Geoderma 271 (2016) 99–114

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

# Chemical and textural controls on the formation of sepiolite, palygorskite and dolomite in volcanic soils

Javier Cuadros [a,*], Jose L. Diaz-Hernandez [b], Antonio Sanchez-Navas [c], Antonio Garcia-Casco [c], Jorge Yepes [d]

[a] Department of Earth Sciences, Natural History Museum, Cromwell Road, London SW7 5BD, United Kingdom
[b] IFAPA, Área de Recursos Naturales, Consejería de Agricultura, Pesca y Medio Ambiente, Junta de Andalucía, 18080 Granada, Spain
[c] Departamento de Mineralogía y Petrología—IACT, Universidad de Granada—CISC, 18071 Granada, Spain
[d] Departamento de Ingeniería Civil, IOCAG, Universidad de las Palmas de Gran Canaria, 35017 Las Palmas de GC, Spain

ARTICLE INFO

*Article history:*
Received 4 September 2015
Received in revised form 4 December 2015
Accepted 31 January 2016
Available online 26 February 2016

*Keywords:*
Calcite
Dolomite
Palygorskite
Sepiolite
Tephra alteration
Volcanic soils

## ABSTRACT

A 3-m deep soil profile from Gran Canaria, Canary Islands, has been studied. The profile is interesting because soil development on mafic tephra produced a pattern of clay mineral and carbonate distribution. Carbonates precipitated abundantly, increasingly towards the bottom, making up 20–90 wt.% of the soil. Sepiolite and calcite are dominant at the top, whereas palygorskite and dolomite are the major components at the lower part of the profile. Quartz is present in low amounts in most of the profile, and smectite and non-crystalline partially altered tephra occur in low amounts towards the bottom. Mineralogical, chemical and textural investigations indicate that sepiolite and calcite precipitated in the space between the original tephra grains, from Ca, Mg and Si dissolved in situ and transported in the runoff. Palygorskite and smectite precipitated within tephra grains, from in situ tephra weathering, as well as dolomite. The distribution of the clay minerals is due to clay composition and ion mobility. Sepiolite, consisting only of Si and Mg, precipitated outside tephra grains, where the mobile Si and Mg ions were abundant in the interstitial waters. Palygorskite and smectite contain Si, Al, Fe, and Mg and only precipitated within the tephra grains, where the immobile Al and Fe were available. Calcite precipitation in solution is kinetically favored over that of dolomite and thus calcite precipitated between the grains. Dolomite precipitated within altering tephra grains and spherical clay structures because tephra and clay generated a viscous medium where dolomite supersaturation increased and the kinetic barrier for precipitation was overcome. These results are relevant to the "dolomite problem", as they illustrate how dolomite can precipitate in surface conditions, and to $CO_2$ sequestration, because dolomite can immobilize higher $CO_2$ amounts (both Ca and Mg are involved and not only Ca) and in a much more stable manner (dolomite is eight orders of magnitude less soluble than calcite).

## 1. Introduction

Chemical weathering of basaltic volcaniclastic rocks leads to the formation of diverse clay mineral assemblages depending on the depositional environment (lacustrine, soils, alluvial terraces and marine fan deltas). Pedogenic alteration constitutes a sub-aerial weathering process involving the combined effect of diverse factors, such as parent material, climate, biota, time and geomorphology. Weathering of a basaltic substrate produces as secondary minerals clays, carbonates, zeolites and Si–Al–Fe oxy-hydroxides (Chamley, 1989). The main clay minerals derived from pedogenically-altered basaltic substrates are smectite (nontronite, saponite or montmorillonite), kaolinite and halloysite (Chamley, 1989). Sepiolite and palygorskite occur in soils derived from several substrates, in particular they are typical of caliches formed in arid and semi-arid areas (Neaman and Singer, 2004). Sub-aerial weathering by meteoric waters of basaltic substrates can provide Si–Mg bearing solutions and suitable physico-chemical conditions (mostly high pH) to precipitate Mg-rich phyllosilicates and carbonates (Singer and Norrish, 1974). Sepiolite and palygorskite are among the most Mg-rich clay minerals (Singer, 2002). Sepiolite contains more Mg than palygorskite and may derive from Mg-leaching reactions affecting palygorskite (Corma et al., 1987; Corma et al., 1990; Singer, 1977).

Altered basalts may constitute geological formations for natural $CO_2$ storage (Oelkers et al., 2008). Particularly, in pedogenic environments, $CO_2$-rich fluids produce the leaching of metals from the basaltic substrate and, under arid conditions, lead to the formation of Ca and Mg carbonates. Although some authors have identified dolomite in soils (e.g., Gile, 1961; St. Arnaud, 1979; Sobecki and Karathanasis, 1987; Botha and Hughes, 1992), there are few reports showing its pedogenic origin. Dolomite pedogeneis has been usually interpreted to take place in saline soils (Shermann et al., 1962; Kohut et al., 1995) and in soils developed on serpentinites and basaltic rocks (Podwojewski, 1995; Capo

---

* Corresponding author.
*E-mail address:* j.cuadros@nhm.ac.uk (J. Cuadros).

http://dx.doi.org/10.1016/j.geoderma.2016.01.042

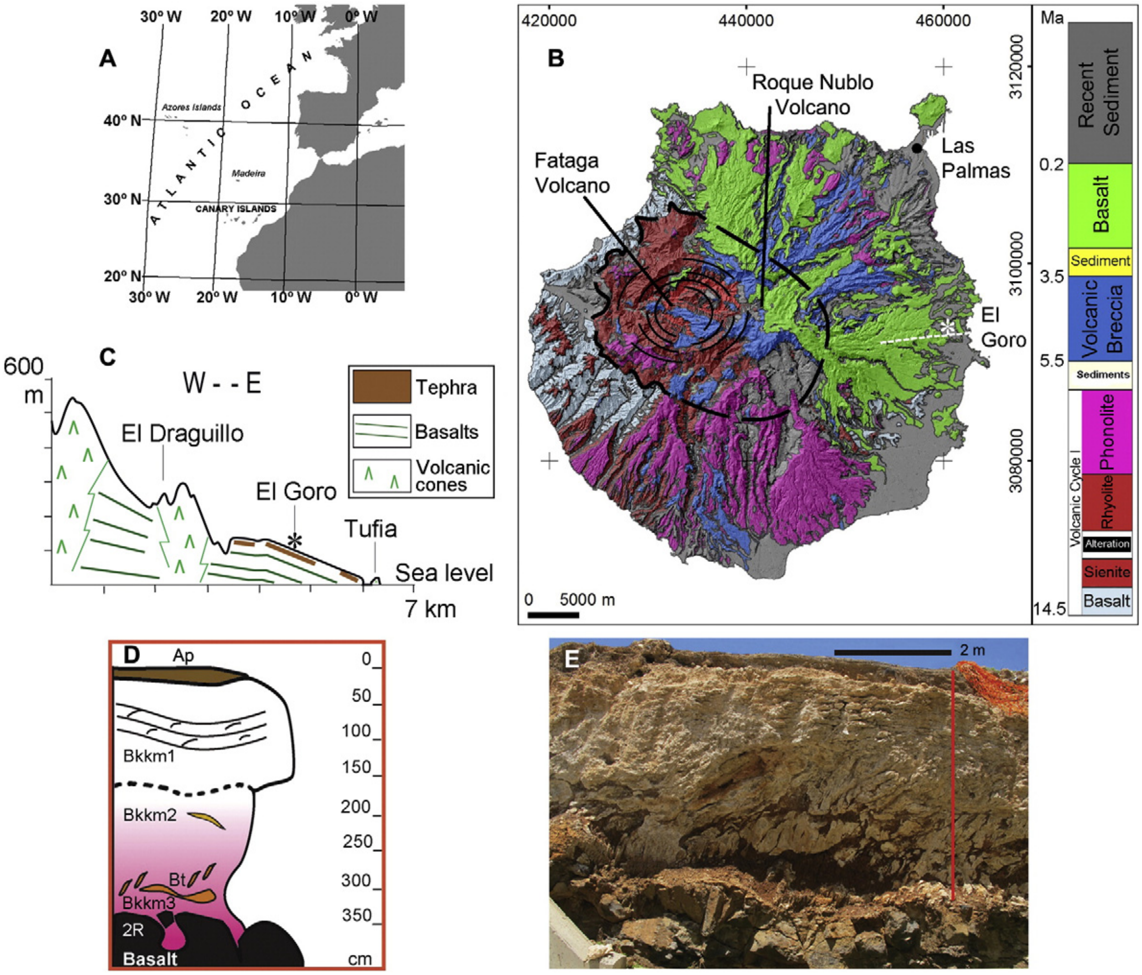

**Fig. 1.** A) Situation of the Canary Islands. B) Geological chart and lithological column of the Gran Canaria Island with indication of the diverse volcanic episodes which formed the island. The studied profile at El Goro (star) developed from tephra deposited on the eastern slopes of the Roque Nublo volcano. C) Cross section indicated in B, showing the spatial relationship between the volcanic cones (e.g., El Draguillo, of the same unit as the tephra where the soil developed), and the deposits of lavas and tephra. D) Sketch and field image (E) of the soil profile with the established horizons: Ap, Bkkm1, Bkkm2 including Bt, and Bkkm3. The basaltic substrate appears at the bottom. The sampled profile is indicated by a vertical line in E.

et al., 2000) as both environments produce or can produce high Mg concentrations. The formation of dolomite in Mg-rich soils has been recently reported by Capo et al. (2000) and Diaz-Hernandez et al. (2013) on a basaltic weathering profile in Hawaii and a clay-rich sediment in southern Spain, respectively. The Mg source was the basalt in the Hawaiian soil and detrital dolomite dissolved in the surface horizons, in the Spanish soil. The scarce formation of dolomite in modern environments contrasts with its abundance in ancient rocks, which together with failure in the efforts to synthesize dolomite in the laboratory under surface abiotic conditions has generated the so-called “dolomite problem” (e.g., Arvidson and Mackenzie, 1999).

Assemblages of Mg- and Fe-bearing clays with Fe–Mg–Ca carbonates have been detected by spectral analysis of NASA's CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) images in some regions of Mars with exposed rock units dating from the Noachian period (Niles et al., 2012). Thus, soils derived from basalts under arid-semiarid conditions constitute a potential Earth analogue to the Mars carbonate and phyllosilicate-bearing rock units. Although sepiolite and palygorskite have not been identified on Mars, their spectral near-infrared features can be very similar to smectite of various Al–Mg–Fe contents, and their presence in Martian rocks is possible. Basalts are also a potential habitat for microbial life (Thorseth et al., 1992) given their abundant inorganic nutrients. Clay-carbonate assemblages on Mars are appropriate targets for the search of life relicts (Michalski et al., 2013) and the study of the bio-geochemical characteristics of Mg-bearing clay-carbonate assemblages on Earth developed on basalt may help the investigation of the possible development of life on Mars during the Noachian period.

In this work we examine a case of formation of sepiolite and palygorskite together with calcite and dolomite from pedogenic alteration of basaltic tephra, in an unusually thick 3 m soil profile. The detailed mineralogical, textural and compositional study shows a mineral distribution consisting of sepiolite and calcite as the major components at the upper part of the profile, palygorskite and dolomite in the lower part, and smectite at the bottom. We discuss this mineral and chemical zoning in the context of the alteration processes taking place in the volcanic deposit and the formation of caliche soil, as well as the role of clay minerals and tephra in the formation of dolomite.

## 2. Geological setting

Gran Canaria is the third largest island of the Canary Islands volcanic archipelago, which is part of the so called Macaronesian region, and is located just off the northwest coast of Africa (Fig. 1A). The Canary Islands are located on the oceanic crust of the African continental margin. Oceanic intraplate alkaline volcanism, probably related to a volcanic plume or hot spot in the mantle, is responsible for the formation of the archipelago. Volcanism in the Gran Canaria island evolved from an old submarine-subaerial stage (14.5–8.0 My; Guillou et al., 2004) which created a large basaltic edifice (the Shield Volcano) and a salic stratovolcano (the Fataga Volcano). The latter then experienced a caldera collapse (Guillou et al., 2004). This first stage was followed by a calm