Catena xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catena

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

Genesis of palygorskite and calcretes in Pliocene Eskişehir Basin, west central Anatolia, Turkey

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A R T I C L E I N F O

Keywords:
Calcrete
Eskişehir
Mudstone
Pliocene
Palygorskite
Turkey

A B S T R A C T

Calcretes are common in the Eskişehir province, and occur as powder, nodules, tubes, fracture-infills, and hard laminated crusts. They are white in color, and developed in the near surface setting of the Pliocene reddish-brown mudstones. Calcrete profiles consist mainly of isolated calcrete occurrences within mudstone. Palygorskite occurs generally as a beige colored layer in the mudstone and also as a minor component in the calcretes. The calcrete nodules are roughly spherical to ellipsoidal in shape with diameters of 3 to 20 cm, and are composed mainly of micrite, locally recrystallized to microsparite and sparite. Detrital quartz and feldspar "float" in the micritic groundmass. Circumgranular cracks, crumbly fractures and rhizoliths are also present. XRD analyses indicate that calcrete samples are comprised mainly of calcite accompanied by small amounts of palygorskite, quartz, feldspar, smectite, chlorite, and locally accessory illite and amphibole. The SEM/TEM images indicate that palygorskite fibers formed singly, as bundles, knitted and/or matted aggregates; either covering calcite crystals or smectite aggregates, or as a meniscus-cement between smectite flakes. The latter are precipitated from meteoric water flushed through the open pore system of the sediments close to the surface. Based on the SEM images, palygorskite is presumed to have formed authigenically by direct precipitation in the vadose zone of a lacustrine environment following precipitation of calcite. The $\delta^{13}C$ and $\delta^{18}O$ values of calcite indicate calcretization from meteoric soil-water in an arid environment. Enrichment of Ba ± Sr, Ni and LREE relative to MREE + HREE, and a negative Eu anomaly, reflect the fractionation of feldspar and amphibole in the parent mudstone. The palygorskite associated with calcretes and mudstone was precipitated from alkaline water rich in Si, Al, Fe and Mg having Mg-rich character with a structural formula of $Si_{7.94}Al_{0.06}O_{20}Mg_{2.96}Al_{0.99}Fe_{0.31}(OH)_2(OH_2)_4Ca_{0.12}K_{0.01}{\cdot}nH_2O$. The required elements were derived from ophiolitic mélange and volcanic units.

1. Introduction

Mineralogical, geochemical, stable isotopic and micromorphological investigations of palygorskite, together with the associated calcretes and mudstones have been studied extensively over the past 30 years (e.g. Singer, 1984; Rodas et al., 1994; Verrecchia and Le Coustumer, 1996; Colson et al., 1998; Pimentel, 2002; Neaman and Singer, 2011), including occurrences in Turkey (e.g. Kapur et al., 1987, 1993; Karakaş and Kadir, 1998; Eren et al., 2004, 2008; Eren, 2007, 2011; Kadir and Eren, 2008; Eren and Hatipoğlu-Bağcı, 2010; Kadir and Akbulut, 2011; Kaplan et al., 2013, 2014). Kadir et al. (2010) and Gürel and Özcan (2016) also provided information regarding the dolocretes of the Çanakkale and Ankara areas respectively. In central Anatolia calcretes and related palygorskite occurrences around Ankara and Kırşehir provinces have been reported by Küçükuysal et al. (2013), Küçükuysal and Kapur (2014) and Kadir et al. (2014). Although palygorskite associated with sepiolite and dolomite within Neogene lacustrine sediments has previously been described (Kadir et al., 2016), until now, there has been no paleoenvironmental data for the Pliocene sedimentation in the Eskişehir basin. The present study aims to determine the mineralogical, geochemical and isotopic characteristics of palygorskite and associated calcretes in near surface setting of the Pliocene mudstones of the Eskişehir province in terms of paleoenvironment, and to assess the influence of climatic on the development of these

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http://dx.doi.org/10.1016/j.catena.2017.09.027
Received 17 April 2017; Received in revised form 10 September 2017; Accepted 26 September 2017

Please cite this article as: Kadir, S., Catena (2017), http://dx.doi.org/10.1016/j.catena.2017.09.027

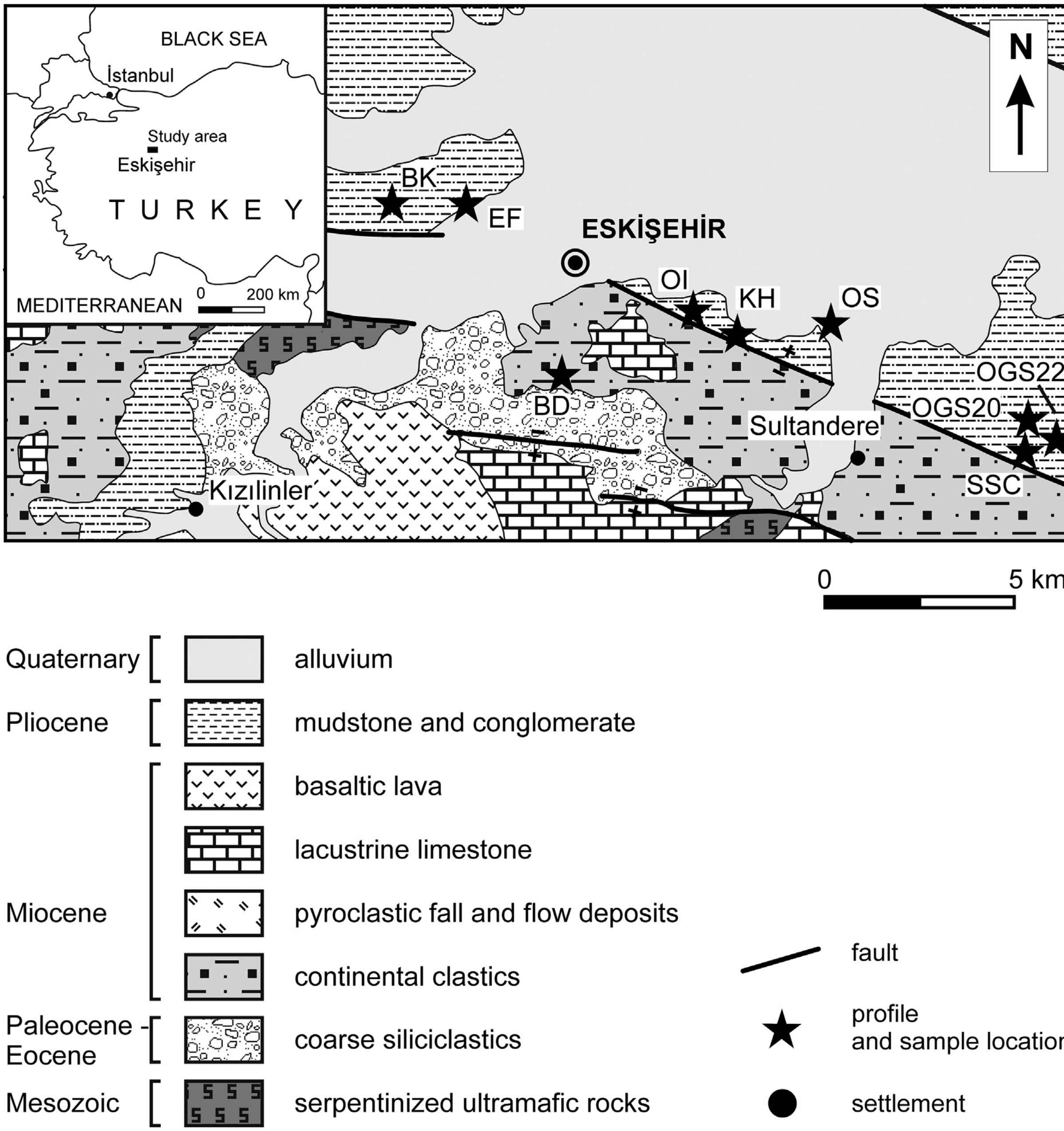

Fig. 1. Geology and location maps of the Eskişehir area.
Modified from Gözler et al. (1996).

sequences and to discuss their origin. This research also provides new data and interpretations to guide the future exploration of the calcretization process in similar environments.

2. Geological setting

The basement rocks in the study area comprise metamorphic (Paleozoic blueschist) and serpentinized ultramafic rocks (Mesozoic) (Figs. 1, 2). The ultramafics are thrust-faulted upon the Paleozoic metamorphics (Kulaksız, 1981; Yılmaz, 1981; Gözler et al., 1996; Gültekin et al., 2003; Kadir and Erkoyun, 2015). The basement rocks are unconformably overlain by Paleocene to Eocene terrestrial, coarse siliciclastic sediments on which Miocene conglomerates rest unconformably. These conglomerates comprise mainly ophiolitic, rarely metamorphic and locally basaltic rock fragments, and pass laterally and vertically into Miocene marls and mudstones. All these formations are overlapped by Late Miocene basaltic lava flows and locally by tephras. Miocene volcano-sedimentary units are unconformably overlain by Pliocene fluvial and lacustrine sediments enclosing calcrete at the upper levels, consisting of brown and reddish-brown, thick bedded mudstones and yellowish-brown conglomerates. The Quaternary sediments are alluvial.

In the Eskişehir province, calcrete occurs as powder, nodules, tubes, fracture-infill, and laminar crusts, in a near surface setting of reddish-brown mudstones of Pliocene age (Figs. 2–4). Calcrete profiles consist of isolated calcrete occurrences within the mudstone, locally covered by hard laminated crust (hardpan). The dome-like appearance of the hardpan indicates a tepee-structure (Eren, 2007).

In the field, calcretes are white in color. The nodules are roughly spherical to ellipsoidal in shape with diameters of 3–20 cm (Figs. 3, 4a). In most places, coalescent calcrete nodules are observed and some of the calcrete nodules show nuclei of mudstone relicts. Calcrete tubes are