, the idiomorphic habit of feldspars, their irregular crystal size, their random orientation and distribution along thin sections, and the fact that feldspars crosscut primary depositional textures, support their authigenic character. This contrasts with anhedral and rounded quartz grains, which suggests a detrital origin.

On the other hand, albite crystals stand by their lack of CL and systematic semi-quantitative cationic analyses show clear compositional differences between the different minerals. In addition, it is relevant the absence of other types of (sedimentary) feldspar such as K-feldspar or plagioclase which could have been the precursor minerals before transformation.

All that would exclude a detrital origin of the albites, supporting a post-depositional diagenetic (authigenic) *in situ* formation by replacement due to the albitization of the limestones. Nevertheless, the formation of stylolites (burial and/or inversion?) clearly postdates the formation of feldspars, incorporating crystals and dissolving them forming clay mineral aggregates.

Albitization timing

Spötl *et al.* (1999) considered a deep burial diagenetic setting and migration of sulphate-bearing brines, which favoured the precipitation of albite and pyrite. The presence of pyrite is also notorious in our samples. However, crosscutting relationships between albites and stylolites are the opposite in our case, favouring a

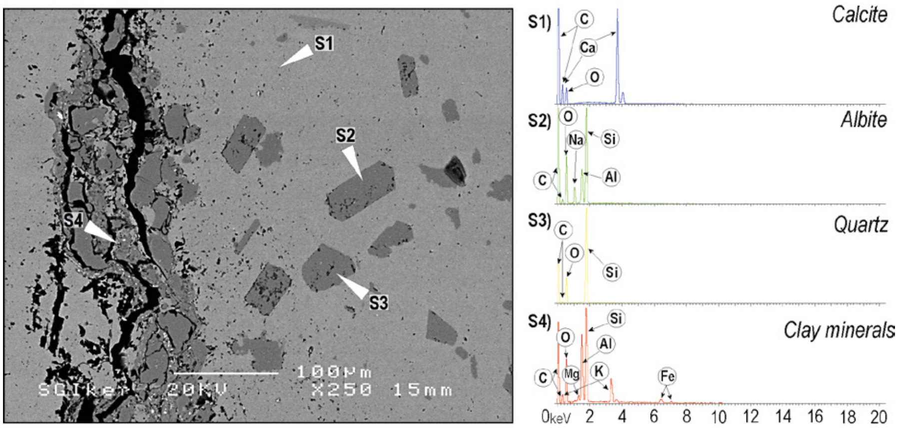

Fig. 3.- Back scattered electron (BSE) image (left) and EDX elemental analysis points with their respective spectrums (right). See figure in colour on the web.

Fig. 3.- Imagen de electrones retrodispersados (BSE) (izquierda) y los puntos de análisis elemental con sus respectivos espectros (derecha). Ver figura en color en la web.

relatively earlier diagenetic process. Therefore, stylolites post-date albites.

As stated by Kastner and Siever (1979), early diagenetic isochemical authigenesis models and fluid-exchange models need pore waters to become enriched in Na^+ and Al^{+3} with respect to H^+ and H^+SiO_4. Apart from that, it is known there is no direct relationship between temperature and albite formation (Kastner and Siever, 1979; Spötl *et al.*, 1999). So, the studied albitization processes could have occurred in early diagenetic stages. Considering the pre- and syn-rift character of the deposits and the more than likely high rate of sedimentation during the mid-Cretaceous (Bodego *et al.*, 2015), early compaction of sediments may have accelerated the release of the elements needed for the saturation of pore waters. Besides, a high permeable scenario where important extensional faulting and salt tectonics occurred (Bodego *et al.*, 2018), could have favoured the release and migration of brines along the fault zones into the younger and less compacted sediments, where albitization has been more intense, favouring crystal growth. Perona (2016) also considered geological structures rooted in Keuper facies and related brine flows for the formation of MVT Zn-Pb deposits in the BCB, where albites were also present.

Although the age of the mineralization remains unclear, the youngest albitized limestone units are, Albian to Cenomanian rocks. Stylolites could have been formed by burial loading or by the action of compressive stress during the Cenozoic tectonic inversion. Since large successions of basin sediments were deposited during the Late Cretaceous and Early Paleogene, dissolution seams probably started to form during the Late Cretaceous post-rift phase, and it could have increased subsequently, when compressive stresses acted. This could rule out an origin related to the migration of albitizing fluids during the Cenozoic tectonic basin inversion.

Conclusions

A petrological study of albite feldspars hosted into Mesozoic carbonates to the northeast of the Bortziriak-Cinco Villas massif has been carried out:

(1) It has been contrasted the pure albitic composition and the authigenic origin of the feldspars.

(2) A possible early diagenetic (replacement) origin has been suggested for their formation, although more data is needed in order to gain certainty in terms of timing, as different scenarios exist.

Author contributions

Ladron de Guevara: conceptualization, coordination, methodology, data acquisition, investigation, writing and visualization. Bodego: conceptualization, supervision, data acquisition, writing, editing and funding acquisition. Iriarte: conceptualization, supervision, data acquisition, writing and editing.

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