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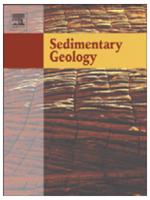

Origins of elements building travertine and tufa: New perspectives provided by isotopic and geochemical tracers

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ABSTRACT

Fluid/rock interaction represents a major process in the formation of calcitic or aragonitic travertine and tufa (CATT). In most cases, CATT is associated to limestone dissolution somewhere along the hydrogeological pathway. However, a wide array of other substratum (basalts, rhyolites, carbonatites, ultramafics, granites, dolomites, evaporites) can act as potential source of elements involved in the formation of CATT. This study reports on the evaluation of potential geochemical tracers linking CATT to their substratum, and unravelling the origin of elements. A large database was established from available literature data as well as new data acquired in the frame of this study for a set of Modern to Recent CATT (Ligurian ophiolites, Italy; the Chaine des Puys, Limagne graben and Paris Basin, France; Reunion Island, Indian Ocean; Jebel Oust, Tunisia). Four most reliable tracing methods are identified (1) $\delta^{13}C$ and $\delta^{18}O$ cross-plot allows distinguishing epigean (min$\delta^{13}C = -27.2$ ‰, max$\delta^{13}C = 0.9$ ‰, mean$\delta^{13}C = -12.3$ ‰ for $N = 314$) from hypogean systems (min$\delta^{13}C = -4$ ‰, max$\delta^{13}C = 11.7$ ‰, mean$\delta^{13}C = -2.87$ ‰ for $N = 198$). Very low $\delta^{13}C$ values (< -12 ‰) and $\delta^{18}O > -4$ ‰ associated to negative $\delta^{13}C$ values are specifically indicative of an ultramafic source rock. (2) Barium and strontium cross-plot helps to discriminate different groups of source rocks amongst the hypogean CATT: (i) source rocks composed of mixed limestones, evaporites, and dolomites are characterised by low barium (<100 ppm) and high strontium (>400 ppm) contents, (ii) mafic and granitic source rocks are undifferentiated and display similar barium (from 15 to 930 ppm) and high strontium (>200 ppm) contents, (iii) the carbonatite group is characterised by its exceptional high barium and strontium values. In epigean CATT, a pure limestone source rock usually relates to very low barium and strontium contents (<50 ppm and <70 ppm respectively), whereas mixed limestone, evaporite and dolomite source rocks generally display low strontium content (<580 ppm) with higher barium content (>50 ppm). (3) Relatively high beryllium content (>30 ppm) in CATT seems to indicate a pure granitoid source. (4) High chromium concentrations (>20 ppm) are systematically documented in Modern CATT located on an ultramafic substratum. The definition of diagnostic compositional fields for actively forming or recently formed CATT is influenced by many factors including water composition, water temperature, dissolved gas composition and concentration, biological activity, position in the sedimentary body and early diagenesis, in addition to substratum lithology. However, the results of this study illustrate that, despite these many factors, the combined use of Ba, Sr, Be, Cr, $\delta^{13}C$, and $\delta^{18}O$ may be valuable to discriminate the rock lithology prevailing in the hydrogeological or palaeo-hydrogeological reservoir of CATT.

1. Introduction

Travertine and tufa are continental carbonate deposits frequently associated with limestone dissolution in superficial (epigean) or deep (hypogean) hydrogeological reservoirs (Fouke et al., 2000; Garnett et al., 2004; Ihlenfeld et al., 2003; Gandin & Capezzuoli, 2008; Kele et al., 2011; Koltai et al., 2012; Makhnach et al., 2004). However, a large variety of other rocks can occur as substratum and source of elements building these carbonates. In Modern and Ancient environments, many studies have shown that igneous rocks (basalts, rhyolites, carbonatites, ultramafics, syenites, granites) and other sedimentary rocks (dolomites, evaporites, marls) may constitute derivative sources for calcium and other elements required for travertine and tufa build-up. Such derivative contributions are generally easy to identify in Modern systems where source rocks are usually known and where fluids (gas and water) can be analysed (Fouke et al., 2000; Crossey et al.,

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2009). On the other hand, it is more difficult to identify and demonstrate the contribution of a non-calcareous supplier in fossil travertine and tufa systems, especially when the lithology of the surrounding or underlying reservoir is poorly known. In such fossil cases, parent fluids of travertine and tufa cannot be analysed. Only primary fluid inclusions preserved in primary calcitic precipitates may provide information on the nature of original fluids (El Desouky et al., 2015). In the last decade, one of the most debated cases has been the deeply buried Lower Cretaceous travertine-like deposits occurring in the South Atlantic, off-shore Brazil, Angola and Congo (Della Porta, 2015; Wright & Barnett, 2015; Harris et al., 2013; Wright, 2012). These deposits belong to the so-called Presalt deposits and are composed of non-marine carbonates accumulated in a rift to post-rift context, on top of rocks of variable nature including ultramafics, basalts, volcaniclastic deposits, lacustrine limestones, claystones and marls (Jones & Xiao, 2013). In this complex buried fossil system, wells rarely reach the underlying substratum of the travertine deposits and numerous hypotheses may be made regarding the lithological origin of the elements used for travertine building.

A number of multidisciplinary studies have been performed since the 70s to characterise processes leading to travertine and tufa deposition (Pola et al., 2014). These studies show that tufa and travertine macro-/microfacies are not always characteristic of the lithologies prevailing in their hydrogeological basin. In fossil situations, macro/microfacies features, mineralogical evidences, plant remains, fossils and sedimentary architectures are sometimes available to constrain factors such as cold or hot waters (Pentecost, 2005), presence of gas bubbles (Chafetz et al., 1991) and hyperalkaline waters (Barnes et al., 1982). But these factors depend much more on the nature of hydrogeological processes, *i.e.* epigean versus hypogean (Lopez et al., in press), than the lithologies involved in the system. Sedimentological and structural approaches are usually used to unravel the processes at stake. Potentially, geochemical tracers could help to. However, studies on major, trace and rare-earth element concentrations in travertine and tufa deposits are largely lacking.

The aim of our study was therefore to establish a geochemical database by compiling major, minor, trace elements and stable isotope concentrations for Modern/Recent travertines and tufas. Our investigation was limited to very young (<50.000 years B.P.) active and inactive deposits in order to avoid late diagenetic over-print. Travertine and tufa have been considered according to the nomenclature of Capezzuoli et al. (2014). According to these authors travertine deposits are related to abiotic processes, and characterised by high depositional rates (cm to m/yrs), calcitic to aragonitic mineralogy and elevated $\delta^{13}C$ signature (>-1 ‰), whereas tufa deposits are linked to biotic processes, and typified by low depositional rates (mm to cm/yrs), mainly calcitic mineralogy and low $\delta^{13}C$ signature (<0 ‰). Capezzuoli et al. (2014) emphasise the uncertainties regarding the interpretation of coeval deposits in cooled thermal waters, where tufa-like deposits are precipitating. Only Modern to Recent calcitic and aragonitic travertine and tufa, here referred as CATT, containing more than 90% $CaCO_3$ were taken into account. Travertine-like siliceous deposits of sinter settings were excluded. The reported database includes data from published literature and new data acquired as part of this research work. The later includes analysed Modern and Recent non-marine CATT derived from the alteration of rocks with various lithologies (ultramafic, mafic, granite, evaporite, limestone) located in the Ligurian ophiolites (Italy), the Chaîne des Puys (France), the Limagne graben (France), the Paris Basin (France), Réunion Island (Indian Ocean) and the Jebel Oust (Tunisia). Each of these occurrences has been classified according to geological setting and investigated for specific geochemical tracers that may help identify the substratum rocks forming the hydrogeological basins of the studied CATT systems. The term “Modern CATT” will be used below as a simplification for currently active or inactive young (Recent) CATT.

2. Geological settings

2.1. Voltri Massif of the Ligurian ophiolites (Italy)

The Voltri Massif in the Ligurian Alps is located in the southernmost part of the Western Alps and to the north of the Apennines system. According to Brouwer et al. (2002), the Voltri Massif represents the relict of a subducted and exhumed lithosphere associated to the Piedmont-Ligurian Ocean, as part of the Mesozoic Tethyan realm. This ophiolitic body is described as the largest of the Alp-Apennine system and is composed of three main units (Chavagnac et al., 2013a,b; Borghini et al., 2007; Hermann et al., 2000; Hoogerduijn Strating, 1991; Fig. 1(A)): (1) a metasediments and metavolcanics unit (Voltri-Rossiglione Unit); (2) a serpentinite unit with highly altered peridotite (Beigua Unit); and (3) a serpentinised lherzolite and harzburgite unit (Erro-Tobbio Unit). Several hyperalkaline springs with travertine deposits have been reported in the Voltri Massif (Chavagnac et al., 2013a,b; Schwarzenbach et al., 2013; Cipolli et al., 2004). The hyperalkaline waters originate from percolation of meteoric water through fractures and water/rock interaction with ultramafic rocks. The travertine precipitation process is described as being related to atmospheric CO_2 uptake and neutralisation of the hyperalkaline waters (Chavagnac et al., 2013a,b).

The spring/travertine systems studied here are mainly located in the Beigua Unit, but near the contact with the Voltri-Rossiglione Unit (Fig. 1(A) and Table 1). One exception is the Gorzente spring/travertine system, which is located directly on lherzolithes of the Erro-Tobbio unit. These springs are always associated to fractures in the bedrock. Field measurements show high pH values (up to 11.2 at Acquasanta and Rio Branaga; Table 1) and low water temperatures ranging from 13 to 23.7 °C. Several authors highlighted high calcium, sodium, and abiotic methane contents associated to low silica and transition metal contents in these waters (Chavagnac et al., 2013b; Boulart et al., 2013; Cipolli et al., 2004; Schwarzenbach, 2013). Also, alkalinity measurements show low values (0.91 to 2.99 meq/l). The carbonate precipitate consists mainly of thin calcium carbonate crusts with micro-terracettes that form relatively small travertine bodies on the ultramafic bedrocks (Fig. 2(A), (B)).

2.2. Réunion Island (Indian Ocean)

The Réunion Island is located in the western Indian Ocean, 700 km east of Madagascar. The island constitutes the subaerial part of an oceanic shield volcano, and is composed of two volcanoes: the dormant Piton des Neiges and the active Piton de la Fournaise. The central part of the Piton des Neiges exhibits three major depressions (Fig. 1(B)) referred to as the cirques of Cilaos, Mafate and Salazie and originating from collapses, landslides and intense erosion (Oehler et al., 2008). Frissant et al. (2003) highlighted the presence of different volcanic units (Fig. 1(B)). The most common volcanic rocks are composed of olivine basalts showing zeolitisation features (Demange et al., 1989). The edge of the three cirques also shows basalts, hawaiites and mugearites, whilst the bottom part locally exhibits trachytic deposits, gabbros, and syenitic intrusive bodies (Frissant et al., 2003).

Thermal springs in the Réunion Island mainly occur in the Salazie and Cilaos cirques, within a few kilometres around the highest point of the island. Some of them are associated with CATT, reported in several studies (Frissant et al., 2003, 2004; Marty et al., 1993; Rançon et al., 1988) but never studied regarding their petrography or geochemistry. In contrast, hydrochemistry of the thermal waters and associated gas has been well documented in studies dealing with volcanology, hydrochemistry, and geothermal energy (Frissant et al., 2003; Moulin et al., 2002; Join & Coudray, 1997; Kluska, 1997; Marty et al., 1993; Demange et al., 1989).

CATT analysed in the present study come from three thermal springs located in the Cilaos cirque and two in the Salazie cirque (Table 1, Fig. 1(B)). These thermal springs are often located in association with