Glauconitic laminated crusts from Jurassic pillow-lava deposits (Betic Cordillera, South Spain)

Costras laminadas glauconíticas de depósitos de lavas almohadilladas del Jurásico (Cordillera Bética, Sur de España)

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ABSTRACT

An exceptional record of Jurassic glauconitic laminated crusts is reported from veins of spaces among pillow-lava bodies in the Middle Subbetic (Betic Cordillera). The veins are composed by green crusts with planar (<36 mm thick), columnar (<130 mm length) and oncoid-like morphologies growing from the pillow-lava walls. Mineralogical and geochemical analyses of the green crusts led us to identify lath-like crystals of glauconite and minority filmy veil-like smectites (saponite and beidellite), calcite and iron oxides. The composition of clay minerals and their association with carbonates reveal whether the alteration occurred under oxidizing or reducing conditions. The main phase of hydrothermal alteration occurred under low temperature oxidizing conditions with a high sea-water/rock ratio, in an open-circulation regime, with precipitation of glauconite. The late phase of alteration is typified by the formation of saponite and calcite, and took place under confined conditions due to the burial of pillow-lava by marine sediment.

Key-words: Clay minerals, hydrothermal alteration, Jurassic, Middle Subbetic.

RESUMEN

Se ha puesto de manifiesto que los materiales que rellenan el espacio entre las lavas almohadilladas jurásicas del Subbético Medio (Cordillera Bética) son costras verdes constituidas mayoritariamente por glauconita. Las costras crecen desde las paredes de las lavas almohadilladas con morfología planar (<36 mm de espesor), columnar (<130 mm de altura) y concéntrica. El análisis mineralógico y geoquímico ha permitido identificar cristales micrométricos de glauconita tabular, esmectitas de naturaleza saponítica y beidellítica, calcita y óxidos de hierro. El tipo de minerales de la arcilla (glauconita y esmectitas) y su asociación con carbonatos sugiere una primera fase de alteración hidrotermal con precipitación de glauconita que aconteció a baja temperatura en un régimen de circulación abierta con alta proporción de agua marina (condiciones oxidantes). Una segunda fase de alteración, bajo condiciones de confinamiento resultado del enterramiento de las lavas por sedimentos marinos carbonatados, dio lugar a la precipitación de saponita y calcita.

Palabras clave: Minerales de la arcilla, alteración hidrotermal, Jurásico, Subbético Medio.

Introduction

Spaces among pillow-lava bodies are commonly filled with a variety of material, including broken-up fragments of glassy-lava, sediments (limestones, marls) and secondary vein minerals. In this research we report on minerals associated with inter-pillow spaces characterized by laminated green crusts, calcite and quartz. Glauconite related to volcanic and hydrothermal processes is scarcely documented in the literature (e.g. Buatier *et al.*, 1989; Clayton and Pearce, 2000) with respect to glauconitic facies from sedimentary environments (e.g. Odin and Matter, 1981; Sánchez-Navas *et al.*, 2008). In both cases –volcanic-hydrothermal and sedimentary-

diagenetic– the glauconite is mainly recorded as peloidal grains. This work reports on green laminated crusts made up mainly of glauconite. Results of mineralogical and geochemical analyses provide a basis for the discussion of possible growth conditions.

Geological setting

The analyzed pillow-lavas come from the Jurassic submarine volcanic rocks of the Middle Subbetic, Betic Cordillera (southern Spain), the westernmost European Alpine chain. The Subbetic is located in the external zones of the cordillera and is constituted mainly by sedimentary marine materials deposited in the Southern Iberian Palaeomar-

gin from the Triassic to the Miocene. During middle-late Jurassic, the southern Iberian Palaeomargin was affected by submarine volcanic activity in wide sectors of the pelagic basin. Pillow-lava flows dominate and are interbedded with pyroclastic rocks and pelagic sediments with a maximum thickness over 300 m (Vera *et al.*, 1997). The Jurassic submarine volcanic rocks of the Middle Subbetic are considered as transitional alkaline, originating in an extensional process of crustal thinning (Portugal *et al.*, 1995). The green laminated crusts of study were obtained from voids developed in inter-pillow spaces. The Campotéjar outcrop (coord. 37°30′12″N, 3°37′50″W) is located close to the A-44 motorway from Jaén to Granada, at km 79 (Granada province) (Fig. 1).
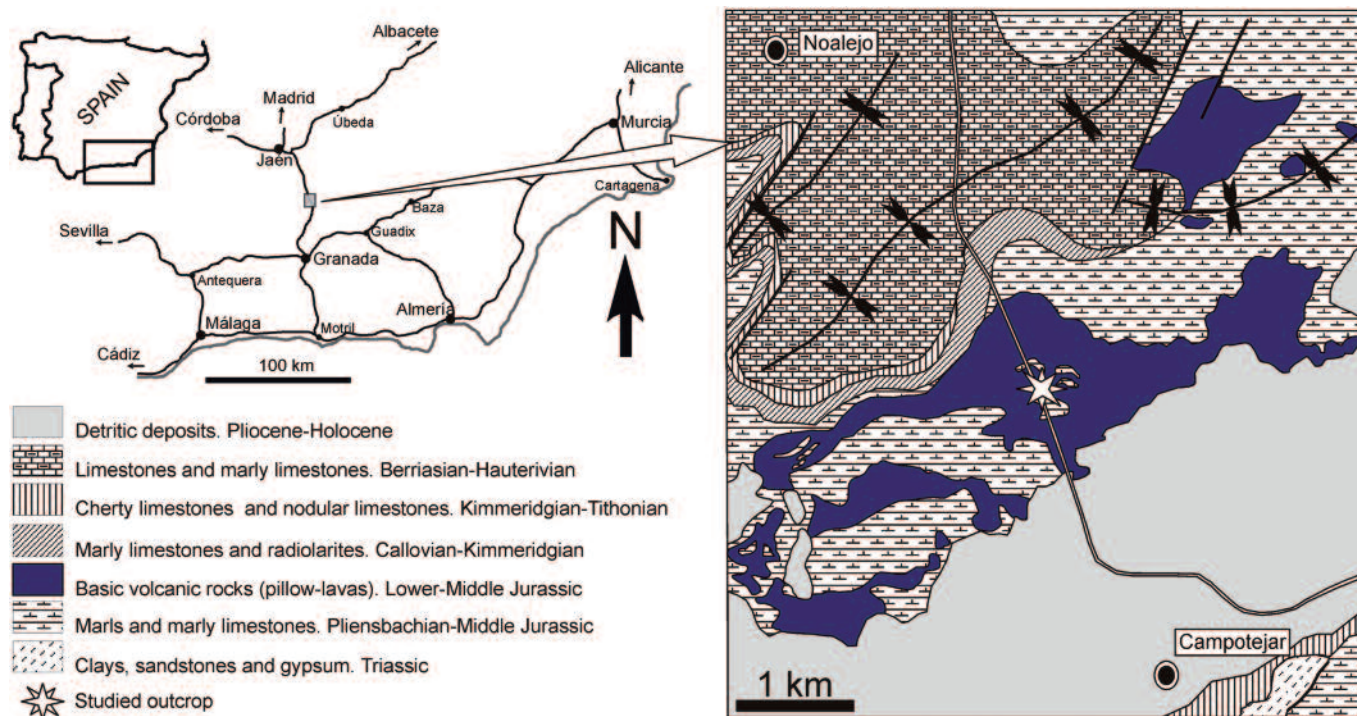
Fig. 1.- Geological setting of the studied outcrop.

Fig. 1.- Localización geológica del afloramiento estudiado.

Methods

Petrographic microscopy as well as magnifying glasses were used to determine the morphology of the crusts on thin and polished sections. Whole-rock samples, oriented aggregates and solvated samples with ethylene glycol (EG) were studied using a Philips PW 1710 powder diffractometer with CuKα radiation, at the Instituto Andaluz de Ciencias de la Tierra (Granada). Samples were examined by Scanning Electron Microscopy (SEM), using back-scattered electron and secondary electron imaging and energy-dispersive X-ray (EDX) to obtain textural and chemical data, with a Leo 1430-VPSEM at the Centro de Instrumentación Científica (CIC) of the Universidad de Granada. To characterize the chemical composition of smectites, analytical electron microscopy (AEM) data were obtained from powdered portions in a Philips CM20 located at CIC and equipped with a solid-state EDX detector. The structural formulae of glauconitic micas and smectites were calculated on the basis of 22 negative charges $O_{10}(OH)_2$ and it was assumed that Fe is present as Fe^{3+}.

Results

White and green crystal growths developed in the inter-pillow spaces. The morphology of these infilling mineralizations is irregular, sometimes stratiform, with length <55 cm. The internal structure of the mineralizations is graded from the walls of the pillow-lava body recovered by planar laminated green crusts (2–36 mm thick). More internal parts of the mineralizations are composed by calcite and secondarily quartz. In some cases, the infilling of the voids was not complete and they are preserved as geodes. The calcite and quartz mass is crossed by green laminated columns (<130 mm length and <26 mm in diameter) growing from the green laminated crusts located on the walls of the pillow-lava (Fig. 2A). Oncoid-like forms (<25 mm diameter) occur inside the calcite mass (Fig. 2B).

The laminae of planar crusts and columns are irregular and not densely packed in surrounding quartz or calcitic crystals. Laminae are 20–60 μm thick and contain cylindrical filaments with a darker core (dark green or black). Some green filaments with dichotomous branching grow perpendicular to the lamination (100–450 μm length) (Fig. 3). Under SEM, the green material is seen to be made up of lath-like crystals (<2.5 μm length, <0.8 μm width) and veil-like crystals (Fig. 4A).

The X-ray diffraction patterns corresponding to the green crusts show glauconite, calcite, and a small amount of smectite with the presence of the 001 reflection only at 16.6 Å after EG solvation. There are no evidences of interstratified glauconite/smectites in the diffractograms. The less-abundant dark green (almost black) material is composed only by smectite and is characterized by a basal spacing of 14.6 Å which expands to 16.6 Å after EG treatment. Micro-chemical analyses (SEM/EDX and TEM/AEM) confirm the presence of glauconite and smectitic grains. Glauconite analyses show a Si content always >3.50 atoms per formula unit (a.f.u.) and an amount of K >0.60 a.f.u. with a sum of interlayer varying in the range of 0.71–0.93 a.f.u. The octahedral sheet is characterized by Fe contents of 0.53–1.27 a.f.u. and Al and Mg contents are in very similar quantities (0.56–0.75 and 0.52–0.78 a.f.u., respectively).

The TEM study performed on the green material corroborates the presence of lath-like crystals of glauconite (Fig. 4B). AEM analyses of smectites reveal the presence of filmy veil-like saponite (Fig. 4C) characterized by an interlayer charge of >0.3 a.f.u. with the predominance of Ca. Less abundant smectites with beidellitic composition were also analyzed, with an interlayer charge of 0.3–0.4 a.f.u. and higher K contents.
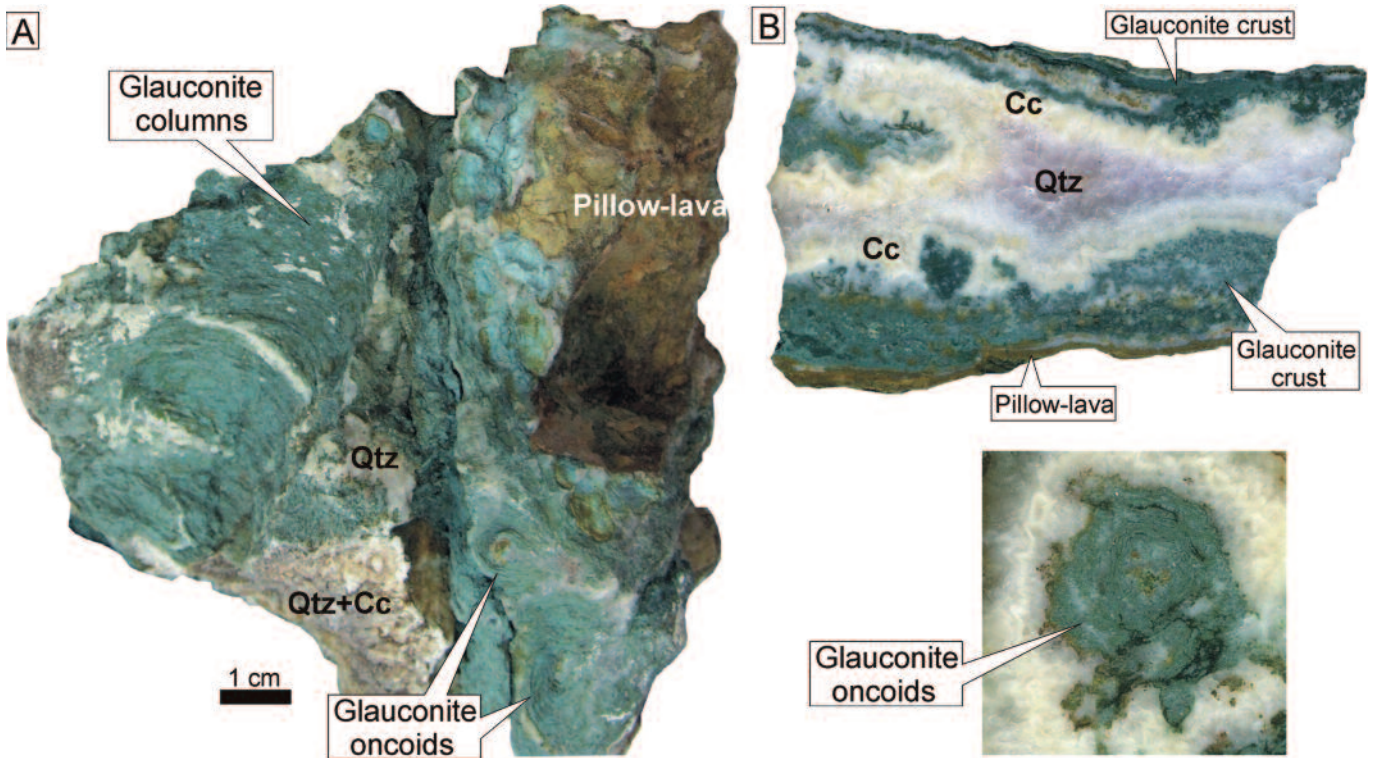
Fig. 2.- Examples of glauconitic crusts. A) Hand sample showing glauconite columns and oncoids. B) Polish section illustrating mineralogical zonation in the inter-pillow spaces infilling. C) Glauconite oncoid surrounded by calcite.

Fig. 2.- Ejemplos de costras glauconíticas. A) Muestra de mano con morfologías columnares y oncoides. B) Sección pulida mostrando la zonación mineralógica de los rellenos entre lavas almohadilladas. C) Oncoide glauconítico rodeado de calcita.

Discussion

Geochemical and mineralogical analyses of the green crusts (planar, columnar and oncoidal morphologies) recorded in the spaces among the pillow-lava bodies confirmed they were glauconite and, less commonly, saponite and beidellite. The glauconite laminated crusts developed principally on the walls of the pillow-lava and constitute the first mineral phase in the infilling of the voids among pillow-lava bodies by hydrothermal precipitates. Other mineral phases occupying more internal parts were calcite and quartz. Veil-like smectites and lath-like glauconite are clearly differentiated by the morphology and geochemistry under SEM and TEM.

The genesis of glauconite is commonly related to sea-bottom confined microenvironments under low sedimentation rate by crystallization of glauconitic smectite (see Odin and Matter, 1981). In these contexts glauconite is an authigenic mineral developed as pelletal facies (mud coprolites, foraminiferal tests and mineral debris) from smectitic precursor to highly evolved glauconite by increasing in K and Fe (e.g. Odin and Matter, 1981; Sánchez-Navas *et al.*,

2008). However, the morphology of the glauconites reported here is different from the traditional classification of glaucony habits (Odin and Fullagar, 1988). Given the type of deposits related to the vein infilling of inter-pillow spaces, the environmental conditions for the genesis of green laminated crusts are associated with hydrothermal fluids.

The composition of the clay minerals from veins filling inter-pillow spaces and their association with carbonates could reveal whether the alteration occurred under

oxidizing or reducing conditions, as a direct consequence of the fluid/rock mass ratio (D'Antonio and Kristensen, 2005). The main phase of hydrothermal alteration of basalts occurred at low temperature under oxidizing conditions with a high seawater/rock ratio, in an open-circulation regime, with precipitation of abundant glauconite. Diffusion of oxygenated seawater along inter-pillow spaces coupled with diffusion into the rock produced the early alteration. In these contexts Fe is mobilized by the breakdown of volcanic glass,
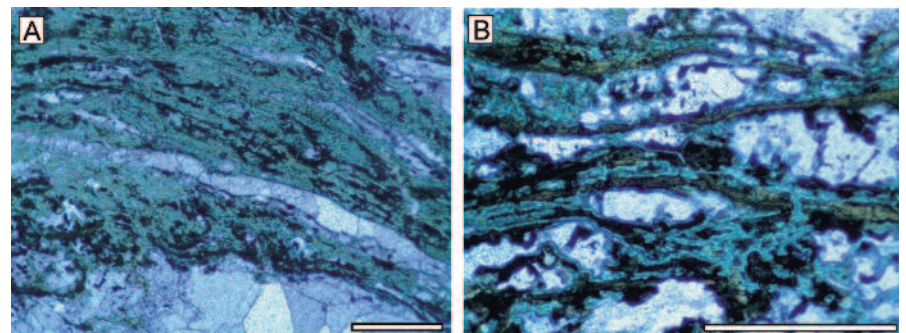

Fig. 3.- Glauconite crusts containing filamentous structures under petrographic microscopy. Scale bar 1 mm.

Fig. 3.- Costras glauconíticas observadas en microscopio petrográfico, que muestran estructuras filamentosas. Escala 1 mm.
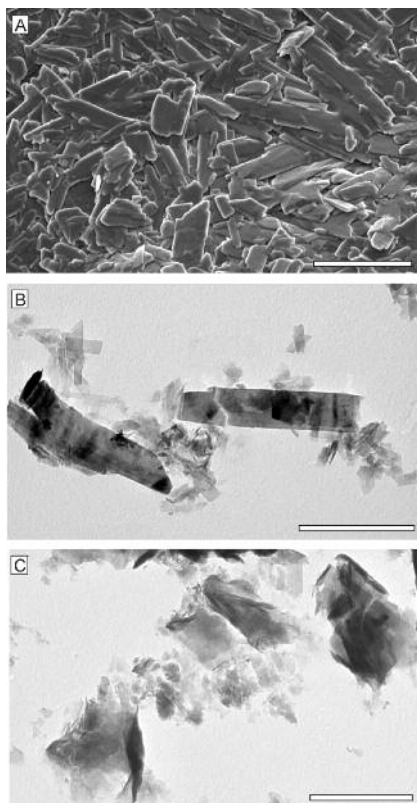
Fig. 4.- Electron microscopy images. A) Lath-like crystals of glauconite (SEM). B) Lath-like crystals of glauconite (TEM). C) Veil-like grains of smectite (TEM). Scale bar 1 µm.

Fig. 4.- Imágenes de microscopía electrónica. A) Cristales tabulares de glauconita (SEM). B) Cristales tabulares de glauconita (TEM). C) Granos tipo velo de esmectita (TEM). Escala 1 µm.

while sea-water must have been an additional supplier of K for glauconite (Clayton and Pearce, 2000; D'Antonio and Kristensen, 2005). However, the volcanic edifices of the Middle Subbetic are composed of K-rich pillow-lavas (Vera *et al.*, 1997). Thus, Fe and K were added to the oxidation zone and fixed in the precipitation of Fe-rich dioctahedral mica (glauconite).

The late phase of alteration is typified by the formation of saponite, beidellite and calcite; and it took place under confined conditions resulting from burial of pillow-lava by marine sediments. There are significant similarities between the products of low temperature hydrothermal alteration in pillow-lava described in this study as compared with those from ocean-ridge basalts and oceanic crusts (Clayton and Pearce, 2000; D'Antonio and Kristensen, 2005), with the presence of early Fe-rich dioctahedral mica (glauconite with some smectite) followed by later saponite and carbonates. The absence of secondary minerals such as chlorite, epidote and albite constrains the temperature of the hydrothermal alteration under zeolite-facies conditions (<100-150ºC). Recently, Clauer *et al.* (2011) recorded a crystallization temperature of 32-63ºC based on $\delta^{18}O$ values in the Galapagos Spreading Center.

Conclusions

The Jurassic pillow-lava from the Middle Subbetic presents characteristic veins made up of glauconitic laminated crusts with planar, columnar and oncoid-like morphologies, calcite and quartz. These laminated crusts developed over the pillow-lava surfaces.

Mineralogical and geochemical analyses of the green laminated crusts make it possible to identify common lath-like crystals of glauconite and minority filmy veil-like smectites (saponite and locally beidellite).

The composition of the veins and their relation with pillow-lava point to a hydrothermal context for the genesis of the studied materials. Two different phases may be differentiated from the clay mineral composition of the veins:

The first phase of hydrothermal alteration occurred under low-temperature oxidizing conditions in an open-circulation regime, with precipitation of glauconite laminated crusts growing directly over the pillow-lava surfaces.

The second phase of hydrothermal alteration occurred after the burial of volcanic rocks by marine sediments, limiting the circulation of sea-water and favouring the formation of saponite and calcite.

Acknowledgements

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