

Editorial

# Editorial for Special Issue “Geochemistry of Travertines and Calcareous Tufas”

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Travertine and calcareous tufa are the lithological terms generally used to describe continental carbonates. They form in subaerial environments, located around groundwater seepages, springs, and along streams and rivers, via the precipitation of calcite/aragonite from waters that range in temperature from ambient to boiling [1]. These deposits exist across all continents, some of them are confined to small, local discharge aprons below spring emergences, whereas others cover extensive areas and form impressive structures (e.g., Tivoli in Italy, Pamukkale in Turkey, Mammoth Hot Springs in USA, Plitvice in Croatia). Travertine and calcareous tufa are complex systems, which are generally investigated using a multidisciplinary approach in order to elucidate the formation processes, environments, depositional models, and diagenesis. The multidisciplinary approach involves geochemistry (elemental and isotope compositions, dating), meso- and macro-scale morphological observations, mineralogy, petrography and sedimentology, and the analysis of biotic content. The active carbonate-depositing systems are natural laboratories, enabling the study of the geochemical characteristics of forming-travertine/tufa and their parental waters. Fossil deposits are important terrestrial archives that are capable of recording past climates, environmental changes, neotectonic activity, and hydrological–hydrothermal circulations. They indicate the possible locations of geothermal resources or contribute to the reconstruction of the carbon cycle.

This Special Issue, entitled “Geochemistry of travertines and calcareous tufas”, includes eleven contributions about travertine and calcareous tufa. The topics discussed included fossil and/or active deposits of natural or anthropogenic origin from three continents (Europe, Asia and America). These carbonate deposits were investigated using several geochemical methods, such as the determination of major and trace element composition, mineralogy, stable (oxygen, carbon, strontium) and clumped isotopes, and radioisotopes (radiocarbon, uranium series). In many cases, the geochemistry of the parental waters of the precipitating carbonates was also considered. Combining different geochemical methods with results from field survey and facies analysis, several contributions aim to determine the genesis of the deposits, the characteristics of the precipitating waters, and the relationship between carbonates and the geological/tectonic settings (Contributions 1, 5, 6, 7, 8, 9, 11). Some studies focus on the use of travertine as a paleoclimate record (Contributions 2, 6, 10), or as an indicator of geothermometric sequence, via the analysis of the Mg/Ca ratio (Contribution 4). With a different purpose, a study on clumped isotopes focuses on a methodological aspect regarding the use of this new technique on carbonate systems of anthropogenic origin (Contribution 3). The main features of these articles are reported in the summary below.

The paper of Porras-Toribio et al. (Contribution 1) investigates the laminated aragonite travertines currently precipitating from a high-temperature hot spring (70 °C) with active degassing on the coast of Tamiahua Lagoon (Mexico). The authors assess mineralogy and petrography, trace elements, stable isotopes (C, O, S) on carbonates, elemental sulfur, and sulphates, as well as the chemical (major and trace elements) and isotopic characterization



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of freshwater and hydrothermal fluids. The authors conclude that aragonitic travertines are generated by CO<sub>2</sub> and H<sub>2</sub>S emanations of deep origin and by oxidation–reduction reactions that are linked to surficial bacterial activity.

The paper of Li et al. (Contribution 2) presents detailed petrographic and mineralogical observations, stable C and O isotopes, and U/Th dating of a travertine dam from Zabuye Salt Lake, which is a semi-dry salt lake located in the southwest of the Tibetan Plateau (China). This study tries to explain the precipitation sequence of Zabuye Salt Lake over the last 800 years (1191–1982 AD), suggesting that travertine might record the evolution of meteoric paleo-precipitation (paleo-monsoon) on a decadal–centennial scale at least.

The paper of Holdsworth et al. (Contribution 3) investigates the clumped isotope values recorded in anthropogenic tufa from high-pH (>10), hydroxylation-related carbonates sampled in northeast England. The authors present the test results of these human-derived carbonates as an archive for evaluating the impact of kinetic fractionations on  $\Delta 47$ .

The paper of Auqué et al. (Contribution 4) focused on the utility of the Mg/Ca elemental ratio of calcite as a temperature indicator in continental carbonates. Recent tufa stromatolite records from four rivers on the Iberian Peninsula are selected for trace element analysis based on six-monthly sampling. The authors report that the seasonal variations in mineralogy, stable isotopes (C and O) of carbonate and water, and hydrochemistry offered the opportunity to decipher the behavior of Mg/Ca ratio in the continental carbonates. The authors concluded that the wide variety of parameters that are involved in the (Mg/Ca)<sub>calcite</sub> limit it as a geochemical thermometer in continental sedimentary environments.

The paper of You et al. (Contribution 5) investigates the lithofacies and stable carbon and oxygen isotopic compositions of banded travertines sampled from the fissure ridge of Xiagei (southwestern China) in order to examine their formation mechanisms. The parental CO<sub>2</sub> and the paleotemperature are determined, and two lithofacies are recognized. The latter show distinct calculated paleotemperatures, suggesting that temperature is a non-negligible control factor in the deposition of the two types of travertines, with important implication for paleo-environment studies.

The paper of Lv et al. (Contribution 6) investigates the Jiuzhaigou calcareous tufa deposit, located at a high altitude (about 2200 m a.s.l.) in the eastern margin of the Tibetan Plateau (China); the study is focused on a profile recently that was exposed by an Mw 7.0 earthquake that occurred in the region on 8 August 2018. Mineralogy, petrography, major/trace element content, stable isotope composition, and radiocarbon dating allow the authors to investigate the origin of this deposit, its paleoclimate significance, and its relationship with the seismic activity of the region.

The paper of Lu et al. (Contribution 7) studies a travertine mound from Sobcha, a high-altitude deposit (about 4700 m a.s.l.) in central Tibet (China). The Sobcha travertines are fossil deposits, but modern hot springs, with alkaline pH and deficient in Ca<sup>2+</sup>, are still present near the studied deposit. Using stable isotopes (C, O, Sr), trace elements including the rare-earth elements (REE), U/Th dating, mineralogy, and petrography, the authors reconstruct the genesis, the paleofluid source(s), and fluid evolution of this deposit.

The paper of Deev et al. (Contribution 8) studies the travertine cements that occur within the zones of active faults bordering two intramontane basin in the Gorny Altay area (Russia). The authors present results for petrography and mineralogy, major and trace elements including REE, stable C and O isotopes. They also perform U/Th dating on carbonates and analyze major and trace elements and stable O and H of present-day waters. Combining the results of their analyses, the authors discuss the origins of paleofluid, the factors influencing the precipitation of calcite and aragonite, the relationship of travertine formation with paleoearthquake and paleoclimate, the possibility of use travertine cement as important tool for paleoseismological research in seismically active regions.

The paper of Giustini and Brilli (Contribution 9) reviews the literature data available on the uranium content and <sup>234</sup>U/<sup>238</sup>U initial activity ratio of 15 travertine and calcareous tufa deposits found in Italy. Using a graphical method, data are interpreted considering the U geochemistry in natural environments as well as the geological, hydrogeological, and

hydrogeochemical features of each site. The paper discusses the factors that appears to affect the U content and  $^{234}\text{U}/^{238}\text{U}$  initial activity ratio in travertine and tufa, such as the availability of U in the aquifer rocks, the redox state of the waters, and the alpha-active radionuclide recoil phenomenon. The results suggest an interpretative model that might contribute to the paleo-environmental reconstruction of fossil travertine and calcareous tufa-depositing systems.

The paper of Brilli and Giustini (Contribution 10) investigates the stratigraphy of a buried travertine deposit, identified in a well at Prima Porta (north of Rome, Italy), using stable C and O isotopes, trace elements, and U/Th dating. The resulting isotope and chemical stratigraphy describe the temporal evolution of events that are correlated with global climatic variability. The authors reconstruct how paleoclimatic changes influenced the hydrological regime and indirectly altered tectonic activity by modulating the emission of deep  $\text{CO}_2$ , the chemistry of the groundwater, and ultimately the precipitation of travertine.

Using stable and clumped isotopes, U/Th dating of carbonates, and the isotopic composition of water sampled at active travertine spring mounds, the paper of Vieira et al. (Contribution 11) proposes a geochemical study of active and fossil travertine mounds found in several localities of Slovakia. The authors outline the age, origin, precipitation conditions, and temperature of these travertines, reconstructing the paleoclimate and paleo-environment during their deposition.

Overall, the contributions published in the Special Issue of *Minerals*, entitled “Geochemistry of travertines and calcareous tufas”, have confirm the ability of geochemical tracers to integrate and deepen the knowledge obtained from the geomorphological and sedimentological studies of travertine and calcareous tufa deposits. We are particularly pleased to present the contributions relating to the new clumped isotope technique and to the use of trace elements which, due to their behavioral complexity, have been outpaced over the years by the more easily interpretable conventional isotopes, with the idea being that “an intelligent application of complementary techniques is a powerful means of constraining the validity of competing theoretical options” [2].

As the Guest Editors of this Special Issue, we hope you enjoy reading these varied and excellent contributions. Our sincere thanks go to the *Minerals* staff for their help and guidance, and to all reviewers for their hard work.

**Conflicts of Interest:** The authors declare no conflicts of interest.

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