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Geochemistry of the Apulian karst bauxites (southern Italy): Chemical fractionation and parental affinities

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ABSTRACT

This study focuses on a late Cretaceous karst bauxite deposit in the Murge area of the Apulia district, southern Italy. The first analysis of the vertical distributions of a wide range of elements (including REEs and selected trace elements) throughout the deposit was shown in order to identify the processes determining element fractionation during the evolution of the bauxite.

The studied karst bauxite deposit exhibits an ooidal texture, is mineralogically homogeneous, and contains higher abundances of boehmite than of hematite, kaolinite, and anatase. The major element composition of the bauxite is dominated by elevated concentrations of SiO_2, TiO_2, Al_2O_3, and Fe_2O_3, and analyses of element mobility within the bauxite indicate that all elements except for Nb and Ni, and to a lesser extent Cr, are depleted relative to the immobile element Ti. R-mode factor analysis revealed a number of key findings: (i) some low-solubility elements (e.g., Zr, Th, Ti, V, Ga) were concentrated in detrital zircon and monazite (Zr, Th), in anatase (Ti, V), and possibly in boehmite and hematite (Ga) during the later stages of bauxitisation; (ii) Fe and Cr were concentrated during wet conditions, whereas Al and Co accumulated during dry conditions; (iii) distributions of the light REEs (LREEs) and the heavy REEs (HREEs) are controlled by the same processes, suggesting that little LREE/HREE fractionation occurred during bauxite formation; and (iv) the behaviour of cerium is different from that of the other REEs, and highly variable cerium anomalies are observed across the deposit, with three characteristic Ce/Ce^* maxima with values of >2. Parisite was the only authigenic cerium mineral detected during this study. Thus, we propose a three-step model to explain the distribution of Ce: cerianite is dissolved by cerium reduction, is transported by downward-moving meteoric water (per descensum), and finally parisite is precipitated. This cycle was repeated several times in the Apulian karst bauxite in response to Eh decreases under alkaline conditions, promoted by fluctuations in the groundwater level. Finally, we used the value of the Eu anomaly to discuss the parental affinity or protolith of the bauxite. The value of the Eu anomaly (min. $Eu/Eu^* = 0.76$, max. $Eu/Eu^* = 0.89$) indicates that the bauxite was not derived from carbonates, but rather, that the majority of the bauxite was influenced by intermediate to mafic magmatic sources. Eu/Eu^* vs Sm/Nd diagram suggests that the parental material for the bauxite was derived from a combination of a distant magmatic source and clastic material derived from a continental margin (northern Africa) to the south.

1. Introduction

A dramatic rise in world demand for selected critical elements, including the rare earth elements (REEs), which are commonly used in electronic devices, has generated great interest in such elements, in part because of uncertainties in their future availability (e.g., Herrington, 2013; Vidal et al., 2013). Bauxite ores are commonly enriched in many of these critical elements, and as such, a significant amount of recent research has focused on the processes that control their distribution within bauxite deposits (Mameli et al., 2007; Zarasvandi et al., 2008; Karadağ et al., 2009; Wang et al., 2010; Boni et al., 2013; Hanilçi, 2013). Analyses of karst bauxites, even of uneconomic bauxite deposits such as those in southern Italy, can provide useful insights into critical element distributions, as such bauxites are analogues for more economically viable bauxite deposits (Mondillo et al., 2011).

Bauxites are residual deposits that generally form in humid tropical to sub-tropical climates (e.g., Bárdossy and Aleva, 1990; Bogatyrev and Zhukov, 2009). The conditions that promoted the formation of currently known European bauxite deposits are related to events occurring between the Cretaceous and the Eocene (Mondillo et al., 2011, and references therein). Most European bauxite deposits formed in karst

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environments developing on exhumed carbonates, where the formation of a karst network provided optimum drainage and preserved the deposits from later surface erosion (Bárdossy, 1982). The southern Italian karst bauxite deposits were formed during a late Cretaceous (late Aptian to early Coniacian) hiatus on a Bahamian-type platform that cropped out within the southern Apennines (Boni et al., 2013, and references therein). These deposits are located in the Abruzzi Mountains, in Apulia (Gargano Peninsula and the area around Murge) and Campania (Matese and Caserta Mountains). The Tethyan realm underwent significant geodynamic tectonism during the Cretaceous which included collision, uplift, and exhumation of ophiolitic suites and sedimentary successions (e.g., Dewey et al., 1973; Channell et al., 1979; Dercourt et al., 1986; Stampfli and Borel, 2002; Schmid et al., 2008; Handy et al., 2010; Schettino and Turco, 2011). This time is contemporaneous with the formation of the bauxite deposits of southern Italy,

This study, which is part of a more comprehensive project examining Apulia geology, focuses on the most representative bauxite deposit of the Murge area located in the Spinazzola district (hereafter named Spinazzola deposit). Previous research on Spinazzola deposit includes an early paper by Bárdossy et al. (1977), followed by subsequent research on the geochemistry of different textural components within the bauxite (Mongelli, 1997), the conditions of ore formation (Mongelli and Acquafredda, 1999), and the palaeoclimatic significance of the bauxite (Mongelli, 2002 and references therein). Here, we present a complete geochemical dataset that allows for the identification of the vertical distribution of a variety of elements, including the REEs and selected trace elements, and we use these data to identify the processes that caused the observed vertical elemental fractionation within the bauxite. These data form the basis of a provenance model of the Apulian karst bauxite, a model that provides evidence regarding the late Cretaceous evolution of the Tethyan realm.

2. Geological setting

The Spinazzola group of bauxite deposits is located in the northern part of the Murge area of Apulia, in southern Italy (Fig. 1). This area forms part of the southern Apennines foreland (Spalluto, 2012, and references therein) and is dominated by a 3-km-thick succession of Cretaceous shallow-water limestones and dolomites, which form a S–SW dipping monocline that is slightly deformed by folds and cross-cut by subvertical normal and transtensional faults (Festa, 2003, and references therein). The carbonate succession was deposited in a low-energy shallow-water environment (Spalluto et al., 2008, and references therein) that developed in the interior of the Mesozoic Apulia Carbonate Platform (ACP). Initiation of collision between Africa and Eurasian in the middle–late Cretaceous meant that the ACP underwent deformation induced by the propagation of intraplate stress during the early phases of the Alpine Orogeny (e.g., Mindszenty et al., 1995). This tectonic deformation of the carbonate platform produced two major regional intra-Cretaceous unconformities that provide evidence of long-lasting subaerial exposures during the Albian–Cenomanian and the Turonian (e.g., Mindszenty et al., 1995). Following the recent plate tectonic model proposed by Schettino and Turco (2011), during the Cretaceous the ACP was within tropical latitudes between 20° and 30°.

The ACP records only the Turonian exposure event, and in the Murge area the bauxite developed as vertical bodies filling deep canyon-like cavities bordered by steep walls. These are mostly local sliding planes related to the karstification process. However, the sub-parallel east–west

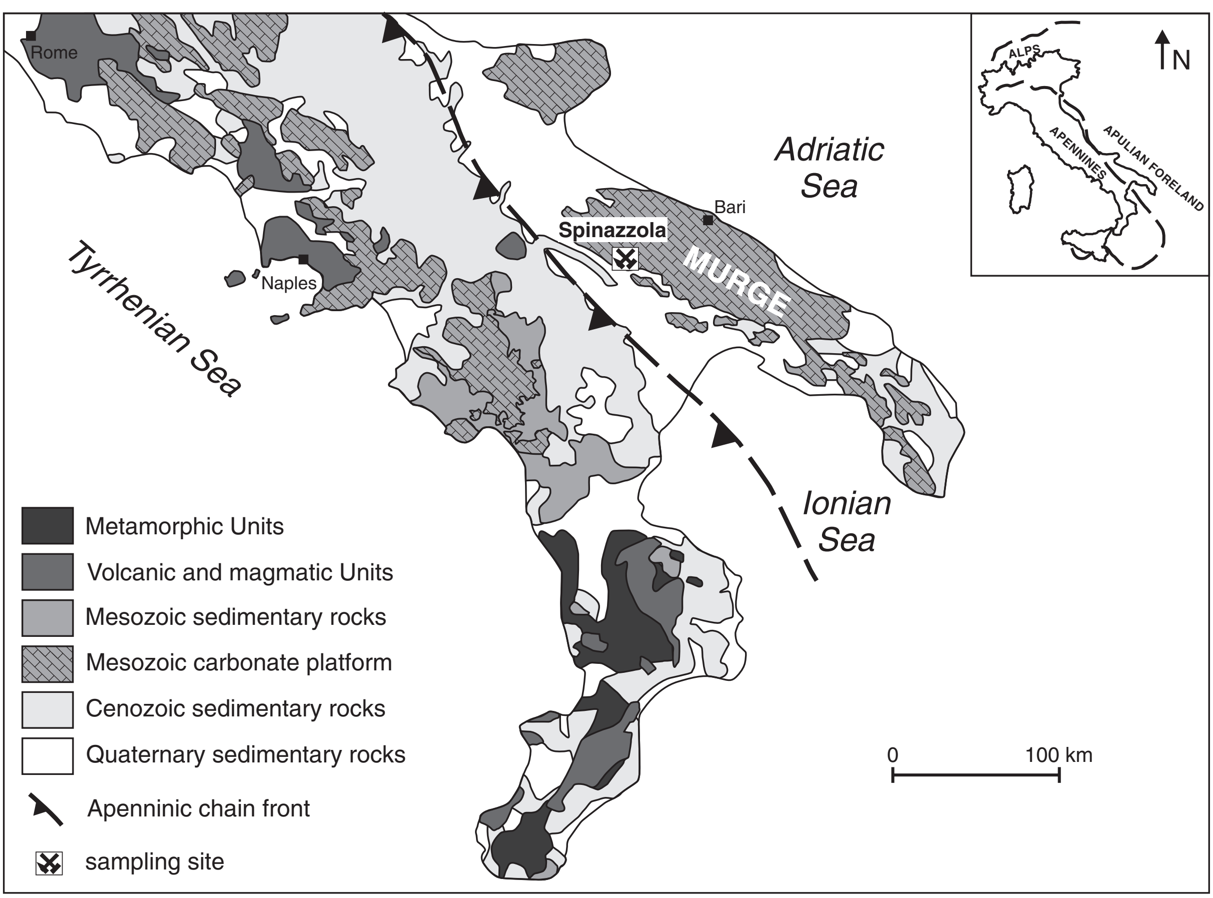

Fig. 1. Geolithological map of the southern Apennines. The sampling site is shown. Modified from Bonardi et al. (2009)