Applied Clay Science 87 (2014) 108–119

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Zeolite occurrence and genesis in the Late-Cretaceous Cayo arc of Coastal Ecuador: Evidence for zeolite formation in cooling marine pyroclastic flow deposits

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A R T I C L E I N F O

Article history:
Received 8 June 2011
Received in revised form 26 July 2013
Accepted 15 October 2013
Available online 18 November 2013

Keywords:
Natural zeolite
Ecuador
Cayo Formation
Geoautoclave
Hydrothermal alteration
Pyroclastic flow deposits

A B S T R A C T

This paper describes the quantitative mineralogy, the mineral chemistry and the distribution of natural zeolites over the outcrop area of the Late Cretaceous Cayo Formation of Coastal Ecuador (>1000 km^2) and develops a model for zeolite alteration in the Cayo volcanic arc. Different zeolite types were identified: Ca-heulandite-type zeolites (clinoptilolite and heulandite), mordenite, laumontite, analcime, stilbite, epistilbite, chabazite, thomsonite and erionite. Zeolites occur over nearly the entire outcrop area and the entire stratigraphical thickness of the Cayo Formation, in percentages varying between less than 20 and nearly 100 wt.%. A substantial amount of the analysed samples (1/8) has zeolite contents higher than 50 wt.% and could potentially be used in agriculture, aquaculture, for waste water treatment or as supplementary cementitious materials. A clear difference in zeolite type and content was observed when comparing the lower and upper units of the Cayo Formation and the distribution of these units determines the zeolite distribution over the outcrop area. In the upper unit, Ca-HEU-type zeolites are the main zeolite minerals and rarely laumontite and analcime occur. A smectite-rich smectite/chlorite (C/S) is the major associated alteration mineral, while quartz contents are relatively low. In the lower unit, the zeolite mineralogy is more variable and mordenite, Ca-HEU-type zeolites and laumontite are common. Stilbite, epistilbite and analcime occur rarely. Further quartz, albite, C/S and celadonite occur as associated alteration minerals. Little burial metamorphism or volcanically induced hydrothermal alteration has affected the deposits of the Cayo formation. Mineral alteration occurred mainly by interaction of hot pyroclastic glass with marine water, present as pressurized steam in cooling pyroclastic flow deposits on one hand or by low temperature diagenesis of already cooled pyroclastic or epiclastic deposits on the other hand. A model similar to the "geoautoclave" model is proposed to explain the genesis of zeolites, in which an autoclave is formed by the hydrostatic pressure exerted by the marine water column overlying the pyroclastic deposits, preventing gas escape and promoting glass dissolution, zeolite formation and, conversion to higher-grade phases possible if heat can be maintained for a long enough period.

1. Introduction

In 1994, zeolites were discovered in the coastal region of Ecuador in Guayaquil, the largest city of Ecuador. Zeolites occur in the Cayo Formation, a Late Cretaceous rock unit composed of marine volcanoclastic rocks. Initially, clinoptilolite and mordenite were identified (Romero, pers. com.) and later heulandite was found (Morante, 2004). The main zeolites occurring in Guayaquil are Ca-heulandites (average Si/Al: 3.30) and Ca-clinoptilolites (average Si/Al: 4.35) and less common are laumontite, mordenite and analcime (Machiels et al., 2008). Zeolites compose 10–60 wt.% of the rocks and a large variability in zeolite type and content exists throughout the beds (Machiels et al., 2008).

Early investigation focussed on the zeolite occurrence in the vicinity of Guayaquil, but preliminary work has shown that zeolites occur throughout the cordillera Chongón-Colonche, a mountain range stretching out west from Guayaquil towards the coastal line, 100 km towards the west (Machiels et al., 2006; Figs. 1 and 2). Nowadays, local zeolitic rocks are used in agriculture and in aquaculture and during the last decades

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http://dx.doi.org/10.1016/j.clay.2013.10.018

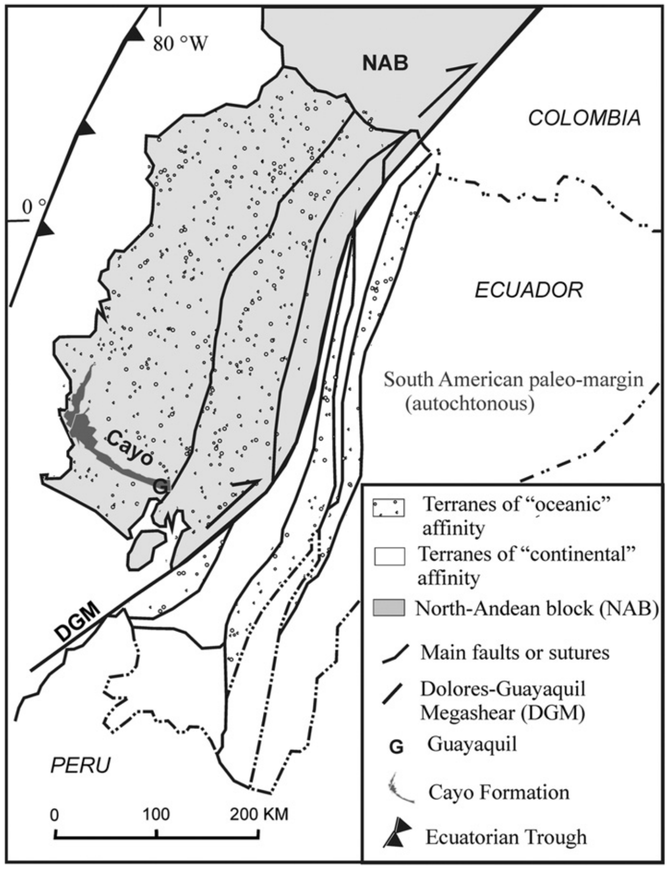

Fig. 1. The oceanic basement of western Ecuador. The entire coastal area and the western Cordillera of the Andes of Ecuador are built up of terranes composed of mafic oceanic crust, derived from the interaction of the Caribbean oceanic plateau with northern South America. The outcrop area of the Cayo Formation, west of Guayaquil (G), is indicated. Modified from Bourdon et al. (2003).

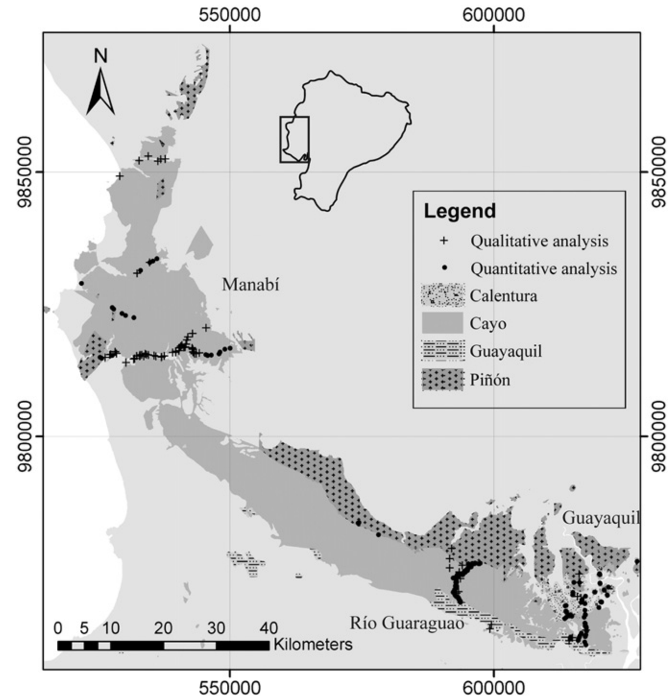

Fig. 2. Localization of the three main sampling areas for X-ray analysis. The Guayaquil area, the Río Guaraguao area and the Manabí area are shown. The underlain geological map is combined from the geological maps of Dirección General de Geología y Minas (1970, 1974a,b,c, 1975a,b, 1980) and ESPOL–ORSTOM (1985). Coordinate system: PSAD 1956. UTM UPS zone 17S.

small quarries have appeared near Guayaquil and throughout the cordillera. However, the exploitation and local application of the minerals are still limited. In the future, zeolitic rocks could be used for the purification of the waste waters of Guayaquil, a city of more than three million inhabitants (Calvo et al., 2009; Garcés et al., submitted for publication; Morante et al., 2010), as fertilizer carriers in banana and coffee plantations, or for the absorption of ammonia from shrimp breeding pools (Morante, 2011). Another possibility is the use of zeolites as supplementary cementitious materials in the local cement industry (Mertens et al., 2009; Snellings et al., 2009).

The objective of the current contribution is to present an overview of the mineralogy, mineral chemistry and distribution of the zeolites in the Cayo Formation over its entire outcrop area throughout the Cordillera Chongón-Colonche and to develop a genetic model explaining zeolite occurrence and distribution, thereby contributing to the understanding of zeolite genesis in the area on one hand, and to the exploitation and application of the minerals on the other hand.

2. Regional and local geology

The western cordillera of the Andes and the Coastal area of Ecuador are built up of accreted fragments of Late Cretaceous mafic oceanic plateau basement (Kerr et al., 2003; Luzieux et al., 2006; Mamberti et al., 2003; Reynaud et al., 1999; Vallejo et al., 2006 — Fig. 1). An intra-oceanic island arc was formed at the edge of this oceanic plateau, which yielded thick sequences of volcanoclastic, volcanic and intrusive rocks (Benítez, 1995; Lebrat et al., 1987; Luzieux et al., 2006; Machiels, 2010; Machiels et al., 2008; Pichler and Aly, 1983; Thalmann, 1946). In the Coastal area, the Late Cretaceous basement crops out in the Cordillera Chongón-Colonche, a NW–SE oriented mountain range occurring west of Guayaquil (Fig. 2). Several rivers cross-cut the cordillera from NE to the SW, perpendicular to the Late Cretaceous beds.

One of the most complete sections of the Late Cretaceous stratigraphy occurs in the Río Guaraguao, a river located 35 km NW of Guayaquil (Fig. 2). The stratigraphical section exposed by the river is shown schematically in Fig. 3. From the north to the south, the following rock units are exposed (Figs. 3–4): the Piñón Formation, of unknown thickness, which forms the mafic oceanic basement of the area, of late Turonian to early Coniacian age (Luzieux et al., 2006); the Las Orquídeas Formation (Van Melle et al., 2008), less than 100 metre thick, composed of submarine volcanic breccia, of early or middle Coniacian age; the Calentura Formation, less than 50 metre thick, composed of fine-grained cherts, limestones and thin-bedded volcanoclastic turbidites, of middle Coniacian age (Ordóñez et al., 2006); the Cayo Formation, 1700 metre thick, subdivided in two units (Machiels, 2010): the lower unit, the Río Guaraguao unit, 700 metre thick and composed of marine pumice-rich pyroclastic flow deposits and minor tuffs and associated epiclastic rocks, of middle Campanian age at the base (Radiolarian zone of *Amphyphyndax pseudoconolus*, Ordóñez et al., 2006) and of late Campanian age (or younger) at the top (Radiolarian zone of *Amphyphyndax tylotus*, Ordóñez et al., 2006); and the upper unit, 1000 metre thick, composed of marine epiclastic rocks, block and ash flow deposits and water-lain tuffs, of late Campanian (or younger) age at the base (Radiolarian zone of Amphyphyndax tylotus, Ordóñez et al., 2006) and of Maastrichtian age (Ordóñez et al., 2006) at the top; and the Guayaquil Formation, 370 metre thick, is composed of fine-grained thin bedded cherts, of Maastrichtian age at the base and of Danian age at the top (Ordóñez et al., 2006; Vilema, 2008). A more extensive description of volcanism and deposition in the Cayo arc can be found in Machiels (2010).