Karst bauxite formation during Miocene Climatic Optimum (central Dalmatia, Croatia): mineralogical, compositional and geochronological perspectives

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Abstract

The Miocene Climatic Optimum (MCO) represents a global warm period (approximately 17–14.7 Ma) interrupting a long-term period of Cenozoic cooling. In order to elucidate if bauxitization took place in southeastern European mid-latitude areas during the MCO, we studied a section of undated massive karst bauxite (Crveni Klanac, CK) in central Dalmatia, Croatia, hosted in Upper Cretaceous limestones and overlain by Miocene Sinj Basin lacustrine deposits. Integrated mineralogical, morphological and geochemical analyses indicate the predominant mineral phases of the homogenous bauxite matrix are authigenic, subhedral to euhedral kaolinite and gibbsite. The *in-situ* mineralization was a consequence of pedogenic processes, indicating the CK bauxites formed autochthonously. *In situ* U-Pb zircon ages of the lower, middle and upper parts of the CK bauxite are very similar, dominated by Miocene and Oligocene ages, indicating they all share similar protolith(s). Subsequent high-precision chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS) analyses indicate a maximum

depositional age (MDA) for the pre-bauxitic material of 16.9576 ± 0.021 Ma (2σ uncertainty, incorporating decay constant uncertainty). This MDA, a maximum age of autochthonous bauxitization, coincides with the onset of the MCO. Based on currently available geochronological constraints, the maximum timeframe for CK bauxitization was less than ~700 ka, which matches the records of the MCO in paleo-mid-latitude Europe. The potential imprint of pre-17 Ma bauxitization and contribution of older (i.e., Upper Paleogene) bauxite deposits resedimented to the CK profile, as well as degree of potential parautochthonous origin of the CK bauxites, is yet to be investigated. More than simply aligning with regional and local reconstructions of continental climatic conditions during the onset and the early stages of the MCO, the high degree of autochthony of the CK bauxites provide a precise climatic constraint. For *in-situ* bauxitization to occur in the southeastern parts of mid-latitude continental Europe, paleoclimatic and paleoenvironmental conditions must have had mean annual temperature greater than 17–22°C and mean annual precipitation of more than 1100–1200 mm.

Keywords: karst bauxite, CA-ID-TIMS zircon geochronology, maximum depositional age, kaolinite and gibbsite, Miocene Climatic Optimum, central Dalmatia

Declarations

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Conflicts of interest/Competing interests

The authors declare no Conflicts of interest/Competing interests

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All data generated or analyzed during this study are included in this article (and its supplementary information files)

Code availability

Not applicable

Author's contributions

All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Mihovil Brlek, Sean Gaynor, Giovanni Mongelli, Blanca Bauluz, Rosa Sinisi, Vlatko Brčić, Irena Peytcheva, Ivan Mišur, Simon Tapster, Nina Trinajstić, Elisa Laita, Alfonso Yuste, Sanja Šuica, Anita Grizelj, Duje Kukoč, and Urs Schaltegger. The first draft of the manuscript was written by Mihovil Brlek and Sean Gaynor and all authors commented on versions of the manuscript. All authors read and approved the final manuscript.

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Introduction

Continental paleoclimate records are essential for reconstructions of past climate changes, better understanding modern climate and potential for future climate change (Bárdossy and Combes 1999; Retallack 2010; Boucot et al. 2013; Retallack et al. 2016 and references therein; Methner et al. 2020; Steinthorsdottir et al. 2021 and references therein). Bauxites are residual deposits which form due to intense chemical weathering in hot and humid zones (generally in humid tropical and sub-tropical climates) and are enriched in Al by removing other cations (e.g., Si, alkali metal and REE; D'Argenio and Mindszenty 1995; Bárdossy and Combes 1999; Bogatyrev et al. 2009; Retallack 2010; Huang et al. 2012; Mindszenty 2016), and therefore these deposits can serve as direct terrestrial paleoclimate indicators, particularly where their temporal record of formation can be well constrained. They are composed of Al hydroxides, with subordinate phyllosilicates (mainly kaolinite), Fe oxides and hydroxides, Ti oxides and a variety of other minerals. The chemical processes involved in formation of karst bauxites, confined to karst zones of carbonate rocks (e.g., Bárdossy 1982; Bárdossy and Combes 1999; Mondillo et al. 2011; Mongelli et al. 2014; Yuste et al. 2015), are almost the same as that for lateritic bauxites, formed as result of a strong chemical weathering of aluminosilicate rocks (e.g., Eggleton et al. 2008; Singh et al. 2018). However, karst bauxites may gain Al from a variety of sources (see also Liu et al. 2013; Liu et al. 2019 and references therein). These include volcaniclastic deposits, as well as resedimented pre-existing bauxite deposits (Comer 1974; Bogatyrev et al. 2009; Kelemen et al. 2017). As suggested by Bárdossy and Aleva (1990) and D'Argenio and Mindszenty (1995), bauxites are unevenly distributed through time, with unusually widespread and intense formation of bauxite (and laterite) associated with distinct temporal peaks identified at approximately 2, 12, 16, 35, 48, 55, 65 and 100 Ma (Retallack 2010). During these peaks, bauxites and laterites are found at unusually high latitudes, and these periods are coeval with CO_2 greenhouse events, times of global high warmth and precipitation, elevated atmospheric carbon dioxide and oceanic anoxia (Bárdossy and Combes 1999; Retallack 2010; Mindszenty 2016). The Miocene Climatic Optimum (MCO; ca. 17–15 Ma) was a CO_2 greenhouse event associated with a global warm and humid climate (Zachos et al. 2001, 2008; Kasbohm and Schoene 2018; Methner et al. 2020 and references therein; Sosdian et al. 2020; Steinthorsdottir et al. 2021 and references therein), and these conditions (just like in the Cretaceous as suggested by Mindszenty 2016) may have allowed for lateritization and bauxitization to potentially extended mid-latitude areas, beyond the tropical modern extent of laterites and bauxites (see also Retallack 2010). Lateritic bauxites associated with the MCO have previously been identified with the Columbia River Basalts (CRB) in Oregon and Washington in the United States (Liu et al. 2013; Retallack

et al. 2016; Kasbohm and Schoene 2018), as well as with intense chemical weathering of Vogelsberg basalts in central Germany (Schwarz 1997).

Central Dalmatian karst bauxites in the Sinj area (Croatia) are found in several stratigraphic horizons (Šušnjara et al. 1990; Sakač and Šinkovec 1991), including massive clayey bauxites hosted predominantly in Upper Cretaceous carbonate platform limestones and underlying the Miocene transgressive Dinaride Lake System Basin deposits (DLSB; Sinj Basin – SB; Šušnjara and Sakač 1988; de Leeuw et al. 2010). Their genesis has been interpreted to reflect Oligocene–Miocene *in situ* bauxitization of mixed detritus, including volcaniclastic material (Šušnjara and Šćavničar 1976, 1978; Šušnjara et al. 1990). These interpretations were based on the presence and abundance of euhedral, prismatic zircon grains found in the heavy mineral assemblage of these bauxites, which are absent from older regional bauxites, but present in Miocene SB volcaniclastic deposits.

In order to define the genesis and age of Central Dalmatian karst bauxites underlying DLSB deposits, we present a multi-proxy approach applied on bauxites from the Crveni Klanac (CK) section. In order to resolve if the CK bauxites were formed *in situ* (autochthonous), or were deposited as the result of recycling of older bauxite horizons, we integrated mineralogical, textural, morphological and geochemical analyses of several bauxite horizons (e.g., Huang et al. 2012; Mongelli et al. 2014; Yuste et al. 2015, 2020; Kelemen et al. 2017, 2020; Singh et al. 2018; Sinisi 2018). These data also yield significant interpretations about the parental affinity and post-genetic modifications for the CK bauxites. In addition, we use detrital zircon U-Pb geochronology to generate the maximum depositional age (MDA) of the bauxite parental material based on the law of detrital zircon: the age of deposition of a sedimentary rock cannot be older than the youngest zircon crystal it contains (Gehrels 2014; Herriot et al. 2019; Sharman and Malkowski 2020). We utilize laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) U-Pb analyses to screen the ages of the detrital zircon (e.g., Liu et al. 2014; Kelemen et al. 2017; Marchand et al. 2021). However, LA-ICP-MS geochronology is relatively limited in precision and accuracy, and therefore the youngest identified population of zircon grains was extracted for further analysis using high-precision chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS) (Schaltegger et al. 2015; Herriott et al. 2019; Sharman and Malkowski 2020). The U-Pb age spectra from these detrital zircon enables preliminary insight into potential regional (e.g., Carpathian-Pannonian Region - CPR - volcanism; Lukács et al. 2018; Brlek et al. 2020) and local magmatic sources that could have provided detrital material to the CK bauxite. Lower–Middle Miocene volcaniclastic rocks, interlaid in lacustrine deposits within the SB and other surrounding intra-montane basins (Šušnjara and Šćavničar 1974), were previously used to construct chronologic framework for the DLSB sediments (de Leeuw et al. 2010; de Leeuw et al. 2012 and references

151 therein). A new high-precision U-Pb zircon date of the oldest volcaniclastic horizon within the SB further refines
152 the depositional history of the basin, and subsequently helps elucidate how bauxite formation may have occurred
153 on a regional scale. This updated model for the geologic history of this region helps to elucidate the weathering
154 processes affected by paleoclimate and prevailing paleoenvironmental conditions during the formation of bauxite
155 mineral associations. These new high-precision zircon geochronology and bauxite compositional data serve as a
156 precisely temporally defined paleoclimatic indicator, and help inform about the climatic conditions during the
157 MCO.
158
159 **Geological and stratigraphic framework of Miocene karst bauxites (central Dalmatia, Croatia)**
160
161 The Sinj Basin (SB) is a NW-SE striking elongated basin located in southeastern Croatia (central Dalmatia) on the
162 SE margin of the External Dinarides, and interpreted to have formed as a pull-apart structure (Fig. 1a, b; Mandic
163 et al. 2008). It is one of numerous, synchronous parallel basins (Fig. 1a) which formed within the Western Thrust
164 Belt of the Dinarides during the Early Miocene as a result of either transpressional tectonics (Mandic et al. 2008),
165 or extension (de Leeuw et al. 2012; van Unen et al. 2019 and references therein; Mandic et al. 2020). These intra-
166 montane basins host MCO-related lacustrine deposits referred to as the DLSB deposits (de Leeuw et al. 2012 and
167 references therein; Mandic et al. 2020). The Dinaric Western Thrust Belt is composed of Mesozoic to early
168 Cenozoic Adriatic–Dinaric Carbonate Platform deposits (Tari-Kovačić 1994; Mandic et al. 2008). With the onset
169 of compressional tectonics during the Eocene, the platform turned into a foredeep, hosting flysch and molasse
170 deposits (Promina Formation; Korbar 2009; Zupanič and Babić 2011), and was subsequently subaerially exposed
171 during the Oligocene. The basin is surrounded by Triassic to Eocene carbonate rocks (also Eocene-Oligocene
172 deposits in its western part), and has been deformed in the western part by the doming of Permo-Triassic evaporites
173 (Fig. 1b; Mandic et al. 2008).
174 The Early to Middle Miocene SB lacustrine succession (palaeobiogeographically part of the DLSB) has an
175 average thickness of 370 m and is divided into 3 main lithological units (Fig. 1b, c; Šušnjara and Šćavničar 1974;
176 Šušnjara and Sakač 1988). The lower unit comprises varicolored marls in the northwestern portion of the basin,
177 and coal-bearing beds and marls with dreissenid bivalves in the southeastern part of the basin (Fig. 1b, c; Šušnjara
178 and Sakač 1988; Mandic et al. 2008; de Leeuw et al. 2010). Although these two types of the basal unit were
179 interpreted as being synchronous, lateral transitions or contacts between the two have not been recorded in the
180 field (Šušnjara and Sakač 1988). The base of the lower unit, and therefore the onset of the lacustrine sedimentation

in the SB, has been previously dated in the northwest portion of the basin via Ar/Ar (biotite) of the Lučane-3 (LUČ-3) volcanoclastic horizon as 17.91 ± 0.18 Ma (de Leeuw et al. 2010, 2012). However, this volcaniclastic horizon only occurs intercalated with the varicolored marls in the northwestern part of the basin (Fig. 1b, c), and therefore only constrains the age of this type of deposit of the lower SB unit. The Lučane-2 (LUČ-2) volcaniclastic horizon, which occurs intercalated with clay-rich limestone's and calcareous marls in the northwestern part of the middle SB unit (with the middle unit lying concordantly on both lithological types of the lower unit), has been dated as deposited at 16.24 ± 0.16 Ma, based on Ar/Ar sanidine geochronology (Fig. 1c; de Leeuw et al. 2010, 2012).

Bauxites hosted by karstified Upper Cretaceous carbonate platform limestones and Paleogene deposits can be found at the southwestern margin (Trilj area; e.g., Crveni Klanac – CK – section) and in the northern part of the SB (Fig. 1b, c; Šušnjara and Sakač 1988; Šušnjara et al. 1990). They are overlain by Miocene SB lacustrine deposits of coal-bearing beds and marls with dreissenid bivalves of the lower SB unit (southwestern margin of the SB) and limestones and marls of middle SB unit (where the lower unit is absent; northern part of the SB). Massive bauxites, ranging from clayey bauxites to bauxitic clay horizons accumulated in pre-Miocene karstified paleo-depressions, which developed due to tectonics, erosion and weathering from the Oligocene to Early Miocene, and formed ore bodies which are defined as irregular, elongated lenses (Šušnjara et al. 1990; Mandic et al. 2008). The formation of the karstic network in Upper Cretaceous rocks provided the optimum conditions for rock leaching and drainage, fostering bauxite formation, and protected these deposits from later surface erosion (e.g., Bogatyrev et al. 2009; Mondillo et al. 2011; Mongelli et al. 2014). The bauxite genesis has been interpreted as an Oligocene–Miocene *in situ* bauxitization of precursor material of mixed origin, including weathered and non-weathered sedimentary, metamorphic and magmatic rocks (Šušnjara and Šćavničar 1976, 1978; Šušnjara et al. 1990; see also Trubelja and Mutić 1991). These interpretations were based predominantly on the basis of the heavy mineral assemblages of the bauxites, with the volcaniclastic origin inferred from predominant presence of euhedral prismatic zircons (e.g., in some horizons of the CK section more than 90% of the transparent heavy mineral grains are zircons; Šušnjara and Šćavničar 1976, 1978). Since zircons from SB volcaniclastic horizons (Šušnjara and Šćavničar 1974) are petrographically similar to zircons of the CK bauxites, and similar zircons are absent in the older bauxites, Upper Cretaceous karstified limestones and Paleogene deposits found in the region, the bauxite zircons have been interpreted as derived from the SB volcaniclastic rocks.

The Crveni Klanac (CK) section of strata, located in the southeastern margin of the SB, contains massive bauxites, bauxitic clays, clays and calcitic clays hosted in karstified Upper Cretaceous limestones, which underlie

the lower SB lacustrine coal-bearing beds and marls with dreissenid bivalves (Fig. 1b, c; Šušnjara and Šćavničar 1976, 1978; Šušnjara et al. 1990). The ore deposit is bounded by faults, which caused the lowering of the relief and enabled bauxite accumulation in the paleo-depression. The original size of the deposit was 200 x 150 m, with a maximum thickness of 30 m. Gibbsite, kaolinite, goethite and hematite are the principal bauxite minerals of CK (Šušnjara et al. 1990).

Analytical methods

Six discrete bauxite levels were identified and sampled from a 14.5 m thick CK bauxite profile, as well as the overlying basal SB lacustrine unit (Fig. 2). The bauxite samples were characterized by a combination of bulk geochemical analyses, X-ray powder diffraction (XRPD) analysis of whole-rock samples and fractions <4μm, optical and field emission scanning electron microscopy (FESEM) and *in situ* LA-ICP-MS U-Pb isotope analyses of accessory zircon, followed by high-precision CA-ID-TIMS U–Pb isotope analyses of the same, polished zircon crystals. High-precision U-Pb isotope analysis was also used for the analysis of zircons from SB oldest volcaniclastic horizon.

Bauxite mineralogy and geochemistry

X-ray diffraction (XRD)

The mineralogy of six bauxite whole rock samples and the <4 μm fractions of six bauxite samples were detected via X-ray powder diffraction (XRPD), using a Siemens D5000 diffractometer equipped with Cu tube (Cu-Kα radiation), automatic divergence slit, and graphite monochromator at the Department of Sciences, of the University of Basilicata (Italy). Random powders were used for the XRD analysis of the whole sample, within the diffraction range between 2° and 70° 2θ. Oriented aggregates were used for the XRD analysis of the <4 μm grain-size fraction, previously obtained by repeated Stokes' Law settling. For the oriented aggregates the 2° to 30° 2θ range was investigated and the analysis was carried out on air-dried, ethylene glycol solvated (overnight at 60 °C), and heated (at 550 °C for 2 h) specimens. The mineral phases identification was completed with X'Pert HighScore Plus software (PANalytical 2001) using the integrated PDF-4 (2006) database. The characterization of clay minerals was done following Moore and Reynolds (1989). To compare the examined samples, an estimation of whole

sample mineral abundances were determined using the reference intensity ratios (RIR) listed in the aforementioned mineralogical database.

Optical and field emission scanning electron microscopy (FESEM)

Thin sections of the bauxite samples were studied by both transmitted and reflected light microscopy, in order to identify mineral phases and their textures. The thin sections of 3 samples, as well as their rock fragments, were analyzed by a Carl Zeiss Merlin FESEM with an Oxford energy-dispersive X-ray (EDS) detector at the University of Zaragoza (Spain). For this, the thin sections were previously carbon-coated. All other bauxite horizons, as well as microfacies of the overlying SB lacustrine limestones and marls, were studied petrographically at the Croatian Geological Survey (Zagreb, Croatia).

Compositional images of the samples were obtained using two types of backscattered electron detectors: angular selective (AsB) and energy selective (EsB). The accelerating voltage used for the AsB and EDS was 15 kV, with a beam current of 600 pA. For the ESB, the accelerating voltage was 4 kV with a beam current of 200-600 pA. Morphological images were also obtained from fragments of the rocks using a secondary electron detector (Inlens), using an accelerating voltage was 3-5 kV with a beam current of 100 pA. In addition, semi-quantitative analyses were carried out using the EDS detector in order to identify mineral chemistry with a detection limit of 0.1%.

Whole-rock geochemistry

Major, trace, and rare earth element (REE) concentrations of six bauxite whole-rock samples were determined by inductively coupled plasma–optical emission spectrometry (ICP-OES) and inductively coupled plasma–mass spectrometry (ICP–MS) at Bureau Veritas Commodities Canada Ltd. (Canada), following their standard procedures. Analytical uncertainties were less than ± 5%, except for elements at a concentration of 10 ppm or lower, for which uncertainties were ± 5–10%. Total loss on ignition (LOI) was determined gravimetrically after heating overnight at 950 °C.

For the purpose of discussion, the rare earth element (REEs) concentrations were normalized to Chondrite standard (McDonough and Sun 1995). The Ce and Eu anomalies were calculated as $Ce/Ce^* = 2Ce_{ch}/\sqrt{(La_{ch}*+Nd_{ch})}$

and $Eu/Eu^* = 2Eu_{ch}/\sqrt{(Sm_{ch}*+Gd_{ch})}$, respectively, where the subscript "ch" refers to normalized values for chondrite. All relevant analytical data can be found in Supplementary Material 1.

Zircon geochronology

Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

First, the samples CK-1 (CKC-Bx3), CK-2 (CKSP-Bx2) and CK-5 (CKSS-Bx1) were crushed and sieved to <500 μm, and separated into a heavy and light fraction using Wilfley table. After the separation of the magnet fraction, the heavy fraction was passed through methylene iodide heavy liquids. Individual zircon grains were handpicked from the heavy non-magnetic fraction under a binocular microscope to obtain the largest variety of grain types (e.g. shape and size). Fifty to sixty zircon crystals from bauxite samples were mounted in epoxy resin and polished to expose the interior domains of individual crystals. These mounts were then imaged by backscattered electron (BSE) and cathodoluminescence (CL) techniques using a scanning electron microscope JSM-6610 LV coupled with an Energy Dispersive X-Max Large Area Analytical Silicon Drifted Spectrometer (Oxford) and CL-detector at the University of Belgrade (Serbia). *In situ* LA-ICP-MS U-Pb isotope analyses were completed using a New Wave Research (NWR) Excimer 193 nm laser-ablation system attached to a Perkin-Elmer ELAN DRC-e quadrupole inductively coupled plasma-mass spectrometer at the Geological Institute of Bulgarian Academy of Science (Sofia, Bulgaria). An in-laboratory designed ablation cell with lowered position effects, a "squid" smoothing device, used an energy density of 7.5 J/cm-2, a repetition rate of 8 s, and ablation craters of 35 μm. The analyses were carried out in blocks of 20-22, using GJ1 zircon (Jackson et al. 2004) as a primary standard reference material (SRM) to correct for fractionation (2 analyses every 6 to 8 analyses), and finally Plesovice (Slama et al. 2008) and 91500 (Wiedenbeck et al. 1995, 2004) as a secondary SRM for controlling systematic errors. Spot analyses were carefully selected based on observation of BSE and CL images in order to avoid mineral inclusions. The results were calculated off-line using Iolite combined with VizualAge, in order to obtain ages and ratios corrected for instrumental drift and down-hole fractionation (Paton et al. 2010, 2011). During the two sessions of analyses in February and May 2020, the Plesovice SRM was measured at 338.9 ±1.7 Ma, and 91500 at 1065 ± 8 Ma, respectively (2s, decay-const. errs included; MSWD of concordance 0.01 and 0.1). All relevant analytical data for age calculations can be found in Supplementary Material 2.

Zircon U-Pb Chemical Abrasion-Isotope Dilution-Thermal Ionization Mass Spectrometry (CA-ID-TIMS)

In order to refine the age of euhedral zircons dated by LA-ICP-MS, samples CK-5 (CKSS-Bx1) and CK-2 (CKSP-Bx2) were selected for high-precision CA-ID-TIMS analysis. Following acquisition of LA-ICP-MS data, zircons with younger $^{206}Pb/^{238}U$ ages were removed from epoxy mounts with a metal tool. In some cases, grains fractured during removal and were then processed as individual sub-grain analyses; these are denoted with a letter following the zircon number. The sub-grains thus represent random fragments, in many cases one analysis would be from just the tip of a zircon (e.g., CKSS-Bx1 Z36b), while the paired analysis included the core (e.g., CKSS-Bx1 Z36a). The zircon grains and sub-grains were then individually annealed in a muffle furnace at 900 °C for 48 hours (Mundil et al. 2004). The annealed grains were then subjected to chemical abrasion at 210 °C for 12 hours in concentrated HF in individual 200 µl Savillex placed in a Parr digestion vessel (Mattinson 2005; Widmann et al. 2019). The abraded material was then transferred to a 3 mL Teflon beaker and leached on a hotplate at 80 °C in 6 N HCL overnight, followed by further cleaning through four rounds of 7 N HNO_3 in combination with ultrasonication. Individual cleaned zircon crystals were then loaded into individual 200 µl Savillex microcapsules, spiked with the EARTHTIME $^{202}Pb + ^{205}Pb + ^{233}U + ^{235}U$ tracer solution (calibration version 3; Condon et al. 2015; McLean et al. 2015) and dissolved with about 70 µl HF and trace HNO_3 in a Parr digestion vessel at 210 °C for 48 hours. Following dissolution, the samples were dried down and converted to a chloride by placing them back in the oven overnight in 6 N HCl. The samples were then dried down again and re-dissolved in 3 N HCl, and purified to U and Pb through anion exchange column chromatography (Krogh 1973). Once purified, the U and Pb fractions were combined in cleaned 7 ml Savillex beakers and dried down with trace H_3PO_4, prior to loading on outgassed zone-refined Re ribbon filaments with a Si-gel emitter.

Uranium and lead isotope analyses were completed on an Isotopx Phoenix TIMS machine at the University of Geneva (Switzerland). Lead measurements were made in dynamic mode using a Daly photomultiplier, and U was measured as an oxide in static mode using Faraday cups coupled to 10^{12} Ω resistors. The $^{18}O/^{16}O$ oxygen isotope ratio in uranium oxide was assumed to be 0.00205 based on previous measurements of the U500 standard. Mass fractionation of Pb and U was corrected using a $^{202}Pb/^{205}Pb$ ratio of 0.99506 and a $^{238}U/^{235}U$ ratio of 137.818 ± 0.045 (2σ) (Hiess et al. 2012). All common Pb was considered laboratory blank and was corrected using the long-termisotopic composition of the Pb blank at the University of Geneva. All data were processed with the Tripoli and Redux U–Pb software packages (Bowring et al. 2011; McLean et al. 2011). All ages were corrected

for initial ^{230}Th disequilibrium in the melt using a magmatic U/Th ratio of 3.5. All relevant analytical data for age calculations can be found in Supplementary Material 3.

In order to better understand the onset of lacustrine deposition within the SB, and therefore constrain bauxite deposition, we also completed CA-ID-TIMS U-Pb zircon geochronology on sample LUČ-3 (Supplementary Material 3). This sample represents the oldest volcaniclastic rock within the SB, and was previously dated by Ar/Ar geochronology of biotite (de Leeuw et al. 2010, 2012; Šegvić et al. 2014). The methods for this sample were very similar to the bauxite grains, and are provided in detail in Brlek et al. (2020).

Results

Bauxite mineralogy, texture, morphology and geochemistry

X-ray diffraction (XRD)

The whole-rock XRD patterns are displayed in Fig. 3a, and the results of the semi-quantitative RIR analysis performed on these samples are presented in Fig. 2. Throughout the deposit, gibbsite and kaolinite are the predominant Al-bearing minerals, ranging in abundance from 7–45% and from 10–31%, respectively. Boehmite is also present in a few samples, and its concentration never exceeds 2%. Goethite and hematite are the principal Fe-bearing phases showing variable contents in different horizons of the studied profile. When these Fe-phases are both present, goethite is always more abundant then hematite, except in the sample CK-1. Calcite, anatase, rutile, 2:1 clay minerals, and gypsum complete the mineralogical association. Among these minerals, calcite shows very high and increasing contents towards the upper part of the section (e.g., 29% in CK-3, 60% in CK-5, and 82% in CK-6; Fig. 2). Other accessory minerals only have a minor presence (between 5% and trace). Further, quartz was detected in small quantities throughout the profile (e.g. up to 3% in sample CK-5). Allophane, imogolite and halloysite were not observed in any of the analyzed CK bauxite samples.

Results of the qualitative XRD analysis of oriented <4μm grain-size specimens indicate similar clay composition for all samples. In detail, comparing the air-dried, ethylene glycol-treated, and 550°C-heated patterns (Fig. 3b), the presence of kaolinite, which was also detected in the whole rock fractions, was further confirmed, and hydroxy-interlayered vermiculite was identified as the sole 2:1 clay mineral of the examined samples.

359 *Optical and field emission scanning electron microscopy (FESEM)*

360

361 The bauxite in samples CK-1 and CK-2 is characterized by a homogeneous texture in an optical microscope, with
362 bauxite textures of a pelitomorphic to microgranular matrix (*sensu* Bárdossy 1982; Fig. 4a, b). The minerals of the
363 fine-grained bauxite matrix of samples CK-1 and CK-2 were too small to be identified under optical microscope
364 resolution (Fig. 4a, b). Occasionally, micron-sized oxides can be observed, and these are more abundant and larger
365 in sample CK-2 (Fig. 4b). In samples CK-3 and CK-5, in contrast, euhedral to anhedral calcite crystals (sparite)
366 are randomly distributed throughout the homogeneous bauxite matrix. The replacement of primary bauxite by
367 calcite is observed in sample CK-6, with previously homogeneous bauxite matrix occasionally embedded in
368 microsparitic to sparitic matrix (Fig. 4c; see Durand et al. 2010). Additionally, the yellowish-brownish part of
369 horizon CK-4 is characterized by fragmented and isolated clasts of bauxite matrix coated, surrounded, and rounded
370 with Fe-oxide films (composition confirmed with FESEM investigation; Fig. 4d). Sparite also occurs in sample
371 CK-4 as a yellowish-brownish infill, and displaces the primary homogeneous bauxite matrix (Fig. 4d).

372 Backscattered and secondary electron images show that samples CK-1 and CK-2 are composed of fine-
373 grained homogeneous matrix with no laminations or other structures present. The matrix of the samples is mainly
374 composed of kaolinite and gibbsite (Fig. 4e, f). Gibbsite has rounded morphologies and is consistently on a
375 nanometer scale (Fig. 4e, f). Kaolinite crystals are heterometric, with subhedral to euhedral platy morphologies
376 which occasionally show pseudohexagonal sections (Fig. 4e, f), and are larger in sample CK-2 (95nm–2μm) than
377 in sample CK-1 (80nm–700nm). Kaolinite booklets are also recognized in both samples, and are up to 4 μm in
378 diameter, and 3.5 μm in longitudinal development (Fig. 4g). The booklets observed in sample CK-2 have their
379 sheets separated and they occasionally occur fractured. In addition, hematite crystals are observed between the
380 booklets sheets in both samples. Some K-rich micas, somewhat broken and deformed, are also observed, with sizes
381 from 25μm to 40μm. Micas occasionally have their sheets open and filled by kaolinite and gibbsite. Rounded
382 nodules were observed, especially in sample CK-2, and are a mixture of clays and iron oxides. Iron and titanium
383 oxides are likely hematite and rutile-anatase, based on XRD data. These minerals either form aggregates (16–100
384 μm), or are disseminated throughout the sample matrix as nanometer scale crystals, with occasional larger crystals
385 (1-5 μm). Finally, CK-5 hosts anhedral to euhedral calcite (sparite, 10–150μm in size) in a fine-grained
386 homogeneous matrix, composed of kaolinite and nanometric gibbsite with rounded morphologies (Fig. 4h, i).
387 These kaolinite crystals are also heterometric, with platy morphologies that occasionally show pseudohexagonal
388 sections (Fig. 4i). They are larger than those in the sample CK-1 and similar to those of the sample CK-2 (80nm–

2μm). Kaolinite booklets are also observed and reach up to 14μm in diameter and 4μm in longitudinal development, and occasionally appear somewhat deteriorated (Fig. 4j).

Whole-rock geochemistry

The bauxite geochemistry exhibits significant heterogeneity in major element composition (SiO_2 average=17.99±7.41; Al_2O_3 average= 24.93±12.73; Fe_2O_3 average=9.23±8.72; CaO average=15.69±18.43) (Fig. 2; Supplementary Material 1). In accordance with the observed calcite in several upper bauxite horizons, several samples are characterized by higher CaO concentrations (Fig. 2; Supplementary Material 1).

Similarly to major elements, concentrations of trace elements are highly heterogeneous, and have a strong correlative trend with CaO concentrations. The concentrations of transition elements (Sc, V, Co, Ni, Cu, Zn), high field strength elements (hereafter HFSE; Ti, Zr, Nb, Hf, Ta,), and large ion lithophile elements (Rb, Cs, Ba, and Pb) all decrease with increasing CaO concentrations (Supplementary Material 1). The REE concentrations in the bauxite samples also parallel this trend, with the total abundance of REE's (ΣREE) decreasing in samples with increased CaO. Strontium is the exception to this trend in trace elements, as its concentration increases in samples with high CaO concentrations (Supplementary Material 1). The light REE to heavy REE fractionation index $(La/Yb)_{ch}$ (average=9.63±2.22) is close to that of the Upper Continental Crust ($(La/Yb)_{ch}$= 9.21, McLennan et al. 2006), similarly to Eu/Eu* index (0.67±0.02, Eu/Eu^*_{UCC}= 0.65) (Fig. 5a; Supplementary Material 1). Finally, the Ce/Ce* index is usually < 1 with the exception of the basal sample CK-1 (Ce/Ce* =1.62; Fig. 5a; Supplementary Material 1).

Elemental mobility during weathering is generally estimated assuming an element as immobile. Among the least mobile and most conservative elements during weathering, Ti can be assumed as largely immobile in karst bauxites (e.g. Mongelli et al. 2017 and references therein). With respect to Ti, Al and especially Si are largely depleted (Fig. 5b; Supplementary Material 1). Iron shows large fluctuations within a general trend of depletion, although it is enriched by ~25% in sample CK-4 (Fig. 5b; Supplementary Material 1).

Zircon geochronology

Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

The U-Pb LA-ICP-MS data are presented in Fig. 6 as well as in Supplementary Material 2, and $^{206}Pb/^{238}U$ zircon ages were used for interpretations of these data. The zircons from CK-5, CK-2 and CK-1 bauxite samples, i.e., from the highest, middle and lower bauxite horizons respectively, have similar age spectra. The youngest and highest abundance temporal populations are Miocene, mainly from 16 to 18.5 Ma, with a secondary peak of Oligocene grains (25-34 Ma), and several Eocene ones of 35-37 Ma (Fig. 6). Inherited cores and older zircon grains yield predominantly Early Paleozoic dates 440-500 Ma, with several Devonian (370-380 Ma) or Permian-Carboniferous dates (270-320 Ma; Fig. 6). The weighted mean $^{206}Pb/^{238}U$ ages of the youngest zircon populations are indistinguishable at the level of uncertainty: 16.56 ± 0.68 Ma (CK-5; n = 5), 16.50 ± 0.43 Ma (CK-2; n = 7) and 16.47 ± 0.58 Ma (CK-1; n = 6).

Zircon U-Pb Chemical Abrasion-Isotope Dilution-Thermal Ionization Mass Spectrometry (CA-ID-TIMS)

Thorium-corrected $^{206}Pb/^{238}U$ zircon date determinations are used for all interpretations of CA-ID-TIMS data, because this chronometer provides the most precise and accurate values for rocks of this age (Figs. 7, 8; Supplementary Materials 3–6). The stratigraphically highest bauxite horizon CK-5 (CKSS-Bx1) yielded seven concordant Miocene dates, two normally discordant dates which plot near the Miocene in Concordia space, two older concordant dates (86.33 Ma and 265.29 Ma), and four older normally discordant dates (Figs. 7, 8; Supplementary Materials 3, 5, 6). Concordant Miocene zircon dates ranged from 16.953 ± 0.032 Ma to 18.587 ± 0.073 Ma, with overlapping dates at 16.96 and 17.13 Ma (Fig. 8). High-precision analyses of the middle bauxite unit CK-2 (CKSP-Bx2) yielded fourteen concordant Miocene zircon dates and two older concordant dates (30.535 and 376.57 Ma) (Figs. 7, 8; Supplementary Materials 3, 4). Miocene zircon ranged from 16.957 ± 0.019 Ma to 18.347 ± 0.040 Ma, with multiple overlapping dates at approximately 16.96 and 17.21 Ma (Fig. 8). The weighted mean value of the youngest population of zircons in each sample yields an age of 16.955 ± 0.013/0.014/0.023 Ma (n = 2; MSWD = 0.13; 2σ uncertainty) for CK-5 (CKSS-Bx1) and 16.960 ± 0.014/0.015/0.023 (n = 3; MSWD = 0.14; 2σ uncertainty) for CK-2 (CKSP-Bx2) (Fig. 8). All five of these analyses are analytically a single age population (16.9576 ± 0.0096/0.011/0.021; n = 5; MSWD = 0.15; 2σ uncertainty). Finally, individual zircon grains from LUČ-3, a volcaniclastic rock located in the basal region of Miocene lacustrine rocks in the SB, yielded dates ranging from 17.307 ± 0.022 to 19.309 ± 0.044 Ma, with three grains yielding overlapping dates at 17.31 Ma (Fig. 8; Supplementary Material 3).

Discussion

Formation of CK bauxites: insights from mineralogy and geochemistry

Massive, homogeneous karst bauxites represent the dominant style of bauxite in the CK profile, with the CK-4 horizon being a heterogeneous exception (Fig. 2). The homogeneous texture of almost all bauxite horizons, with pelitomorphic to microgranular matrices, is highly indicative of an authigenic origin of the massive bauxites (*sensu* Bárdossy 1982). Gibbsite and kaolinite, the predominant CK bauxite mineral phases (Figs. 2–4), are typical bauxite minerals. Electron microscopy shows that the CK bauxites have a fine-grained matrix of kaolinite and gibbsite, with minor proportions of hematite, goethite and rutile-anatase (Fig. 4) (Bardossy 1982; Bardossy and Combes 1999). The rounded nodules in samples CK-1 and CK-2 indicate that pedogenic characteristics are recorded in both samples, as these nodules could be considered as incipient pisoid precursors (roundgrains *sensu* Bárdossy 1982; Tilley 1994). The subhedral to euhedral and occasional pseudohexagonal morphologies of the platy kaolinite crystals of the bauxite matrix indicate that kaolinite is authigenic and not detrital, since erosion and transport processes would have modified them (Fig. 4; e.g., Bauluz et al. 2014; Yuste et al. 2015, 2020; Laita et al. 2020). The kaolinite booklets are also indicative of an authigenic origin, as this morphology is not robust enough to survive any significant transport. Furthermore, the apparent growth of kaolinite and gibbsite between the sheets of detrital micas also suggests that both kaolinite and gibbsite have been formed *in situ*. Therefore, the association of authigenic phases, such as kaolinite and gibbsite associated with Fe and Ti oxides, suggests that all were formed *in situ* as a consequence of pedogenic processes that enabled the autochthonous bauxite formation (e.g., Bauluz et al. 2014; Yuste et al. 2015, 2020). These bauxites and their representative mineral associations formed during warm and humid tropical to sub-tropical climate that promoted intense chemical weathering with the dissolution of primary silicate minerals (e.g., the observed micas) and crystallization of aluminium-rich phases and oxides (Muggler et al. 2007; Eggleton et al. 2008; Fernández-Caliani and Cantano 2010; Huang et al. 2012; Bauluz et al. 2014; Yuste et al. 2015, 2020; Singh et al. 2018). In contrast, the largest-sized kaolinite booklets, which occasionally have sheets which are separated and broken (Fig. 4), seem to have undergone minor transport due to potential reworking processes. Fragmentation of homogeneous bauxite matrix with formation of Fe-oxide films and coatings around and including the isolated matrix parts in the CK-4 horizon (Fig. 4), can also be interpreted as result of an *in situ* process, that took place either during bauxitization or diagenesis (Bárdossy 1982; see also Achyuthan and Fedoroff 2008; Yuste et al. 2015, 2020; Laita et al. 2020).

The field observations are in accordance with mineralogical and geochemical data: the amount of calcite in the bauxite horizons increases upward throughout the CK section (Fig. 2). The occurrence of authigenic carbonate throughout the profile, with the notable exception of the basal horizons (CK-1 and CK-2), indicates that diagenetic modifications affect also bauxites (as previously suggested by Šušnjara et al. 1990; Figs. 2, 3; Supplementary Material 1). Carbonate precipitation in the surface realm depends on the aqueous medium, particularly solute contents, pH, Eh, and P_{CO2} (e.g., Kirk et al. 2015 and references therein). Neogene sediments overlying bauxites are lacustrine limestones and marls, where secondary calcite likely precipitated from percolating water during lacustrine sedimentation, filling voids and displacing homogeneous bauxite matrix (especially CK-4 and CK-6 horizons; Fig. 4; Bárdossy 1982; Laita et al. 2020; see also Wang et al. 1994 and Durand et al. 2010). The groundmass of soils and sediments affected by diagenesis commonly hosts isolated calcite crystals with rhombohedral to acicular morphology, such as those observed in horizons CK-3, CK-4 and CK-5 (Fig. 4). This suggests a period of stable environmental and geological conditions, which promoted low nucleation density and slow growth of calcite as already suggested for different buried soils of the Kalahari Desert (Mees and Van Ranst 2011).

The geochemistry of the CK bauxite samples also leads to significant interpretations concerning the CK bauxite formation and its post-genetic modifications. The (La/Yb)ch values of the bauxite samples affected by carbonate addition (CK-2 to CK-6: average $(La/Yb)_{ch}$=9.40±2.41) are close to that of basal CK-1 sample which was not affected by diagenetic modifications ($(La/Yb)_{ch}$=10.77) (Fig. 5a). Furthermore, the samples have $(La/Yb)_{ch}$ values similar to the average upper continental crust ($(La/Yb)_{ch}$= 9.21, McLennan et al. 2006) (Fig. 5a). This suggests that later percolating water, which caused carbonate precipitation, did not affect the $(La/Yb)_{ch}$ geochemistry associated with bauxitization. Despite acidic pH is an essential condition triggering the chemical weathering of silicate minerals (Loughnan 1969), according to several authors (Pourret et al. 2010; Abedini and Calagari 2013; Mongelli et al. 2014), the $(La/Yb)_{ch}$ values of the CK samples suggest alkaline pH soil solutions as the prevalent condition in the Crveni Klanac section from the bauxitization to the carbonate addition. Alternatively, recorded $(La/Yb)_{ch}$ values may reflect a shift to more alkaline pH (and slightly reducing Eh) conditions in the early diagenetic phreatic environments probably related to gradual establishment of lacustrine environments (leading to deposition of the overlying SB lacustrine deposits), subsequent to original dominantly acidic pH conditions (and oxidizing Eh) that prevailed during bauxitization in vadose environments (Thiry and Simon-Coinçon 1999; A. Mindszenty personal communication). The Ce/Ce* index has been largely used in order to track the paleo-redox evolution during bauxitization, as cerium enrichment and positive Ce anomalies are driven by oxidation (e.g.,

509 Mongelli et al. 2014; Khosravi et al. 2017). The basal horizon (CK-1) has a positive Ce anomaly (Fig. 5a),
510 suggesting oxidation and precipitation of cerianite (CeO_2), according to a well-documented mechanism in karst
511 bauxites (e.g., Abedini et al. 2020). In the other parts of the section affected by diagenetic modifications, the Ce
512 anomaly is always <1 (Fig. 5a), indicating that the redox conditions either promoting cerium oxidation, or the
513 stability of cerianite, during bauxitization did not occur on burial.

514 Although carbonate successions host karst bauxite deposits, the dissolution of carbonate bedrock is not
515 considered suitable for the formation of karst bauxite, and instead, a large variety of protoliths likely contributed
516 material for bauxitization (e.g., Comer 1974; Bárdossy 1982; Bárdossy and Combes 1999; Abedini et al. 2020 and
517 references therein). Among the several proxies used to identify the parent rock(s) of karst bauxites, the Eu anomaly
518 (an index of chemical differentiation affected by minor fractionation during intense weathering) is commonly used
519 in order to elucidate the parent material of karst bauxite deposits (e.g., Mongelli et al. 2014, 2016; Khosravi et al.
520 2017; Sinisi 2018; Abedini et al. 2020). The samples from the CK section have similar Eu/Eu* values (Eu/Eu*:
521 0.67 ± 0.02, n=6), which is close to the upper continental crust composition (UCC: Eu/Eu*=0.65; Post Archean
522 Australian Shales: Eu/Eu*=0.66; Taylor and McLennan 1985), and therefore it is likely that the same protolith(s)
523 contributed the Al-rich detritus throughout the development of the various horizons of the CK bauxite. The heavy
524 mineral assemblage of these bauxites includes staurolite, andalusite, kyanite, garnet and zircon (Šušnjara and
525 Šćavničar 1976, 1978), and therefore detritus incorporated in the formation of the CK bauxites had to involve
526 multiple sources, including magmatic, metamorphic and sedimentary rocks. Therefore, although CK bauxites show
527 a broad consistence of the average Eu/Eu* values with the Miocene volcaniclastic deposits of the SB (and regional
528 Carpathian-Pannonian Region; e.g., Šegvic et al. 2014; Lukács et al. 2018; Brlek et al. 2020), these rocks cannot
529 be confirmed nor excluded as being the dominant CK bauxite precursor material, in accordance with a mechanism
530 that was suggested for other (Cretaceous) karst bauxites of the Mediterranean region that involves volcanic ash
531 (Mondillo et al. 2011; Boni et al. 2013; Putzolu et al. 2018). Instead, based on currently available data, a
532 combination of Oligocene–Miocene volcaniclastic material and siliciclastic detritus (Mongelli et al. 2014, 2016;
533 Sinisi 2018) represents a more realistic model for CK precursor material.
534
535 High-precision zircon geochronology
536
537 *Age interpretation of Sinj Basin volcaniclastic rocks*
538

539 Individual zircon dates from the volcaniclastic horizon from the SB range over 2 Ma, and yield an MSWD in
540 excess of that expected for a single population at the level of precision, and therefore require interpretation to
541 determine the eruption age of these volcaniclastic rocks. It is common for high silica rocks to incorporate a
542 moderate to high amount of antecrystic and xenocrystic zircon, which may host autocrystic overgrowths and
543 therefore have euhedral appearances because of their recent magmatic history (e.g., Lipman and Bachman 2015;
544 Gonzales 2015; Samperton et al. 2015; Rosera et al. 2021). While Pb-loss could artificially extend the age spectra
545 by yielding young ages, a 12-hour chemical abrasion has been demonstrated as a robust measure to limit Pb-loss,
546 and was used in this work (Widmann et al. 2019). Therefore, we interpret that the youngest population of zircons
547 in this sample reflects the age of final crystallization, with older grains representing a mix of antecrystic and
548 xenocrystic zircons (e.g., Wotzlaw et al. 2018; Szymanowski et al. 2019; Gaynor et al. 2019; Ellis et al. 2019;
549 Brlek et al. 2020; Rosera et al. 2021). The weighted mean and uncertainty for this interpretation is 17.312 ±
550 0.015/0.016/0.024 Ma for LUČ-3 (Fig. 8; 2σ uncertainty given as: internal only/internal with tracer
551 calibration/internal, tracer calibration and with ^{238}U decay constant). Previous ^{40}Ar/^{39}Ar geochronology of this
552 volcaniclastic deposit, intercalated within the lowest lacustrine unit of the SB, indicated that it was deposited at
553 17.91 ± 0.18 (de Leeuw et al. 2010, 2012). Our new age is approximately 600 ka younger than the previous biotite
554 geochronology suggesting that deposition of lacustrine sediments did not begin as early as previously interpreted.
555
556 *Interpreting zircon age spectra and maximum depositional ages (MDA's) in CK bauxites*
557
558 Zircon age spectra in all three samples analyzed via LA-ICP-MS (CK-1, CK-2 and CK-5) is dominated by Miocene
559 ages (16 to 18.5 Ma), with a lesser, secondary peak in the Oligocene (25–34 Ma and a few Late Eocene ages) (Fig.
560 6; Supplementary Material 2). Volcanic and volcaniclastic rocks, representing the products of regional Late Eocene
561 to earliest Miocene volcanism, are recorded both in the Balkan Peninsula (including the Inner Dinarides) as well
562 as in the Alps, Slovenia, Croatia and Hungary (vicinity of the Periadriatic and Mid-Hungarian Fault Zones) (Fig.
563 1a; e.g., Harkovska et al. 1998; Singer and Marchev 2000; Pamić and Balen 2001; Benedek et al. 2004; Schefer et
564 al. 2011; Bergomi et al. 2015; Danišík et al. 2015; Cvetković et al. 2016; Kelemen et al. 2017, 2020), and could
565 represent the sources of predominantly Oligocene zircon dates recorded in CK bauxites. The Miocene CK bauxite
566 zircons targeted by individual grain and sub-grain analyses by CA-ID-TIMS of the upper two bauxite samples
567 (CK-2 and CK-5) reveal a more complex distribution of dates within the Early Miocene zircon domains; these
568 analyses yield spectra with high zircon age scatter (Figs. 7, 8; Supplementary Material 3). Both the LA-ICP-MS

569 and CA-ID-TIMS data reveal the presence of inherited, xenocrystic components in these Miocene zircons that
570 potentially inhibit the direct translation of the zircon date to the timing of the magmatic system it formed within.
571 While *in situ* analyses have an advantage when dealing with inherited cores, LA-ICP-MS is limited by both
572 precision and accuracy relative to CA-ID-TIMS (e.g., Schaltegger et al. 2015; Herriott et al. 2019). Therefore, in
573 order to overcome this zircon inheritance, we prescreened the grains using SEM and LA-ICP-MS prior to ID-
574 TIMS, in some cases also doing sub-grain analyses, and we subsequently based much of our interpretations of the
575 bauxite U-Pb zircon data upon these CA-ID-TIMS data, although these data do not represent the full age spectra
576 of all zircon found within the bauxite horizons. These analyses indicate either: (1) that the Early Miocene (i.e.,
577 ~17–18.5 Ma) zircon grains are mostly sourced from several regional Early Miocene volcanic events and/or from
578 a heterogeneous suite of local volcaniclastic material (e.g., Pécskay et al. 2006; de Leeuw et al. 2010, 2012; Lukács
579 et al. 2018; Brlek et al. 2020), or (2) that the protolith for these bauxite horizons was predominately an individual
580 regional eruption event and/or individual local Miocene volcaniclastic deposit with complicated zircon
581 geochronology.

582 There are a number of regional volcanic events as well as local volcaniclastic rocks that could have
583 potentially provided zircons matching the ages sampled in this study, and therefore could have contributed the
584 protolith material to the depositional zone of the bauxites (see also Kelemen et al. 2017, 2020). The Carpathian-
585 Pannonian Region, located in the northeastern part of the Alpine–Mediterranean region of eastern Central Europe,
586 hosted compositionally diverse, post-collisional magmatism over the last 20 Ma (Pécskay et al. 2006; Seghedi and
587 Downes 2011). This extension-related volcanism started with the eruption of the silicic pyroclastic rocks during
588 the Early Miocene, highlighted by the eruption of regional-scale ignimbrites at 18.060 ± 0.012 Ma, 17.5 ± 0.3 Ma,
589 17.05 ± 0.055 Ma and 16.816 ± 0.059 Ma (Lukács et al. 2018; Brlek et al. 2020; Fig. 1a). There are volcaniclastic
590 rocks in other intra-montane lacustrine basins (DLSB) proximal to the SB, including a horizon previously dated at
591 17.00 ± 0.17 Ma via Ar/Ar in the nearby Livno Basin (de Leeuw et al. 2012 and references therein). Importantly,
592 there are Lower–Middle Miocene volcaniclastic rocks intercalated throughout the SB lacustrine succession within
593 ~30 km of the CK bauxite location that have been interpreted as sourced from the Carpathian-Pannonian Region
594 (Šušnjara and Šćavničar 1974; de Leeuw et al. 2010; Šegvić et al. 2014; Fig. 1a). The zircon geochronology from
595 LUČ-3, one of the lowermost SB volcaniclastic rocks, yielded CA-ID-TIMS zircon ages that overlap with CA-ID-
596 TIMS zircon dates of the bauxite samples, and therefore may have contributed detritus into the depositional
597 environment of the bauxite (Fig. 8). This would require contributions from additional volcanic horizons, however,
598 as the bauxites have a significant population of zircons younger than any found in LUČ-3. There are multiple other

599 units that have been identified as being intercalated within the basal SB lacustrine unit that are stratigraphically
600 younger than LUČ-3 (Šegvić et al. 2014), and could therefore contribute further zircon, and protolith material to
601 the CK bauxites. In this scenario it is probable that one of these as yet undated events would represent the zircon
602 population that defines the MDA of the CK precursor material. As illustrated by the zircon age distributions within
603 LUČ-3, it should also be taken into consideration that any single unit within the SB would not only carry zircon
604 that capture the eruption age, but also antecrystic zircon that can capture zircon growth that can be many 100s ka
605 prior to the eruption age. These complex zircon age spectra could be further mixed between volcaniclastic units
606 prior to being sequentially washed into the final CK depositional zone, providing the complexity in age
607 distributions with a low probability of sampling zircons related to the 'youngest' units within the bauxites.
608 The alternative hypothesis is that the complex age range in the CK bauxite samples is a function of igneous
609 processes and a large xeno- and antecrystic crystal cargo in a single volcanic eruption and/or volcaniclastic unit
610 that was sequentially deposited in the CK depositional zone and was the dominant source of Miocene zircons. Due
611 to the mixing of xenocrystic, antecrystic and autocrystic zircon crystallization within individual mineral grains and
612 then averaged by whole grain dissolution, individual ignimbrite eruptions dated with CA-ID-TIMS can reveal
613 concordant zircon ages with >1 Ma of protracted zircon dates within individual eruptive events (e.g., Wotzlaw et
614 al. 2013; Szymanowski et al. 2019; Ellis et al. 2019).Therefore, a single ignimbrite eruption could reasonably yield
615 protracted ranges in zircon dates similar to the samples dated in this study. It is possible that the old ages reflect a
616 xenocrystic component in a relatively homogeneous igneous source material for the bauxite horizons, rather than
617 a mixed detrital input. CA-ID-TIMS analyses indicate that there are normally discordant grains with Miocene
618 $^{206}Pb/^{238}U$ ages, which suggests subtle components of inheritance present in some grains. More reliable provenance
619 reconstructions require building a large database of geochronological data for the region, both for bauxite deposits
620 and potential volcanic sources, as well as application of additional proxies, such as zircon petrochronology (e.g.,
621 Liu et al. 2014; Szymanowski et al. 2016, 2019; Ellis et al. 2019; Lu et al. 2019).
622 Regardless of the nature of the detrital source of the volcanic material, both samples dated by CA-ID-TIMS
623 have consistent, indistinguishable dates at the youngest identified ages in each sample, and therefore we interpret
624 that these dates are not outliers resulting from Pb-loss, but capturing the primary zircon crystallization ages, and
625 therefore the maximum depositional age (MDA) for the protolith and the maximum age of bauxitization. The
626 weighted mean value of the youngest population of zircons in each sample yields an MDA of 16.955 ± 0.023 Ma
627 (n = 2; MSWD = 0.13; 2σ uncertainty) for CK-5 (CKSS-Bx1) and 16.960 ± 0.023 Ma (n = 3; MSWD = 0.14; 2σ
628 uncertainty) for CK-2 (CKSP-Bx2) (Fig. 8; all uncertainties are reported at 2σ uncertainty, and incorporate internal,

tracer calibration and with ^{238}U decay constant uncertainties). All five of the analyses interpreted to determine MDA's for the two samples are analytically a single age population (16.9576 ± 0.021 Ma; n = 5; MSWD = 0.15; 2σ uncertainty incorporating internal, tracer calibration and with ^{238}U decay constant uncertainties), indicating that while CK-5 is younger due to stratigraphic relationships, an absolute age difference between the formation of the two horizons is unresolvable using our zircon dates.

As mentioned above, it is not uncommon for high silica magmatism to crystallize zircon with an abundance of xenocrystic components, and this may not be readily observed during SEM imagery. Whole grain analyses, as commonly done in U-Pb ID-TIMS geochronology, may bias the accuracy of individual dates, and yielding artificially older ages in some geological settings. While this method does not allow for replicate analyses when compared to breaking the grains evenly (e.g., Heriott et al. 2019), for samples ranging from those with subtle antecrystic cores to those with obvious xenocrystic cores these young exterior zircon domains represent the most precise, accurate target for MDA's. Therefore, we suggest that subsequent studies which require strong temporal control using MDA's consider utilizing sub-grain ID-TIMS analyses in order to generate the most accurate high-precision ages.

Model and duration of bauxite formation, implications for SB evolution and climatic implications

The Upper Cretaceous limestones hosting CK bauxite deposits belong to the Adriatic-Dinaridic Carbonate Platform (Tari-Kovačić 1994; Mandic et al. 2008). With the start of compressional tectonics during the Eocene, the platform turned into a foredeep with deposition of flysch and molasses (Promina Formation), and was subsequently subaerially exposed during the Oligocene (Mandic et al. 2008). Accordingly, these rocks could have begun to undergo the combined effects of tectonic deformation, erosion and weathering beginning in the Oligocene (perhaps even from Late Eocene), allowing for the gradual development of the karstified paleo-depressions suitable for trapping bauxite precursor material (Šušnjara et al. 1990; see also Bárdossy 1982; Bogatyrev et al. 2009). Based on geochronological and geochemical data, the same protoliths provided the bauxite precursor material for all CK bauxite horizons. CK bauxite geochronology (Fig. 6) seems to be consistent with the regional geological framework: the euhedral zircons of Oligocene (and Late Eocene) age probably represent the initial volcanic material having reached the newly formed pre-Miocene paleorelief and accumulated in the paleo-depressions, with accumulation of new material, including younger volcanic zircon, up until the Early Miocene.

Our high-precision maximum depositional age (MDA) of 16.9576 ± 0.021 Ma (Fig. 8; 2σ uncertainty) of the CK bauxite parent material provide chronologic constraint on its true depositional age and on the maximum age of bauxite formation. The bauxite precursor detritus appears to be relatively homogenized throughout the CK profile based on similar geochemistry, mineralogy and zircon age spectra (Figs. 6, 7), and was subjected to autochtonous bauxitization.

At the time of the maximum bauxitization age (~17 Ma), certain areas of the SB carbonatic basement were still exposed, specifically the Upper Cretaceous limestones hosting the Miocene bauxites in the southeastern region of the SB. This is in contrast with previous work, which interpreted that lacustrine environments had covered the entirety of the SB by this point, based on 17.91 Ma Ar/Ar geochronology of a volcanic horizon intercalated in lacustrine sediments (LUČ-3; de Leeuw et al. 2010, 2012). Our revision of this date indicates that SB lacustrine sedimentation in the northern portion of the basin began at 17.312 ± 0.024 Ma (Fig. 8). This volcaniclastic horizon occurs intercalated only with varicolored marls in the northwestern part of the basin (Fig. 1), however the lower SB stratigraphy is comprised of coal-bearing beds and marls with dreissenid bivalves overlying Miocene bauxites in the southeastern part of the basin (Fig. 1; Šušnjara and Sakač 1988; Šušnjara et al. 1990; Mandic et al. 2008; de Leeuw et al. 2010). Although the two types of sedimentary rocks of the basal unit of the SB have been interpreted as synchronous, lateral transitions or contacts between the two have not been observed in the field (Šušnjara and Sakač 1988). Therefore, while lacustrine environments existed in the northwestern part of the SB by 17.3 Ma, there was still subaerial exposure in the southeastern portion of the basin. This implies there was significant paleorelief in the SB during Early Miocene, and that the lacustrine flooding across the SB was diachronous, with flooding first in the northwest and later in the southeast.

The minimum age of bauxite formation can be inferred by stratigraphic relationships and Ar/Ar dating within the SB. Since there is no high-precision geochronological data for the lower SB stratigraphy in the southeastern portion of the basin overlying the CK bauxites, we instead rely on a 16.24 Ma using $^{40}Ar/^{39}Ar$ sanidine date from an overlying lacustrine section of the middle SB stratigraphy to provide a minimum age for bauxitization (LUČ-2; de Leeuw et al. 2010, 2012). These upper and lower stratigraphic geochronology constraints indicate that bauxitization must have taken place in 700 ka or less (Fig. 9), which agrees with the estimated 10^5–10^6 years required to develop strong oxisols, soil analogues for bauxites, and the formation timeframes of ancient bauxites during tropical and subtropical humid weathering (Birkeland 1984; D'Argenio and Mindszenty 1995; Retallack 2001, 2010; Bogatyrev et al. 2009; Huang et al. 2012; Retallack et al. 2016). This age range coincides remarkably with the onset and the early stage of the Miocene Climatic Optimum (MCO; Fig. 9; Kasbohm and Schoene 2018;

688 Methner et al. 2020; Sosdian et al. 2020; Steinthorsdottir et al. 2021), implying that the *in situ* bauxitization in
689 mid-latitude European areas occurred during the Cenozoic period of elevated atmospheric CO_2 levels and global
690 warming. The possibility that some *in situ* bauxitization of CK precursor material might have been taking place
691 before ~17 Ma (e.g., during Late Oligocene Warming and/or during Early Miocene; Zachos et al. 2001, 2008;
692 Mossbruger et al. 2005; Ivanov et al. 2011; Scotese et al. 2021; Steinthorsdottir et al. 2021), as well as potential
693 contribution of SB range Upper Paleogene bauxite horizons (i.e., underlying Upper Eocene–Lower Oligocene
694 Promina Formation deposits; Šušnjara et al. 1990) resedimented to the CK profile, with subsequent dominant
695 MCO bauxitization of the protolith (including potential pre-17 Ma bauxites) is not excluded and is yet to be
696 investigated (e.g., Hall et al. 2015; Kelemen et al. 2017; Mathian et al. 2019). In addition, degree of potential
697 parautochthonous origin of CK bauxites should also be evaluated (Bárdossy 1982; Sakač et al. 1987; Valeton
698 1991).
699
700 Correlation of CK bauxite formation to the Miocene Climatic Optimum
701
702 The MCO represents the 14.7–17 Ma warm period (global mean annual temperatures 5˚C–6˚C warmer than present
703 day) interrupting long-term Cenozoic cooling and declining pCO_2 levels, and reduced continental ice volume (Fig.
704 9; e.g., Kasbohm and Schoene 2018; Methner et al. 2020; Sosdian et al. 2020; Steinthorsdottir et al. 2021 and
705 references therein). The MCO is a part of the Monterey carbon isotope excursion (MCIE) - a prolonged ~1.0 ‰
706 positive carbon isotope excursion ($\delta^{13}C$) of the global oceans (e.g., Zachos et al. 2001; Holbourn et al. 2015;
707 Sosdian et al. 2020). There is a growing evidence for elevated and variable pCO_2 levels of 350 to 630 ppm during
708 the MCO global warm period (e.g., Kasbohm and Schoene 2018; Methner et al. 2020; Sosdian et al. 2020;
709 Steinthorsdottir et al. 2021; see also Retallack 2009 as well as Retallack and Conde 2020). The MCO may therefore
710 have similarities in the magnitude of global change we are currently observing in the present-day, with rise in
711 global atmospheric pCO_2, global temperature and decrease in polar ice volume, and therefore is crucial to better
712 understand it (e.g., Retallack 2009; Kasbohm and Schoene 2018; Methner et al. 2020; Retallack and Conde 2020;
713 Sosdian et al. 2020; Steinthorsdottir et al. 2021).
714 Although continental paleoclimate records from the MCO are essential for assessing past global climate
715 change, they are far less common than the available marine record (Methner et al. 2020). The 15.7 Ma old lateritic
716 bauxites (Oxisols) developed on Columbia River Basalts (CRB, weathered to bauxite to depths of 18m) in western
717 Oregon (and Washington) in the United States have been directly correlated to the MCO (Fig. 9; e.g., Liu et al.

718 2013, Retallack et al. 2016). In contrast, the contemporaneous intra-basaltic Alfisols in eastern Oregon have been
719 interpreted to reflect that local rainfall variations could have also determined the local expressions of weathering
720 during MCO (e.g., Sheldon et al. 2003; Retallack 2010; Retallack et al. 2016). Intense chemical weathering of
721 Vogelsberg basalts (central Germany) during MCO is held responsible for lateritic bauxite development in these
722 mid-latitude European areas (Figs. 1, 9; 51° paleolatitude; Schwarz 1997; Retallack 2010). Formation of terrestrial
723 kaolin deposits trapped in Transdanubian Range (Pannonian Basin, Hungary) Miocene karstic sinkholes was
724 interpreted as partially related to *in situ* weathering of wind-borne material (mainly tephra) during the MCO (Figs.
725 1, 9; Kelemen et al. 2020). Optimum climatic conditions during MCO also stimulated lake formation in the
726 Dinarides (Mandic et al. 2020 and references therein). The high relative percentage of warm pollen taxa
727 (thermophilous plants) throughout the SB lacustrine stratigraphy is indicative of a warm subtropical and a yearlong
728 humid climate for this area (in accordance with other European areas, such as the Pannonian Basin) during Early
729 and early Middle Miocene (Jiménez-Moreno et al. 2006, 2008 and references therein).
730 Although the temporal and causative relationships between the CRB and the MCO is still debated, and there
731 are still outstanding concerns regarding the most reliable age models for climate proxy records across the MCO,
732 it is generally accepted that the MCO began at approximately 17 Ma (Kasbohm and Schoene 2018; Methner et al.
733 2020; Sosdian et al. 2020; Fig. 9). The onset of the MCO is not clearly resolved in North Alpine Foreland Basin
734 (NAFB, Switzerland; Fig. 1) paleosols, however, the timing of central European warming agrees with the onset of
735 the MCO at high latitudes between 17.4 and 16.9 Ma, and the NAFB paleosol carbonates indicate (based on
736 clumped isotope data) there was a warming period between 17.4 and 16.6 Ma (Methner et al. 2020; Fig. 9). The
737 peak of MCO-related warming was 30.6 °C at 16.59 Ma, with temperature declining to 23.4 °C by 16.38 Ma, and
738 terrestrial temperatures remained below 25 °C between 16.4 and 15.8 Ma, coinciding with the Miocene cooling
739 interval (Methner et al. 2020; Fig. 9). This first warming peak recorded in NAFB paleosols correlates with climatic
740 evidence in other regional and global terrestrial and marine environments, such as increased $\delta^{13}C$ marine carbonate
741 values after 16.7 Ma and increased pCO_2 levels (e.g., Holbourn et al. 2015; Methner et al. 2020 and references
742 therein). Although this timing is 400 ka later than the reconstructed maximum bottom water temperatures recorded
743 at ~17.0 Ma, it correlates well with the timing of minimum global ice volume (Lear et al. 2015; Methner et al.
744 2020).
745 MCO-related CK bauxitization provides an independent evaluation of paleotemperature and paleorainfall
746 calculations at comparable latitudes in Europe during the ~700 ka during which the CK bauxites formed, which
747 indicate elevated mean annual temperatures (MAT) and mean annual precipitation (MAP). In NAFB (southern

748 Germany; Fig. 1), during the period from 17 to ~16.3 Ma, the MAT and MAP values (based on silicified woods)
749 had a range from 15.7 to 20.5 °C and from 1138 to 1355 mm, respectively (Fig. 9; e.g., Böhme et al. 2007, 2011;
750 Bruck et al. 2007, 2011). Pollen-based data from the SB and the larger DLSB indicate that the Early Miocene had
751 a warm subtropical and humid climate, favorable for bauxite formation (Jiménez-Moreno et al. 2008). In order for
752 *in situ* bauxitization to occur, the temperatures must have been warmer than 17–22°C, with more than 1100–1200
753 mm of annual precipitation, which gives direct paleoclimate constraints to mid-latitude European continental
754 settings during the early stages of the MCO (Fig. 9; Bárdossy 1982; Bárdossy and Combes 1999; Bogatyrev et al.
755 2009; Retallack 2008, 2010; Mondillo et al. 2011). Along with agreeing with reconstructions of climatic conditions
756 during the onset and the early stages of the MCO, CK bauxites provide also a distinct geochronological constraint
757 on the onset and the early stages of the MCO in European continental settings, and a unique insight into prevailing
758 conditions during Early Miocene in parts of southeastern Europe (central Dalmatia; Fig. 9).
759
760 **Conclusions**
761
762 New zircon geochronology data, integrated with compositional, mineralogical and morphological data from central
763 Dalmatian (CK section) karst bauxites provide a unique insight into their genesis and formation. The subhedral to
764 euhedral morphologies of the kaolinite crystals, together with gibbsite, are the predominant mineral phase of the
765 homogeneous matrix of the bauxite, and these morphologies indicate that they are authigenic. Their *in situ*
766 formation, a consequence of the pedogenic process under prevailing alkaline pH conditions based on $(La/Yb)_{ch}$
767 values (or alternatively reflecting phreatic early diagenetic processes taking place under gradually more alkaline
768 pH conditions superimposed on initial vadose bauxitization taking place under dominantly acidic pH conditions),
769 indicates that the CK massive karstic bauxites are autochthonous. The presence of authigenic calcite throughout
770 the profile, together with geochemical data, indicate that late-diagenetic modification affected these bauxites. *In*
771 *situ* LA-ICP-MS zircon age spectra of the lower, middle and upper parts of the CK bauxite are dominated by
772 Miocene and Oligocene ages, and together with their similar geochemistry throughout the profile we interpret that
773 all of the CK bauxite horizons had the same precursor materials. Individual zircon and sub-grain analyses by CA-
774 ID-TIMS also revealed protracted Miocene zircon age spectra of the CK bauxites, as well as a MDA of 16.9576 ±
775 0.0096/0.011/0.021 Ma (2σ uncertainty) for the CK bauxite parent material. In addition, zircon geochronology of
776 a volcaniclastic horizon from the northeastern portion of the Sinj Basin (SB) indicates that there was significant
777 paleorelief within the basin during the Early Miocene, and that lacustrine flooding across the SB was diachronous.

The MDA for the parental material of the bauxite, which also serves as the maximum age of autochthonous bauxitization, coincides with the onset of the MCO. Based on currently available geochronological constraints, the maximum timeframe for CK bauxitization was less than ~700 ka. The potential imprint of pre-17 Ma bauxitization and contribution of older (i.e., Upper Paleogene) bauxite deposits resedimented to the CK profile, as well as degree of potential parautochthonous origin of the CK bauxites, is yet to be investigated. Continental proxies from several European mid-latitude areas indicate that there was a warming period between approximately 17–16.3 Ma, correlating with climatic evidence archived in regional and global terrestrial and marine environments. More than simply aligning with regional and local reconstructions of continental climatic conditions during the onset and the early stages of the MCO, the CK autochtonous bauxites provide a precise climatic constraint. In order for *in situ* bauxitization to have occurred, the mean annual temperature must have been higher than 17–22°C, with more than 1,100–1,200 mm of precipitation per year between 16.95–16.24 Ma in some southeastern parts of mid-latitude continental Europe. High-quality data provided in this study strengthen the view (suggested already by D'Argenio and Mindszenty 1995 with the Cretaceous in their focus) that periods of unusually widespread bauxite formation, beyond their modern distribution within the tropics, is correlated with times of global high warmth and precipitation, as is the case of the MCO.

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Figure captions

Fig.1 a Geographical position of the Sinj Basin (SB) and Dinaride Lake System Basins. The position of volcanic and volcaniclastic rocks representing the products of regional Late Eocene to Early Miocene volcanic episodes, as well as locations of continental mid-latitude central European Miocene Climatic Optimum (MCO) records, is also provided. **b**, **c**: Schematized geological map (**b**) and generalized stratigraphic columns (**c**; lower and middle units) of the SB (modified after Šušnjara and Sakač 1988; de Leeuw et al. 2010; Šegvić et al. 2014), with positions of some Miocene bauxite localities and SB Lower Miocene volcaniclastic rocks. Subdivision and lithostratigraphic units according to Šušnjara and Sakač (1988).

Fig. 2 Vertical section (geological column) of the Crveni Klanac (CK) section, represented by variously colored massive bauxite horizons (CK-1, CK-2, CK-3, CK-5) and CK-4 horizon with films and coatings, hosted in the Upper Cretaceous limestones and overlain by the lower SB lacustrine deposits. Variations in bulk mineralogical content and geochemical composition throughout the bauxite profile are shown.

Fig. 3 Whole-rock (**a**) and clay fraction (**b**) XRPD patterns obtained from CK bauxite samples (from the bottom horizon CK-1 to the top horizon CK-6). Ant = anatase; Bhm = boehmite, Cal = calcite, Gbs = gibbsite, Gt = goethite, Hem = hematite, HIV = hydroxy-interlayered vermiculite, Kln = kaolinite, Qtz = quartz, Rt = rutile.

Fig. 4 Transmitted light optical microscopy (**a**–**d**) and FESEM (E–J) images of CK bauxite samples. **a**, **b** Homogeneous bauxite texture of samples CK-1 and CK-2 composed of pelitomorphic to microgranular matrix, with micron-sized Fe oxides (**b**). Parallel nicols. **c** Replacement of primary bauxite by calcite (sample CK-6) with previously homogeneous bauxite matrix embedded in microsparitic to sparitic matrix. Crossed nicols. **D** The

yellowish-brownish part of the horizon CK-4 with fragmented and isolated bauxite matrix coated, surrounded and rounded with Fe-oxide films. Sparite infilling voids can also be observed. Parallel nicols. **e**, **f** Secondary electron images showing subhedral to euhedral kaolinite crystals and gibbsite with rounded morphology composing the CK-1 and CK-2 bauxite homogeneous matrix. **g** Backscattered electron image of kaolinite booklets in sample CK-1. **h** Backscattered electron image showing anhedral to euhedral calcite (sparite) in a fine-grained homogeneous bauxite matrix (sample CK-5). **i** Secondary electron image showing heteromorphic kaolinite crystals with platy morphologies and nanometric gibbsite with rounded morphologies composing homogeneous matrix of the sample CK-5. **j** Backscattered electron image showing somewhat deteriorated kaolinite booklets of the sample CK-5. Hem = hematite, Gib = gibbsite, Kln = kaolinite, Cal = calcite

Fig. 5 a $(La/Yb)_{ch}$ and Ce/Ce* values, as indicators of pH of the soil solution and paleo-redox conditions, respectively, of the bauxite samples affected at various degree by carbonate addition. **b** Mobility of the chemical elements as change % relatively to the Upper Continental Crust composition and assuming Ti as an immobile element. See text for further details.

Fig. 6 Probability distribution function (PDF) graphs of $^{206}Pb/^{238}U$ LA-ICP-MS zircons dated in this study, highlighting that age spectra from all three dated samples are dominated by Early Miocene zircon analyses, with a subordinate peak in the Early Oligocene.

Fig. 7 SEM imagery of zircons dated using CA-ID-TIMS in this study. All ages are Th-corrected $^{206}Pb/^{238}U$ ages, and individual grains or subgrains which yielded normally discordant ages are indicated with a blue *. All zircons were previously analyzed by LA-ICP-MS, and had a significant volume of material ablated from the grain prior to CA-ID-TIMS and therefore the volume of zircon analyzed by CA-ID-TIMS is less than shown here. Grains which were fractured during removal from the LA-ICP-MS mount and analyzed separately are denoted with a red line which indicates where they broke, and which portion of the grain refers to individual ages. Grains most commonly fractured along the laser ablation pits.

Fig. 8 Rank order plot of ID-TIMS Th-corrected $^{206}Pb/^{238}U$ ages from Miocene-aged detrital zircon hosted in CK bauxite horizons, and volcanic zircon from sample LUČ-3, an ash bed intercalated within the lower lacustrine unit

of the SB. Unfilled boxes/data points represent $^{206}Pb/^{238}U$ age of normally discordant analysis. See text for discussion of how these ages are interpreted.

Fig. 9 Compilation of Crveni Klanac (CK) *in situ* bauxitization and other continental mid-latitude Miocene Climatic Optimum (MCO) records (modified from Methner et al. 2020). **a** Statistical onset of the MCO and the duration of the subsequent Middle Miocene Climatic Transition (MMCT; after Methner et al. 2020). **b** MCO (orange) and MMCT (blue) in Central Europe as inferred by Methner et al. 2020. **c** Geochronological constraints on the timing of the onset and the maximum timeframe for the CK bauxitization, with implied mean annual temperatures (MAT) and mean annual precipitation (MAP) in southeastern parts of mid-latitude continental Europe (central Dalmatia) during MCO (this study). **d** Clumped isotope temperature record (pedogenic carbonate) and paleofloral-based MAT of the North Alpine Foreland Basin (NAFB; Böhme et al. 2007; Methner et al. 2020). **e** Other Central European and North American mid-latitude records of intense chemical weathering during MCO (CGLB, Central German lateritic bauxites – Schwarz 1997; TBR kd, Transdanubian range kaolin deposits – Kelemen et al. 2020; CRB bx, Columbia River Basalts lateritic bauxites – Liu et al. 2013).

Electronic Supplementary Material captions

Supplementary Material 1

ICP geochemistry table

Supplementary Material 2

LA-ICP-MS geochronology table

Supplementary Material 3

CA-ID-TIMS geochronology table