Manifestations of syn-eruptive fluid circulations on carbonate veins, Central Anatolian Volcanic Province

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Abstract

Although there are several attempts to compare the age distributions on travertines with episodes of surrounding volcanism, the correlation between the precipitation record of carbonate veins and the fractural pattern around a volcanic conduit has not yet been examined. In this study, we investigate the geochronological, geochemical and isotopic characteristics of two travertine deposits (Balkaya and Sarıhıdır) surrounded by many eruption centers in the central Anatolia with ample paleoeruption records. High-resolution carbonate precipitation records revealed by U-series dating are well correlated with the compiled dataset on Acıgöl caldera and Erciyes stratovolcano eruptions with regard to fractural positioning to the volcanic centers. Syn-eruptive carbonate precipitation is thought to occur because of sudden flux of CO_2-rich fluid along the extensional fracture systems aligned tangential to the related volcanic conduit and, therefore, may be an alternative technique for the reconstruction of paleoeruptions. $\delta^{18}O$ and $\delta^{13}C$ values of the travertine sites are within the range of meteogene fluids and $\delta^{18}O$ values show a similar trend to climate proxies preserved in different depositional environments throughout the world. It is likely due to that studied carbonates were precipitated under similar fluid conditions which are represented by high rate of dilatation followed by the meteoric water influx into the extensional fracture systems.

1. Introduction

The internal structure of thermogenic carbonate veins is composed of alternated vertical bands that are precipitated from CO_2-rich hot waters through the fracture systems around the geothermal areas (Pentocost, 2005; Uysal et al., 2007; Brogi and Capezzuoli, 2014; Karabacak et al., 2017). The formation of these bands is closely linked to repeated precipitation episodes that require reopening of previously sealed fractures within the bedrock, favouring a temporary hydrothermal fluid circulation. Every band of the vein presents a limited time that corresponds to the period starting just after the event until sealing (Williams et al., 2017; Capezzuoli et al., 2018; Karabacak et al., 2019). Thus, since carbonate veins are highly suitable for direct dating of calcite, they provide an opportunity to understand the history of fluid circulation in a region of seismic or volcanic unrest.

Most of the previous studies devoted to carbonate veins focus on the interaction with fluid circulation and active crustal deformation (e.g. type and direction of regional stresses, dilatational rate) (e.g. Altunel and Karabacak, 2005; Uysal et al., 2007; Brogi et al., 2017). In recent works, their relations with earthquake strain cycles are also addressed (Uysal et al., 2011; Brogi and Capezzuoli, 2014; Williams et al., 2017). Moreover, it is proven that the age distributions of vertical bands in a carbonate vein supply direct dates of the nearby fluid flow circulation in the areas of seismic unrest (Karabacak et al., 2019). These features make the carbonate veins quite attractive for the active tectonic studies.

In volcanic regions, deformation is caused by shear failure, tensile failure or fluid pressurization process that produce ruptures at the tip of a magma body during strain cycles (Anderson, 1951; Rubin and Gillard, 1998; Azzarro, 1999; Glen and Ponce, 2002; Zobin, 2003). Stress in a radial-pattern spreading generates extensional fractures positioned tangential to volcanic conduits (e.g. Anderson, 1951; Macdonald, 1972; Park, 1989; Borgia et al., 2014) thus creating deep migration pathways for the fluids. During strain cycles, changes may also occur in deep aquifers (Montgomery and Manga, 2003; Wang et al., 2004) that are loaded by great elastic strain at depth (Seed and Idriss 1971), resulting in a relatively large expulsion of depressurized CO_2-rich hot waters. Therefore, subsurface hot fluids are mobilized in deeply penetrating fractures that act as conduits for hot waters and as a result, carbonates are precipitated around the volcanic eruption centers.

The previous studies asserted the temporal correlation between carbonate precipitation and volcanism with random sampling strategies on travertine deposits, carbonate veins and speleotherms (e.g. Tuccimei et al., 2006; Priewisch et al., 2014; Karabacak et al., 2017; Weinstein et al., 2020). For example, Priewisch et al. (2014) suggest that the deposition ages of voluminous travertines overlap with the episodes of basaltic volcanism in New Mexico and Arizona. Karabacak et al. (2017) compare U-series geochronology of carbonate veins with previous volcanic eruption records and achieve to resolve independent events on two different eruption centers. In the literature, however, there is a lack of studies focusing on continuous precipitation record to compare the syn-eruptive fluid circulations and carbonate vein ages. Furthermore, none of the previous studies assessed the correlations regarding the fractural pattern and volcanic conduit position.

In this study, we investigate a continuous precipitation records of carbonate veins in the Central Anatolian Volcanic Province (CAVP) and evaluate precise U-Th ages, mineralogy, and geochemical and isotopic characteristics of alternated bands. We compare our results with paleo-eruption records from major volcanic centers (Figure 1). Our correlations are discussed with regard to fractural positioning to the eruption centers to discriminate the event origin. Furthermore, oxygen isotope and rare element compositions of vein samples provided us with a great opportunity to examine temporal variations in the temperature and source of fluids that precipitated the studied travertines in the region.

2. Material and Method

Mineralogical and petrographic determinations of carbonate samples were carried out at the Geology Department (YEBIM Center) of the Ankara University. Porosity types and textural characteristics of samples were studied with Leica DMLP model polarizing microscope. Mineralogical composition of carbonates was determined with Inel Equinox 1000 X-Ray Diffractometer. Raman spectroscopy analysis on selected samples was conducted with DXR brand using laser beam of 780 nm.

Carbon and oxygen isotope analyses of carbonate samples were carried out with micromass Isoprime dual inlet isotope ratio mass spectrometer (DI-IRMS) at the Environmental Isotope Laboratory of the University of Arizona. Samples were reacted with dehydrated phosphoric acid (H_3PO_4) under vacuum at a temperature of 70^0C. The isotope ratio measurement is calibrated based on replicate measurements of international standards NBS-19 and NBS-18. The analytical precision is ±0.1‰ for $\delta^{18}O$ and ±0.08‰ for $\delta^{13}C$ (1σ).

The trace element analyses of the carbonate samples were performed at the Radiogenic Isotope Laboratory, the University of Queensland on a Thermo X-series ICP-MS with instrument conditions as described in Lawrence and Kamber (2006), after dissolving the carbonates in a 2% HNO_3 solution embed with internal standards. The raw data were corrected for the low, detectable blank, internal and external drift, and for oxides and doubly charged species. Instrument response was calibrated against two independent digests of the USGS reference W-2, and confirmed by analysis of other inter-lab references, treated as unknowns. Corrections were applied for oxides using formation rates determined from pure single element REE standards.

Carbonate samples were dated by U-series technique at the Radiogenic Isotope Laboratory at the University of Queensland using a Nu Plasma HR Multicollector Inductively Coupled Plasma Mass Spectrometer (MCICP- MS) following the analytical protocols described in Zhao et al. (2001) and Ünal-İmer et al. (2016). $^{230}Th/^{238}U$ and $^{234}U/^{238}U$ ratios were calculated using decay constants given by Cheng et al. (2000). U-series ages were estimated using the DensityPlotter 8.5 (Vermeesch, 2012).

3. Geological Setting

3.1. Central Anatolian Volcanic Province

The tectonics of the Anatolian Block is governed by interactions between three major plates; African, Arabian and Eurasian plates. Owing to this outstanding location, the Anatolian block represents an intraplate deformation resulting from the northward convergence of the Afro-Arabian plates to the Eurasian plate. As commonly expected within intraplate domains controlled by collisional margins, the central part of Anatolia has witnessed an intense Neogene-Quaternary volcanic activity associated mainly with subduction events (Innocenti et al., 1975; Aydar et al., 1994; 1995; Piper et al., 2002).

The central Anatolia is shaped by a triangular frame controlled by Quaternary faults; NW-SE-trending Tuzgölü Fault Zone (TFZ) in the west, NE-SW-trending Ecemiş Fault Zone (EFZ) in the east and the Central Kızılırmak Fault Zone (CKFZ) in the north. The TFZ and EFZ consist of Holocene faults with strike-slip component (Dirik and Göncüoğlu, 1996; Emre et al., 2011). The CKFZ present a southward arc-shape geometry through the Kızılırmak River (Toprak, 1994). It consists of Quaternary normal faults and linements of faults with strike-slip component (Dirik and Göncüoğlu, 1996; Emre et al., 2011) and constitutes the northern margin of the CAVP (Toprak, 1994). The region of triangular frame, so called the CAVP, is surrounded by a number of eruption centers such as major composite volcanoes and monogenetic cones with voluminous volcanic products (Toprak and Göncüoğlu, 1993). In this province, Quaternary eruption development has been controlled by three main eruption centers (Acıgöl caldera, Hasandag and Erciyes stratovolcanoes) within an area of 40 km radius. Hasandağ and Erciyes composite volcanoes were formed along the TFZ and EFZ (Pasquare et al., 1988; Toprak and Göncüoğlu, 1993). The Acıgöl Caldera area lies in the central part by monogenetic cones. Paleoeruption events on extrusive materials in the region were dated by a range of methods (for the last 190 ka) (Table S1).

3.2. Balkaya and Sarıhıdır travertine sites

In the current study, we focus on fracture systems and their carbonate veins in Balkaya and Sarıhıdır travertine sites around the Avanos town that is surrounded by well-known volcanic centers between the Acıgöl caldera and Erciyes stratovolcano. In the area, Kızılırmak River flows towards west by drawing a southward arc.

Figure 2 presents the geological setting of the study area that was improved from Köksal and Göncüoğlu (1997) and Koçyiğit and Doğan (2016) authors' field observations. In the study area, Mesozoic-aged metamorphites (Köksal and Göncüoğlu, 1997) comprise the basement and are overlain by the Upper Cretaceous-Lower Paleocene granitoid-syenitoid and Middle-Upper Eocene limestones (Koçyiğit and Doğan, 2016). Volcaniclastic sediments consisting of tuffaceous fluvial deposits (Upper Miocene-Pliocene) form a huge platform at the south of

Kızılırmak River and become thinner to the north (Köksal and Göncüoğlu, 1997; Koçyiğit and Doğan, 2016). The Upper Miocene-Lower Pleistocene fluvial and lacustrine deposits are represented by tectonically controlled margins and lie on the hanging walls of the normal faults (Koçyiğit and Doğan, 2016). The studied travertines are exposed as separate bodies at the Sarıhıdır and Balkaya sites in northern part of the Avanos town.

3.3. Syntectonic fluid circulation

During seismic release, deep aquifers are loaded by larger elastic strain which causes a relatively huge expulsion of depressurized CO_2-rich hot waters (Montgomery and Manga, 2003; Wang et al., 2004; Berardi et al., 2016; Karabacak et al., 2017) giving rise to carbonate precipitation within fractures that serve as conduits for CO_2-charged groundwater (Sibson, 1987; Altunel and Karabacak, 2005). Although both high flux of CO_2 and large rate of groundwater discharge are the ultimate drivers of carbonate vein precipitation in deeply-penetrating fractures, climate-driven near-surface hydrological changes may also play an important role in episodic CO_2-rich fluid circulation. Recent studies have shown that the timing of vein formation coincides preferentially with colder and drier climate regimes (Uysal et al., 2019). Such carbonate vein precipitation is, therefore, a direct record of the seismic release during glacial periods (Uysal et al., 2007; 2011; Brogi and Capezzuoli, 2014).

The internal structure of carbonate veins formed in alternated bands is closely linked to repeated crustal reactivation that requires fluid circulation (Uysal et al., 2007; Nuriel et al., 2012; Brogi and Capezzuoli, 2014; Karabacak et al., 2017; Williams et al., 2017). Karabacak et al. (2019) review the cycles of banded carbonate vein precipitation in tectonically active areas (Table 1) and suggest that 1) *coseismic period* involves the opening/reopening of fractures due to seismic release. Simultaneous fluid circulation in fracture systems and expulsion of depressurized/supersaturated hot water are resulted in rapid precipitation of carbonates on both walls of the fracture (planar). The band is formed as whitish microcrystalline calcite that is related to abundant fluid inclusions with high-CO_2 degassing, 2) during the *post-seismic period,* saturated fluids still discharge with relatively slow flow rate until the fracture is completely plugged. Because of slow degassing rates, light-transparent macrocrystalline calcites are precipitated and 3) until the next seismic event no more carbonate could be precipitated under slow-flowing conditions. This *interseismic period* forms a hiatus with the former carbonate band.

4. Results

4.1. Sampling

We investigated the structural features reported in the previous studies in the neighborhood of study area (i.e. Toprak, 1994; Köksal and Göncüoğlu, 1997; Emre et al., 2011a; 2011b; Koçyiğit and Doğan, 2016) using digital elevation data at ca. 29-m ground pixel resolutions (AsterGDEM v2) (Figures 1, 2 and S1). The key morphological lineaments were determined by satellite images (from Google Earth software) and confirmed by field observations (Figure 2). Accordingly, main lineaments controlling the northern margin of the Kızılırmak valley are found to extend in E-W direction with a southward arc-shape geometry.

There are two travertine sites (Balkaya and Sarıhıdır) formed on these lineaments in a few km distance. Balkaya travertines occur on a dilational jog between the NW-SE-trending dipslip faults with length of about 3 km (Figures 2 and S1b). They display a normal fault morphology on which the southern blocks have moved downward. Travertines with a well-protected morphology, consist of a main central fissure filled with carbonate vein (vertically banded compact travertines), and porous bedded travertines dipping away from the central fissures. Fracture analyses on carbonate veins show the presence of two dominant stress orientations spanning the range of 70° to 130° (Figure 2). They are controlled by two conjugated sets displaying a hybrid fracture feature.

The Sarıhıdır travertines are formed on a jogging area between a NE-SW-trending left-lateral oblique fault and a NE-SW-trending morphological lineament (Figures 2 and S1a). Most of the fissures in this site have been filled with carbonate material. Field observations and bi-directional rose diagrams plotted for the Sarıhıdır fissures and veins reveal two conjugate sets in a range of 40° to 120° (Figure 2).

For isotopic and geochemical analyses, using microdrilling technique we sampled 36 bands from four selected carbonate veins at Sarıhıdır (locations 1 and 2) and Balkaya (locations 3 and 4) sites (Table S2, Figures S1-4). We selected veins that are suitable for sampling across their entire width (wall to wall) or at least from wall to the fissure center. The sampling strategy is focused on relatively thick, detritus-free crystalline bands along the veins. All samples were labelled and signed onsite to indicate the first precipitation sides.

4.2. Mineralogical and petrographic analyses

Carbonate band samples were cut parallel to their deposition directions. The samples were polished and cleaned ultrasonically. Before the analysis, two sets were prepared: one of the sets was used to investigate the whole rock mineralogy and microtexture by XRD and another was for thin section petrography.

Carbonate samples from the Balkaya and Sarıhıdır locations are divided into several subgroups concerning their textural features and mineral sizes (Table S3, Figures S5-S8). The first subgroup of the Balkaya samples is represented by well-developed banded and flow textures and composed chiefly of idiomorph, coarse crystalline, needle-shaped calcite minerals accompanied by trace amount of kaolinite (Figure S5a, b). Results of confocal Raman spectroscopic (CRS) and electron probe microanalysis (EPMA) studies indicate that bands are made up of rhodochrosite (Figure S7) and cryptocrystalline quartzs comprise the porous parts of carbonates. The porosity type is burrowing. The second subgroup of Balkaya samples has granular (mosaic) texture with different sized xenomorphic calcite minerals (Figure S5c, d) represented by fenestral type porosity. The third group is comprised by both flow and granular textures with shelter porosity (Figure S5e, f). The fourth group shows fine crystalline granular texture with shelter and fenestral porosity (Figure S5g, h). Balkaya carbonates are formed within the cracks and fractures of micritic limestone, which consists of calcite with rare quartz. The existence of quartz may indicate occasional erosion and sediment transport by surface runoff to the deposition site.

Concerning texture types, the Sarıhıdır samples are divided into three subgroups. The first group has finely banded (flow) and granular textures and consists of fine to coarse crystalline calcite with rare quartz, pyroxene (augite), epidote and clay minerals (Figure S6a, b and S8). They typically have shelter type porosity. The second group of carbonates is characterized by finely crystalline granular texture and shelter type porosity (Figure S6c, d). Samples of this group are composed of calcite, quartz, feldspar (bytownite) and opaque minerals (manganese dioxide) (Figure S6c, d and S8). The third group presents very finely banded and well-developed flow textures with shelter and fenestral type porosity (Figure S6e-h). Clay minerals occur in the carbonate bands.

Idiomorph and coarsely crystalline, needle-shaped calcites indicate rapid crystallization from the fluid. Coarse crystalline calcite minerals grow toward the fluid direction whereas fine crystalline calcites point to crystallization under a stagnant flow regime (Rizzo et al., 2019). Because of heterogeneous crystallization, calcites show various crystal sizes. The flow rate of fluids forming this subgroup is quite varied. Sarıhıdır samples contain mineral fragments of volcanic or intrusive rocks exposed in the study area. The banded texture of Balkaya carbonates is much better developed than the Sarıhıdır samples and Mn-bearing bands are thicker for the former. Cataclastic texture recognized within the Sarıhıdır carbonate veins indicates that seismic event probably postdates the carbonate formation.

4.3. U-Th geochronology

Based on the results of XRD and microscopy studies, collected carbonate samples are coarsely crystalline and consist of almost 100% calcite minerals. Calcite fabrics are generally observed as long elongated and open columnar forms. The discontinuities between the bands (hiatus) are quite noticeable ensuring no contamination in adjacent generations (Figure 3). Most of the bands display two crystalline zones: 1) towards fracture wall, whitish microcrystalline calcites that are related to abundant fluid inclusions with high-CO_2 degassing, 2) towards fracture center, light-transparent macrocrystalline calcites that are related to slow degassing rates. For U-Th dating, carbonate vein bands were microdrilled from the whitish microcrystalline parts, immediate nearest location of the band to the fracture wall (Figure 3).

$^{230}Th/^{232}Th$ ratios of most samples (more pronounced for the Sarıhıdır samples) are lower than 10 showing the presence of detrital ^{232}Th in Balkaya and Sarıhıdır sites (Tables 2 and S4). The samples have very low U contents (6.6 to 37.4 ppb). This may imply that there might be a time gap between the vein formation and the commencement of carbonate crystallization, which led to clastic material to accommodate at the deposition site.

Regarding Sarıhıdır carbonates, U-Th dates of location 1 vary from 7.5 to 29 ka and those of location 2 are rather older and range from 66 to 82 ka within analytical errors. Location 3 from the Balkaya site yields U/Th ages in the range of 33 to 73 ka. Location 4 at this site gives a wide range of age data from 14.9 to 171 ka.

4.4. Rare earth element contents

Rare earth element + Y contents of studied travertine samples are shown in Table S5. Total REY of samples fall in a wide range from 176 to 23509 ppb. REY contents of Balkaya travertines (2.4 to 23.5 ppm) are significantly higher than those of Sarıhıdır travertines (0.2 to 2.1 ppm). REY patterns of both sample sets are 1 to 3 orders of magnitude lower than the PAAS (Post-Archean Australian Shale) values (Taylor and Mclennan, 1985) (Figure 4a). REY concentrations of Balkaya samples steeply descend from La to Y and continue with a nearly flat pattern across the HREEs. However, REY patterns of Sarıhıdır travertines maintain a horizontal position from La to Lu, except for a sharp positive Eu anomaly, which might be due to replacement of calcium by this element (e.g. Rankama and Sahama, 1950).

In the PAAS-normalized diagram, REY contents of Balkaya and Sarıhıdır travertines are compared to those of volcanic and granitoid rocks exposing in the region (Toksoy-Köksal et al., 2008). It is shown that host rocks with REY concentrations greater than travertines display a flat trend that slightly descends from La to Lu.

4.5. Stable isotopes

$\delta^{18}O$ and $\delta^{13}C$ values of Balkaya and Sarıhıdır samples are given in Table 2. Carbon isotope composition of Balkaya carbonates is in the range of 11.5 to 13.2‰ (VPDB) and those of Sarıhıdır carbonates varies from 8.7 to 11.0‰ (VPDB). Oxygen isotope values of Balkaya and Sarıhıdır samples are from -11.6 to -9.5‰ (VPDB) and from -16.2 to -11.6‰ (VPDB). The data indicate that carbon-oxygen isotope systematics of Balkaya samples are higher than Sarıhıdır carbonates.

5. Discussion

5.1. Origin of fossil fluid circulations

Carbon isotope compositions of Balkaya (11.5 to 13.2‰) and Sarıhıdır carbonates (8.7 to 11.0‰) yield similar ranges. These values are higher than the array suggested for the marine limestones (±3‰; Clark and Fritz, 1997) but within the range of meteogene fluids (–3 to +8‰; Pentecost, 2005). In a previous study by Karabacak et al. (2017), $\delta^{13}C$ values of Ihlara carbonates between the Hasandag volcano and Acıgöl Caldera are reported between 7.64

and 9.31‰, which are closely consistent with the values of carbonate veins from Balkaya and Sarıhıdır sites.

As shown from the $\delta^{13}C$ vs. $\delta^{18}O$ diagram (Figure 4b), the vein systems of Balkaya and Sarıhıdır sites, although nearly 10 km apart, are represented by different carbon-oxygen isotope systematics. For example, carbonate samples of locations 1 (r^2 = 0.99) and 2 (r^2 = 0.93) from the Sarıhıdır site show a very strong positive correlation. However, location 4 from the Balkaya area is characterized by a rather low correlation with r^2 = 0.61. Figure 4b also implies that heavy isotope enrichment of samples is not restricted only to carbon but also oxygen isotope. Previous studies show that travertines deposited during rapid CO_2 degassing resulting from seismic events are enriched in both ^{18}O and ^{13}C (e.g. Pentecost, 2005; Uysal et al., 2009; Yıldırım et al., in press). According to Ercan et al. (1995) and Güleç et al. (2002), mantle-derived He contributed to the thermal fluids in the central Anatolia is almost 35% of total helium inventory. Therefore, it is likely that volcanism is the major process accounting for the high volatile inventory of the fluids in this region. $\delta^{13}C$ values of fumaroles (CO_2 gas) emitting in central Anatolia (-1.9‰) fall in the range of limestones (Mutlu et al., 2018). The difference between carbon isotope values of fumaroles and travertines in the region is attributed to CO_2 degassing from hot springs, which resulted in carbon isotope fractionation. This gave rise to the participation of heavy carbon isotope (^{13}C) into carbonate phase and enrichment of light carbon isotope (^{12}C) in the gas phase. Precipitation from isotopically enriched waters explains the isotopically heavy character of the Balkaya and Sarıhıdır carbonates.

Unlike carbon isotopes, oxygen isotopes can be used to estimate the isotope composition and/or equilibrium temperature of waters that precipitated the carbonates (Friedman and

O'Neil, 1977). The temperatures of hot spring issuing in the Sarıhıdır site and a thermal water produced from a well drilled in the same area are 29^{0}C and 44^{0}C, respectively. Assuming that discharge temperatures of thermal waters in the region have not significantly changed in the studied time interval and using the oxygen isotopic fractionation between calcite and water ($\Delta^{18}O_{calcite-water}$) proposed by Kele et al. (2015), we calculated δ^{18}O values of waters that precipitated Balkaya and Sarıhıdır carbonate veins (Table S6). Oxygen isotope composition of fluids at 29^{0}C is found in the range of -16.0 to -11.2‰ (average: -13.8‰) for the Sarıhıdır samples and from -11.2 to -9.1‰ (average: -9.9‰) for the Balkaya samples. δ^{18}O values estimated at 44^{0}C are -12.9 to -8.1‰ (average: -10.3‰) and -8.1 to -5.9‰ (average: -6.7‰) for the respective fields. These values indicate a meteoric origin for the paleowaters.

Assessment of temporal variations in oxygen isotope systematics of Balkaya carbonate veins indicates a significant decrease around 133 ka BP (Figure 6 and Table 2). Nearly 2‰ decline of δ^{18}O is most probably due to meteoric water influx into the deposition site. It is driven either by a high rate of dilatation which increased the meteoric water component of fluids or by an enhanced rainfall event in the Eastern Mediterranean land and sea regions (e.g., Bar-Matthews et al., 2003).

Throughout the late Pleistocene, the Earth has experienced periods of glacial climate terminations (glacial-to-interglacial transitions) on both orbital and millennial time scales. The long term changes in orbital parameters have led to quasi-periodic fluctuations in the eccentricity, obliquity and precession of the equinoxes with frequencies at around 100, 41 and 19/23 ka BP, respectively (e.g. Milankovitch, 1941; Berger, 1978). These quasi-cycles are originated from astronomically driven changes in the latitudinal and seasonal distributions of the solar energy (Berger and Loutre, 2004). Among these cycles, those recurring every 100-ka are prominently recorded in atmospheric CO_2 from Vostok (Petit et al., 1999), benthic $\delta^{18}O$ from the ocean cores (Martinson et al., 1987; Cortijo et al., 1994), continental ice sheets in the Northern Hemisphere (Bender et al., 1994) and speleothems throughout the world (Bar-Matthews et al., 1997; 2003; Drysdale et al., 2009). These variations are widely accepted to control the commencement of late Pleistocene glacial terminations, which are found at 23, 139, 253, 345, 419, 546 and 632 ka BP (Schulz and Zeebe, 2006).

Termination II among others received intense research over the last two decades as high-resolution U-series dates became available on carbonate meterials for which radiocarbon dating method is only possible for the last 40-50 ka. Consequently, the beginning of Termination II was elaborated by a number of studies on speleothems and benthic carbonates (136 to 129 ka BP; Gallup et al., 2002; Landais et al., 2013). In these studies, $\delta^{18}O$ was reported to decrease during warmer (interglacial or interstadial) periods. An attempt is made here to compare oxygen isotope data on Balkaya carbonate veins with records of marine benthics (Lisiecki and Raymo, 2005), and speleothems of Soreq cave (Bar-Matthews et al., 2003), Antro del Corchia cave, (Drysdale et. al, 2005), Kesang cave (Cheng et al., 2012), Buraca Gloriosa cave (Denniston et al., 2018) (Figure 5). There is a striking similarity between isotope records of travertines and global benthic and cave compilations. This implies that $\delta^{18}O$ values of carbonates deposited under open air conditions are well correlated with those of marine and subterraneus carbonates and therefore they can be used as a proxy for the climate studies.

The diagram depicted in Figure 6 yields two shoulders of $\delta^{18}O$ decrease for the carbonate veins; the first is at 122.3 ka (sample G-3) and another clustering at around 133 ka (samples

E-2, F, G-1, G-2 and H-2). These negative anomalies are separated by a relatively cooler period at 130 ka represented by a 1‰ increase (sample D1). Our data indicate that the interglacial period which started at 133 ka BP proceeded only 3 ka and then demised at 130 ka BP. This was followed by a deglaciation with a duration of 8 ka (Figure 5). Interstadial reversals are common for the glacial Termination II. The lag periods between the interglacial periods are reported 1 ka to 10 ka (e.g. Schulz and Zeebe, 2006; Moseley et al., 2015).

Alternatively, high rate of dilatation is another mechanism responsible for depleted $\delta^{18}O$ values recorded in the Balkaya travertines. The $\delta^{18}O$ of meteoric waters is strongly latitude dependent and falls in the range of −2 to −20‰ (SMOW) (Craig, 1961; Kendall et al., 1995). It is reported that during major earthquakes stable isotope ratios measured in groundwater significantly changed which cannot be explained with water-rock interaction process (e.g. Claesson et al., 2004; Reddy and Nagabhushanam, 2012; Skelton et al., 2014). These changes are caused by crustal dilatation associated with stress build-up before the seismic event, which facilitated different groundwater components to mix. Although similar isotopic variations are not previously reported in areas of volcanic unrest, it is likely that crustal deformation or high rate of dilatation during the volcanic activity may increase the rate of mixing between thermogene and meteoric waters that precipitated the travertine deposits. To test this, we examine oxygen isotope compositions of mineral waters in the Gümüşkent area (nearly 20 km NW of study area). $\delta^{18}O$ values of Gümüşkent springs fall in the range of -10.5 to -9.71‰ (Afşin, 2002) which are consistent with the estimated average oxygen isotope composition of fluids (-9.92‰ at 29°C) that formed the Balkaya carbonate veins. These values are within the range proposed for meteoric waters. It is important to note that samples with high rate of dilatation have the lowest $\delta^{18}O$ values (–10,9‰ for sample G-1) (Table 2). Assuming that $\delta^{18}O$ of springs has remained unchanged in the studied time interval, there might be significant amount of cold water influx to the deposition site of Balkaya travertines. Although limited data available, among the samples witnessed high dilatation rate, G2 and H2 are characterized by notably low rare earth element compositions (Figure 4a). This might indicate rapid ascent of meteoric waters without sufficient interaction with the host rocks (Yıldırım et al., in press).

In regard to texture and crystal size, sample D1 (dated at 130 ka) from the Balkaya travertine shows quite different mineralogical features. This sample that does not contain any banding consists of calcites with different sizes (Figure S9). In this sample, needle-shaped small calcite crystals occur along the cracks (Figure S9). The remarkable heterogeneous crystallization indicates that the continuous fluid flow with high discharge rate resulted in carbonate deposition in a turbulent environment.

We conclude that although $\delta^{18}O$ values of Balkaya travertines fall in a relatively low range, they show similar trend to climate proxies preserved in different depositional environments throughout the world. If the climatic variations are neglected, this might indicate that studied carbonates were precipitated under similar fluid conditions (by means of origin and pathway) which are represented by high rate of dilatation followed by the invasion of meteoric waters. In other words, all the samples investigated are the manifestation of crustal deformation in the region.

5.2. Manifestation of paleo-eruptions on the carbonate veins

Current deformation of the Central Anatolia measured by GPS studies is not uniform (e.g., Aktuğ et al., 2013; Simao et al., 2016). In any case, however, a regional dilatation dominates despite variations in stress directions in the CAVP (Karabacak et al., 2017). Specifically, as shown by principle strain and horizontal velocity field analyses, a tension stress striking WNW-ESE is evident around Balkaya and Sarıhıdır sites (e.g., Aktuğ et al., 2013; Simao et al., 2016). Our field analyses show that both travertine sites set on the dilational jog area along the same fault zone (i.e. along the CKFZ with 10 km-distance) and all fractures in Balkaya and Sarıhıdır sites represent notable opening features (Mode I extension fractures). There are no slickenlines on their planes and no evidence for compressional tectonics. Thus, it is concluded that the fractures were formed under the tensile stress-normal trending NNE-SSW in Balkaya and NNW-SSE in Sarıhıdır. However, although carbonate veins in extensional fractures along the same fault zones indicate close-epicenter paleoearthquakes (Karabacak et al., 2019), vein precipitation periods favouring a temporary hydrothermal fluid circulation due to seismic unrest are completely different in both travertine sites. Consequently, it cannot be asserted that Sarıhıdır and Balkaya fractures are fully controlled by the regional dominant stress orientations and/or activity of CKFZ, i.e. it requires other mechanisms. One of the main reasons of Quaternary crustal deformation in the study area is the growth of magmatic crests and associated eruptions within a fairly close region (i.e. Acıgöl caldera and Erciyes stratovolcano). Therefore, it is possible to observe the manifestations of crustal deformations related to eruptive activity in the vicinity of study area.In the volcanic regions, pressure change at the tip of magma body results in shear and tensile failures or fluid pressurization (Rubin and Gillard, 1998; Azzarro, 1999; Glen and Ponce, 2002; Zobin, 2003) and the deformation produces three types of fractures around volcanoes, i.e. radial, cone sheet and ring types (Anderson, 1951). Inflation/deflation of magma chamber or volcanic spreading form σ3 in a radial pattern and generate extensional ring fractures (e.g. Anderson, 1951; Macdonald, 1972; Park, 1989; Borgia et al., 2014). This setting forms ideal deep penetrating pathways for fluid circulations during strain cycles. Thus, the extensional fracture systems aligned tangential to the volcanic conduits could present unique manifestations of syn-eruptive fluid circulations. For example, Karabacak et al. (2017) focused on two different fracture systems in the Ihlara site (central Anatolia) and indicated different fluid migration pathways for each. The dates of carbonates in each system are correlated well with the eruptive history of the Acıgöl caldera and Hasandag stratovolcano. Assessment of their data indicates that the formation of these fracture systems in the Ihlara site is controlled by various eruption centers where they are positioned tangentially. If we consider the geometric setting of the fracture systems, Balkaya and Sarıhıdır carbonate veins have positioned tangential to the Acıgöl caldera and Erciyes stratovolcano, respectively (Figure 6). Therefore, the correlation of the timing of carbonate precipitation with paleo-eruption records in CAVP may provide significant supplementary geochronological data.

Figure S10a-c displays the U-series age distribution of carbonate veins in the Balkaya and Sarıhıdır travertine sites. The age data indicate that the vein precipitations clustered in 3 major periods in last 190 ka (i.e. 5-35, 60-100, 120-170 ka BP) (Figure S10c). Accordingly, the crustal deformation intensified during 2 different periods at about 9, 82 ka BP in Sarıhıdır (Figure S10a) and during at least 7 different periods at about 15, 22, 73, 94-100, 119, 133, 145-150, 164 ka BP in Balkaya (Figure S10b). Carbonate vein from Location 4 in Balkaya also presents a detailed continuous precipitation record for the region (Figure S11a). Figure 6a displays the U-series ages with respect to distance from the vein center to the wall. If we order the coeval bands, the graph revolves to U-series age vs. the band widths (Figure S11b) and displays that the vein has 8 rapid dilatation periods at 15, 22, 67-73, 94-100, 119, 133, 145-155, and 164-171 ka BP coherent to picks of relative probability graph (Figure S10b).

Figure S10d displays the paleo-eruption dating records in CAVP for the last 190 ka compiled from the previous studies (Table S1). Results show that the eruptions took place across the region episodically in 3 major periods (i.e. 5-40, 75-115, 145-190 ka BP) are compatible with carbonate precipitations around Sarıhıdır and Balkaya (Figure S10c). Accordingly, each eruptive period in the CAVP lasted approximately 35-45 ka and is followed by an episode of volcanic unrest of around 30 ka. Comparison of the carbonate precipitation periods (i.e. intensified crustal deformation periods) with the eruption records in the surrounding area yields that there is a great affinity between the Sarıdır results and Erciyes eruptions and between the Balkaya results and Acıgöl eruptions. For example, Holocene eruption on Erciyes Stratovolcano of 8.8±0.6 ka BP (Sarıkaya et al., 2006; 2017) was recorded at Sarıhıdır carbonate veins (sample 04; 8.8±3.8 ka BP). Similarly, an eruption dated at 22.3±1.1 ka BP in the Acıgöl Caldera region (Karnıyarık cone, 24 km distant from Balkaya) (Schmitt vd., 2011) was almost perfectly recorded in the Balkaya site (sample B; 22.4±2.1 ka BP). Table 3 summarizes the results of U-Th ages of the carbonate veins respect to the timing of volcanic eruption events in the surrounding region.

6. Conclusions

In the volcanic regions, while pressure change of magma chamber generates extensional ring fractures forming ideal deep penetrating pathways for fluid circulations, the extensional fracture systems positioned tangentially to eruption centers could present manifestations of fluid circulations during volcanic strain cycles. In the suitable areas, thus, high flux of CO_2-rich fluid discharge precipitates syn-eruptive carbonate veins in the fractures. Here we propose a model, carbonate veins of the extensional fracture systems positioned tangentially to a volcanic conduit provide a substantial late Quaternary paleo-eruption record for that center (Figure 6).

$\delta^{18}O$ and $\delta^{13}C$ values of travertine sites of CAVP are within the range of meteogene fluids. The significant decrease in oxygen isotope values of Balkaya carbonate veins is likely due to meteoric water influx into the deposition site. It is driven either by a high rate of dilatation that increased the meteoric water component of fluids or by an enhanced rainfall event triggered by a change in the climate regime.

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Figure Captions

Figure 1. a. Generalized tectonic setting of the Anatolian Block (yellow arrows show the plate motions). b. Shaded relief map of the Central Anatolian Volcanic Province (generated using the WorldImagery data merged to SRTM-3arc-second resolution digital data) (black lines show the Quaternary faults, blue circles show

Neogene activity while the yellow circles show Quaternary activity on stratovolcanoes). B: Balkaya site, S: Sarıhıdır site, I: Ihlara site.

Figure 2. Geological setting of the study area and locations of the travertine sites (simplified from Köksal and Göncüoğlu, 1997; Koçyiğit and Doğan, 2016 and authors' field observations) (base map is taken from GoogleEarth). Red line indicates the trace of the faults.

Figure 3. A representative thin section from the carbonates (sample A-2, location 4, Balkaya). The discontinuities in between the bands (hiatus) are noticeable (yellow lines). Arrows show the elongation of calcite fabrics (red lines indicate microcrystalline, blue lines indicate macrocrystalline) (right image is cross-polarized, while the image at the left is plane-polarized). Note that, we drilled preferentially microcrystalline parts for dating.

Figure 4. a. PAAS normalized NTE+Y patterns of Balkaya and Sarıhıdır carbonate samples and host rocks (Taylor and Mclennan, 1985) (host rock data from Toksoy-Köksal et al., 2008). b. δ 18O vs. δ 13C systematics for Balkaya and Sarıhıdır carbonate samples (blue cross: location 1, red cross: location 2, red circle: location 3, blue circle: location 4).

Figure 5. Comparison of oxygen isotope data on Balkaya carbonate veins with various climate records. Marine benthic record (Lisiecki and Raymo, 2005), Soreq cave, Israel (Bar-Matthews et al., 2003), Antro del Corchia cave, Italy (Drysdale et. al, 2005), Buraca Gloriosa cave, Portugal (Denniston et al., 2018), Kesang cave, China (Cheng et al., 2012).

Figure 6. Model on correlations of carbonate veins with the paleo-eruption records in the meaning of fractural positioning to the eruption centers in CAVP. B: Balkaya travertine site, S: Sarıhıdır travertine site, I: Ihlara travertine site.

Table Captions

Table 1. The cycle of episodic carbonate vein (banded) precipitation in tectonically active areas: fluid-rock interaction (modified from Karabacak et al., 2019).

Table 2. Geochronologic and stable isotope data.

Table 3. Comparison between the carbonate ages investigated in the study area and the volcanic eruption events in the surrounding region from the literature.

Figures.

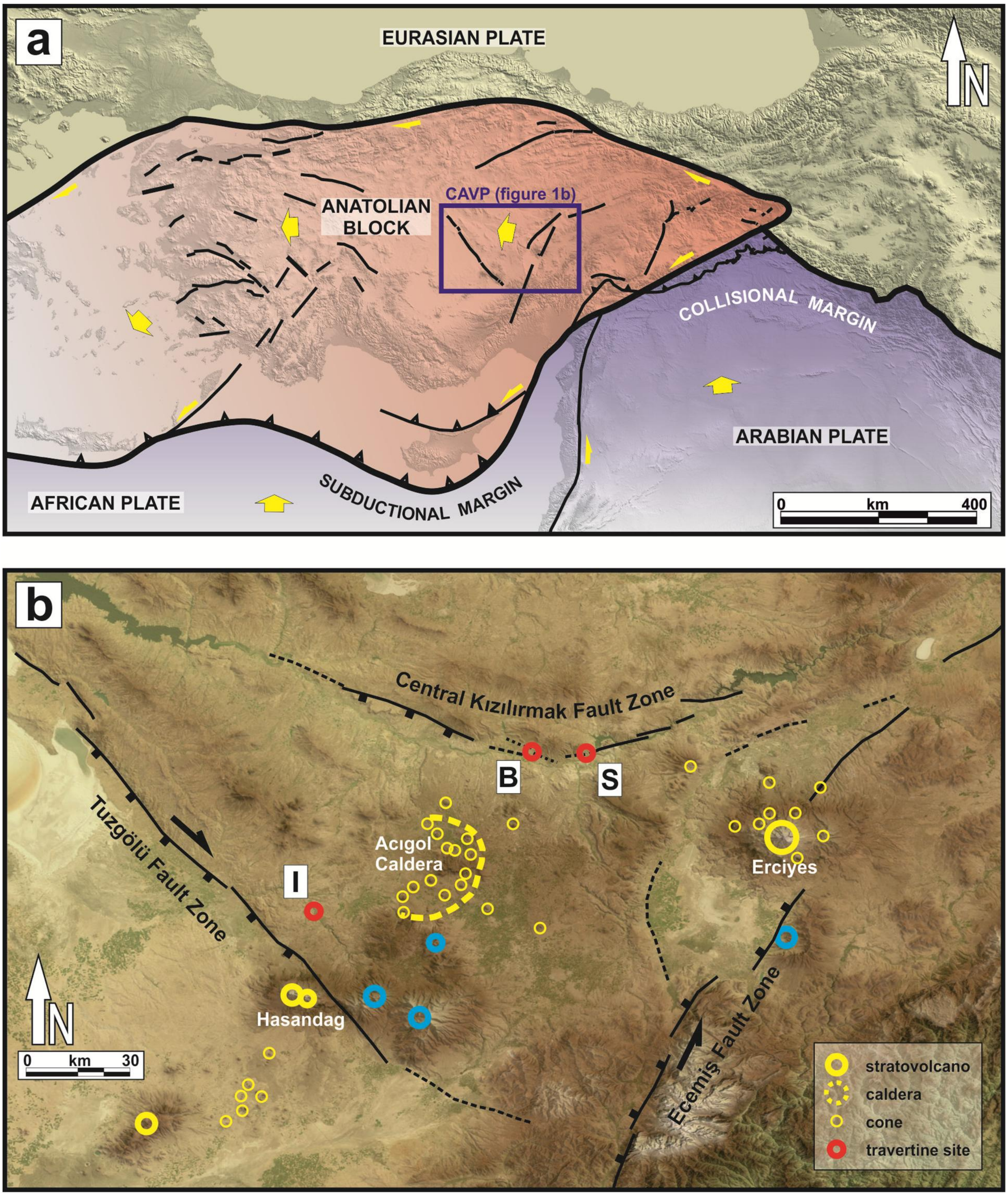
a
EURASIAN PLATE
ANATOLIAN BLOCK
CAVP (figure 1b)
COLLISIONAL MARGIN
ARABIAN PLATE
AFRICAN PLATE
SUBDUCTIONAL MARGIN
0 km 400
N
b
Central Kızılırmak Fault Zone
B
S
I
Tuzgölü Fault Zone
Acıgol Caldera
Erciyes
Hasandag
Ecemiş Fault Zone
0 km 30
N
stratovolcano
caldera
cone
travertine site

Figure 1

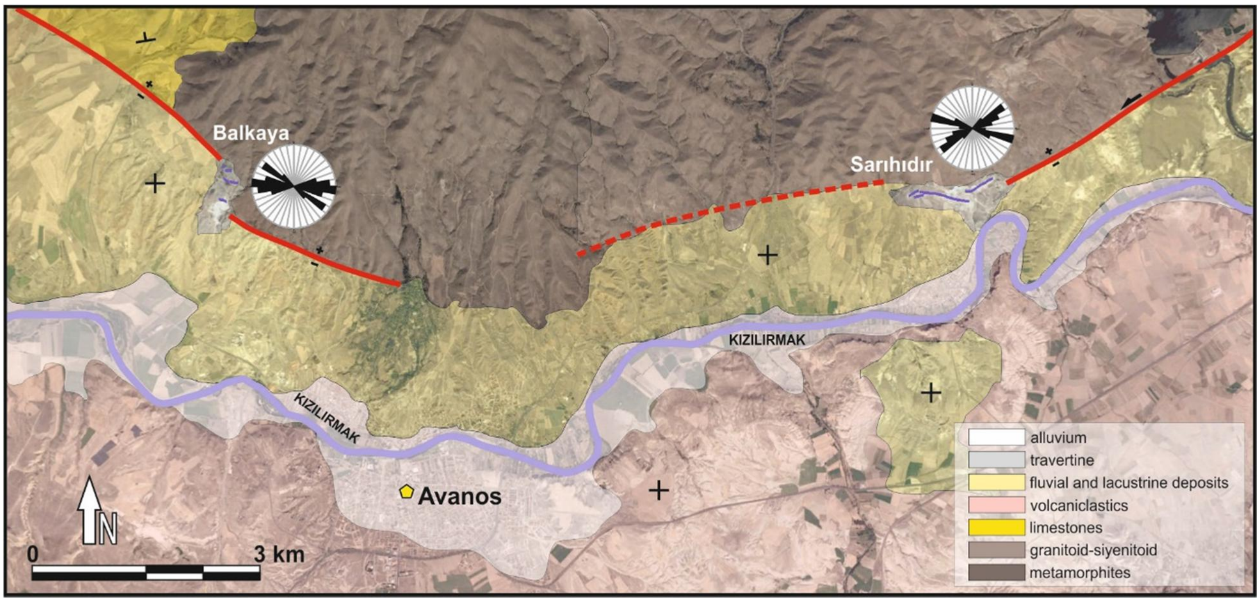
Balkaya
Sarıhıdır
KIZILIRMAK
KIZILIRMAK
Avanos
N
0
3 km
alluvium
travertine
fluvial and lacustrine deposits
volcaniclastics
limestones
granitoid-siyenitoid
metamorphites

Figure 2.

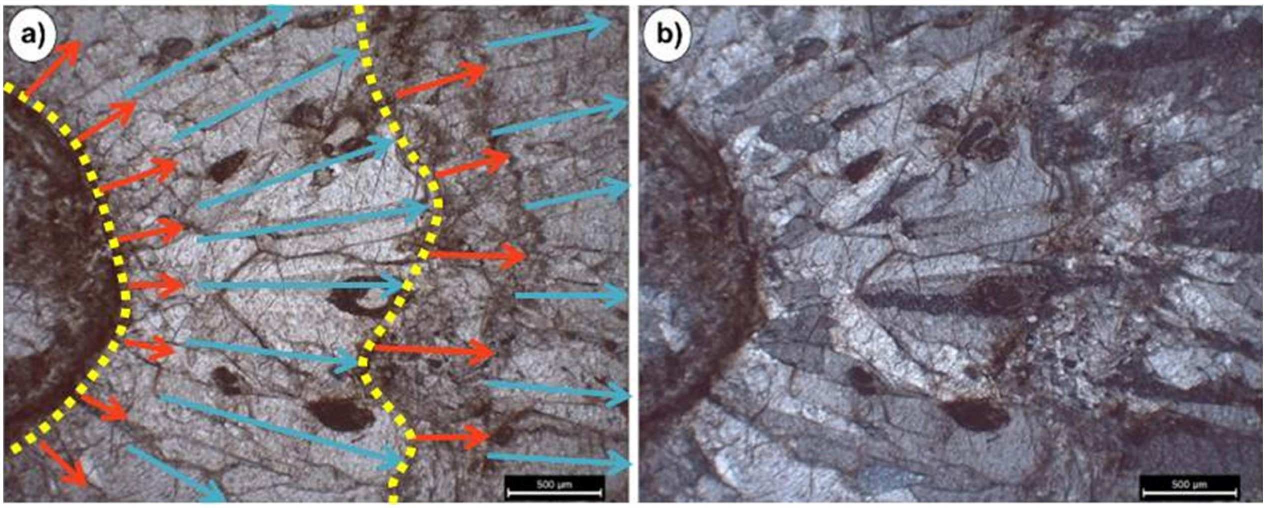

Figure 3.

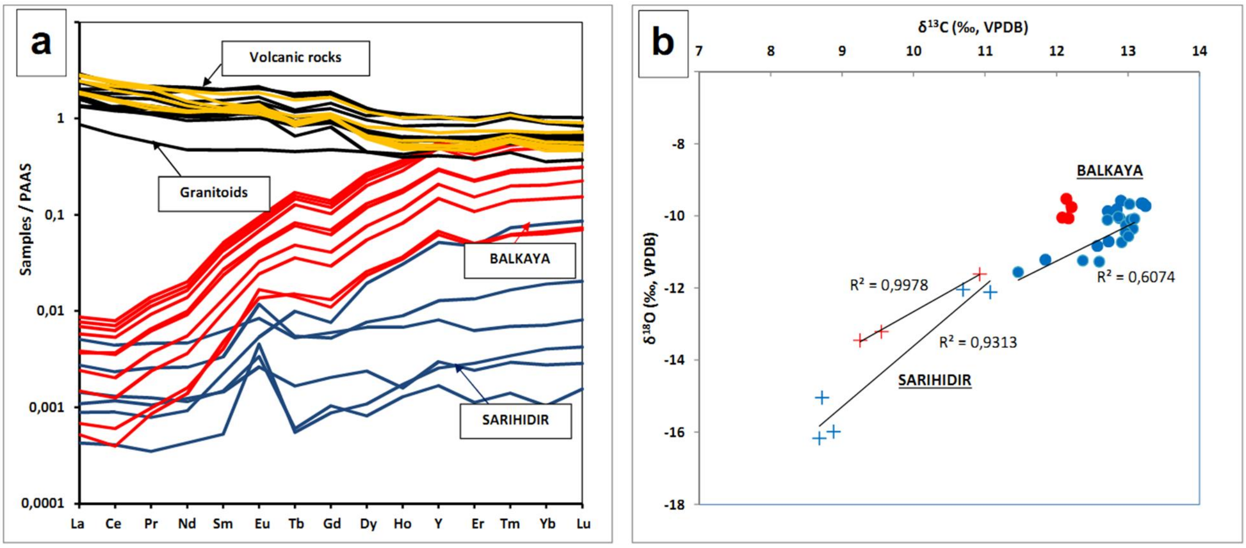
a
Volcanic rocks
Granitoids
BALKAYA
SARIHIDIR
Samples / PAAS
1
0,1
0,01
0,001
0,0001
La
Ce
Pr
Nd
Sm
Eu
Tb
Gd
Dy
Ho
Y
Er
Tm
Yb
Lu
b
δ13C (‰, VPDB)
δ18O (‰, VPDB)
BALKAYA
SARIHIDIR
R² = 0,9978
R² = 0,9313
R² = 0,6074
7
8
9
10
11
12
13
14
-8
-10
-12
-14
-16
-18

Figure 4.

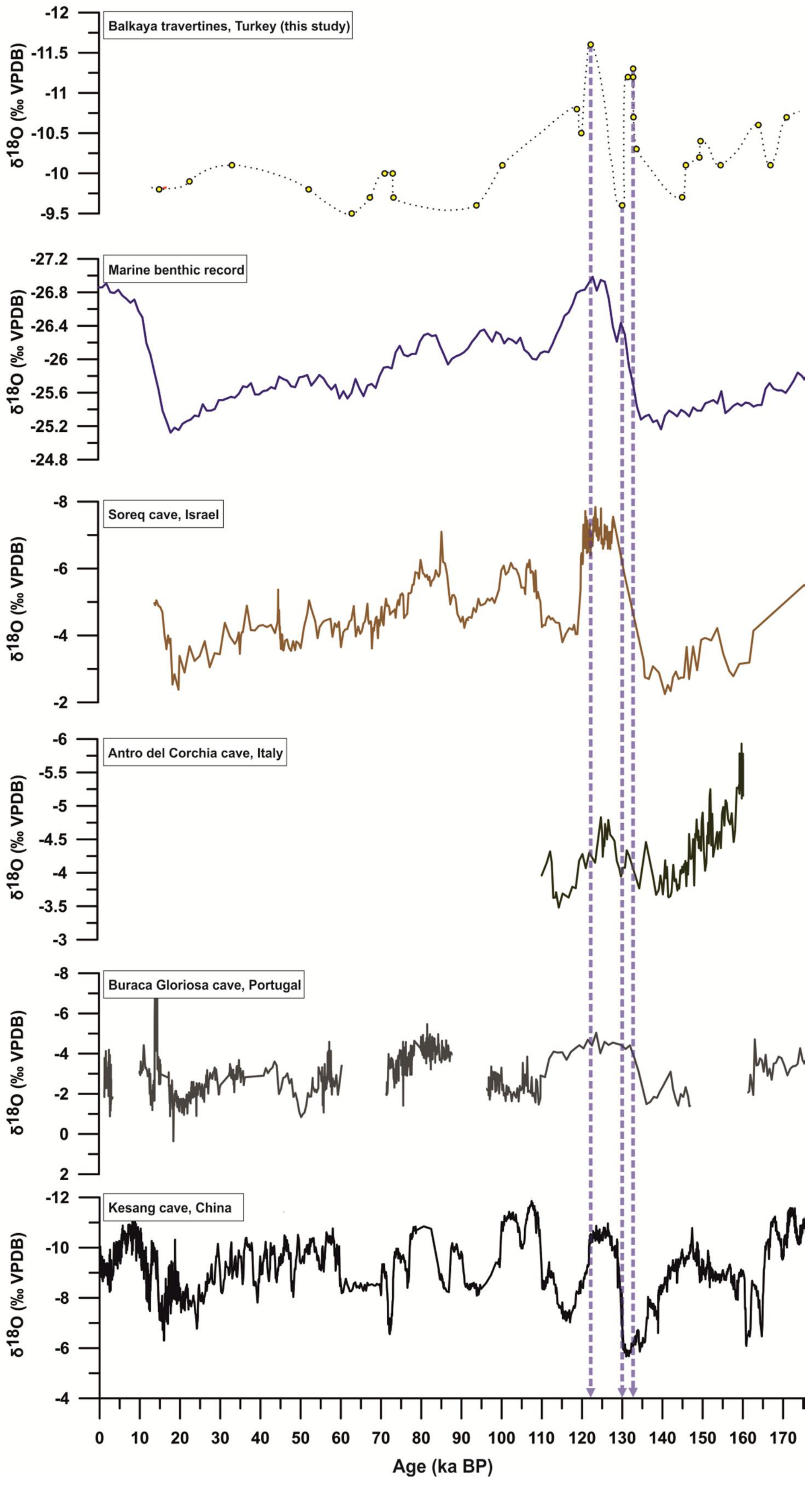
Balkaya travertines, Turkey (this study)
Marine benthic record
Soreq cave, Israel
Antro del Corchia cave, Italy
Buraca Gloriosa cave, Portugal
Kesang cave, China
δ18O (‰ VPDB)
Age (ka BP)

Figure 5.

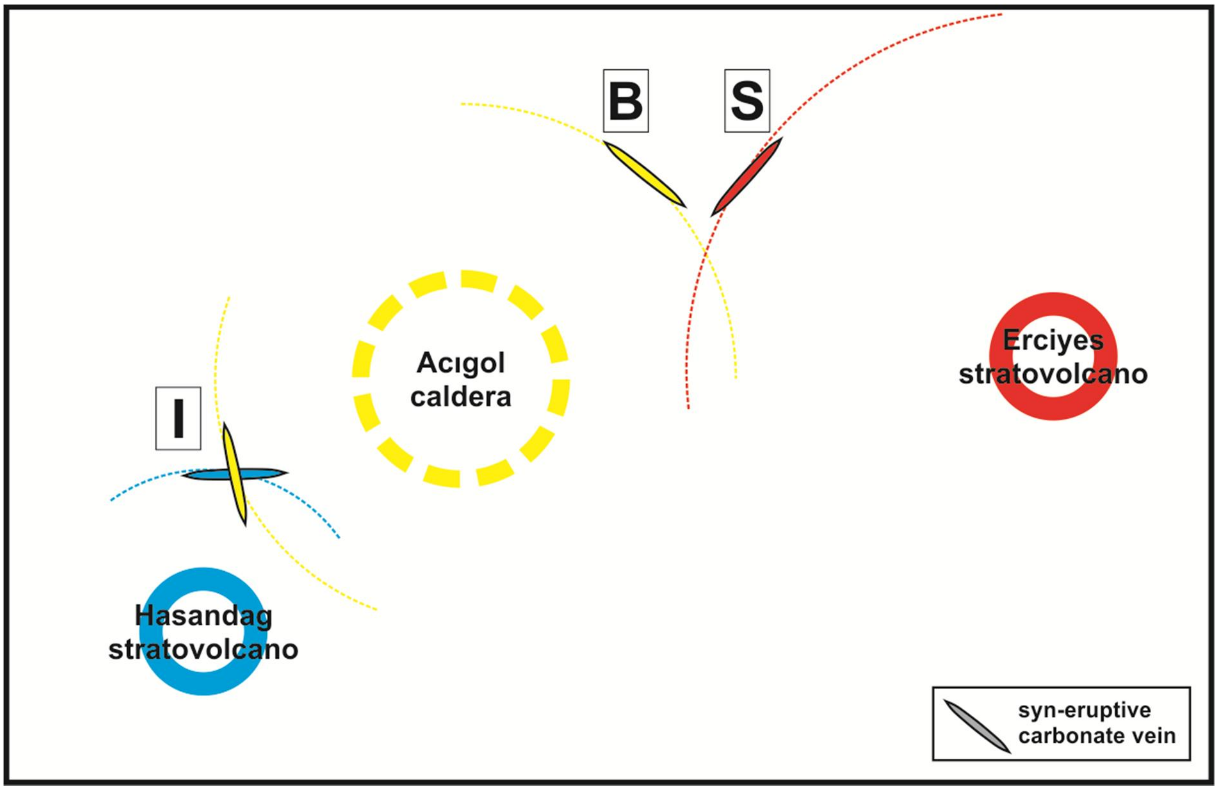
B
S
Acıgol
caldera
Erciyes
stratovolcano
I
Hasandag
stratovolcano
syn-eruptive
carbonate vein

Figure 6.

Table 1. The cycle of episodic carbonate vein (banded) precipitation in tectonically active areas: fluid-rock interaction (modified from Karabacak et al., 2019).

<table>
<tr><th>period</th><th>event</th><th colspan="2">result</th><th>evidence</th></tr>
<tr><td rowspan="2">coseismic</td><td>seismic release</td><td colspan="3">opening/reopening of fractures</td></tr>
<tr><td>simultaneous fluid circulation in fracture systems and expulsion of depressurized/supersaturated hot water</td><td rowspan="2">single carbonate band</td><td>rapid precipitation of banded carbonate on both walls of the fracture (planar)</td><td>whitish microcrystalline calcite that is related to abundant fluid inclusions with high-CO_2 degassing</td></tr>
<tr><td>postseismic</td><td>saturated but relatively slow fluid flow</td><td>plugging of the fracture along the carbonate vein</td><td>light-transparent macrocrystalline calcites that are precipitated at slow degassing rates during the time up to sealing</td></tr>
<tr><td>interseismic</td><td>unsaturated and slow fluid flow</td><td colspan="2">shifting spring points (pipes) along the sealed fracture</td><td>hiatus (no precipitation)</td></tr>
</table>

Table 2. Geochronologic and stable isotope data.

site	location	sample	corr. age (ka)	±2s	$\delta^{13}C$ (VPDB)	$\delta^{18}O$ (VPDB)	$\delta^{18}O$ (VSMOW)
SARIHIDIR	1	01	29	50	10,7	-12,0	18,5
		02	8,4	5,7	8,9	-16,0	14,5
		03	11,3	6,0	8,7	-15,0	15,5
		04	8,8	3,8	8,7	-16,2	14,3
		05	7,5	9,8	11,1	-12,1	18,4
	2	06-1	82	121	9,3	-13,4	17,1
		06-2	66	39	10,9	-11,6	18,9
		06-3	81	16	9,5	-13,2	17,3
BALKAYA	3	11A	52,1	8,4	12,2	-9,8	20,7
		11B	62,8	8,4	12,1	-9,5	21,0
		12C	33	10	12,2	-10,1	20,4
		12D	73	13	12,1	-10,0	20,5
	4	A-1	67,3	5,6	13,2	-9,7	20,8
		A-2	14,9	3,2	12,8	-9,8	20,7
		B	22,4	2,1	12,7	-9,9	20,6
		C-1	93,8	3,9	13,2	-9,6	20,9
		C-2	73,2	2,6	13,2	-9,7	20,8
		D-1	130,1	4,9	12,9	-9,6	20,9
		D-2	100,3	3,2	12,9	-10,1	20,4
		E--1	118,8	2,9	12,6	-10,8	19,7
		E--2	132,9	2,7	12,7	-10,7	19,8
		F	132,8	3,9	11,8	-11,2	19,3
		G-1	132,8	3,5	12,6	-11,3	19,2
		G-2	131,5	2,1	12,4	-11,2	19,3
		G-3	122,3	1,1	11,5	-11,6	18,9
		H-1	149,3	7,5	13,0	-10,2	20,3
		H-2	133,6	3,5	13,0	-10,3	20,2
		H-3	154,6	6,0	13,0	-10,1	20,4
		H-4	149,6	5,8	13,1	-10,4	20,1
		H-5	119,9	8,7	13,0	-10,5	20,0
		H-6	171	18	12,9	-10,7	19,8
		H-7	164	27	13,0	-10,6	19,9
		I-1	167	15	13,1	-10,1	20,4
		I-2	145	10	13,0	-9,7	20,8
		J-1	71	15	12,9	-10,0	20,5
		J-2	146	15	12,7	-10,1	20,4

Table 3. Comparison between the carbonate ages investigated in the study area and the volcanic eruption events in the surrounding region from the literature.

U-series age data of studied carbonates			volcanic events dated around the study area		
site	sample	corr. age (ka BP)	eruption date (ka BP)	eruption center and evidence	reference
BALKAYA	A-2	14,9±3,2	14	Acıgöl - sediment cores in the late Pleistocene Eski Acıgöl maar, tephra layer (radiocarbon)	Kuzucuoglu et al., 1998
			16	Acıgöl - Acıgöl maar (U-Th)	Roberts et al., 2001
	B	22,4±2,1	22,3±1,1	Acıgöl - Karnıyarık, rhyolitic lava nearly aphyric (U-Th/He)	Schmitt et al., 2011
	12c	33±10	32±3*	Acıgöl - south of Kocadağ (K-Ar)	Türkecan et al., 2004
	12d	73±13	75	Acıgöl – Taşkesik Hill, lava dome	Bigazzi et al., 1993
	C-2	73,2±2,6			
	C-1	93,8±3,9	93±2*	Acıgöl - Boğazköy (obsidian)	Türkecan et al., 2004
	D-2	100,3±3,2	96,0±13,0	Acıgöl - basaltic lava (Karnıyarık Hill) (Ar-Ar)	Doğan, 2011
	E-1	118,8±2,9	117±4	Acıgöl - Alacasar, rhyolitic pumice aphyric (U-Th/He)	Schmitt et al., 2011
	H-5	119,9±8,7			
	I-2	145±10	147±8*	Acıgöl – Taşkesik Hill, rhyolitic lava nearly aphyric (U-Th/He)	Schmitt et al., 2011
	J-2	146±15			
	H-1	149,3±7,5			
	H-4	149,6±5,8			
	H-7	164±27	163±7	Acıgöl - upper Acıgöl tuffs Boğazköy, rhyolitic pumice aphyric (U-Th/He)	Schmitt et al., 2011
	I-1	167±15			
SARIHIDIR	05	7,5±9,8	7,2±0,9	Erciyes - lava-flow (Karagüllü) (cosmogenic ^{36}Cl)	Sarıkaya et al., 2017
			7,7±0,4	Erciyes - lava-flow (Perikartın) (cosmogenic ^{36}Cl)	Sarıkaya et al., 2017
	02	8,4±5,7	8,8±0,6	Erciyes - lava-flow (Dikkartın) (cosmogenic ^{36}Cl)	Sarıkaya et al., 2017
	04	8,8±3,8			
	03	11,3±6,0	13±5	Erciyes - cinder cone basalt (K-Ar)	Doğan-Külahcı, 2015
	06-03	81±16	80±10	Erciyes - augite-hypersthene andesite, lava-flow (Karigtepe) (K-Ar)	Notsu et al., 1995
	06-01	82±121			

* the eruptions of Acıgöl caldera dated from carbonate veins of Ihlara travertine site (Karabacak et al., 2017).