Calcareous Tufa

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The term calcareous tufa, or freshwater travertine, is widely used in the scientific literature to describe carbonate deposits precipitated from cool groundwaters of meteoric origin enriched in CO_2 (carbon dioxide) by percolating through organic soils.

calcareous tufa climate change ground thermal gradient

1. Calcareous Tufa

The term calcareous tufa, or freshwater travertine, is widely used in the scientific literature to describe carbonate deposits precipitated from cool groundwaters of meteoric origin enriched in CO_2 (carbon dioxide) by percolating through organic soils and, therefore, capable of attacking $CaCO_3$ (calcium carbonate) in limestone aquifers and dissolving it as Ca $(HCO_3)_2$ (calcium bicarbonate) according to the equation: [1]

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca + (HCO_3)_2$$

Calcareous tufa deposits form from the degassing of carbon dioxide and related shifting of the above equation induced by flowing water turbulence and the photosynthetic process by vegetal organisms typical of aquatic environments such as bacteria, blue-green algae, and mosses whose remnants are usually present in the deposit structure [1][2][3] together with fossil fauna such as ostracods and mollusk shells [4][5]. Similar in origin to calcareous tufa are cave speleothems [6]. Carbonate deposits precipitated from geothermal waters highly enriched with concentrations of CO_2 are called thermogene travertines [6] or, more simply, travertines [7]. Calcareous tufa deposition has taken place in various environmental conditions since the earliest geological times [6], even though most deposits are referred to the Middle-Upper Pleistocene and Holocene ([8][9][10][11] and references therein).

2. Calcareous Tufa Deposition/Erosion and the $CaCO_3 \cdot CO_2 \cdot H_2O$ System

The dissolution rate of $CaCO_3$ in water is very low [12]. However, if the solution includes some CO_2, $CaCO_3$ is easily dissolved as $Ca(HCO_3)_2$. The dissolved free carbon dioxide (not combined in the previous equation) is called equilibrium CO_2 [13]: With concentrations of dissolved CO_2 lower than the equilibrium values, precipitation of $CaCO_3$ will occur, while with higher concentrations, further dissolution of CaCO3 will be possible. The carbon dioxide concentration above the equilibrium value is called independent CO_2 [12].

The solubility of $CaCO_3$ in water directly depends on the partial pressure of CO_2 in the surrounding atmosphere [14][15]. It is very low in the open air but strongly increases in soils, where the partial pressure of CO_2 produced by biological processes and the decay of organic matter can attain values up to 1000 times higher than in the atmosphere [16]. The temperature also controls the CO_2 solubility: Water at 0 °C dissolves CO_2 about three times more than at 30 °C [12]. Then, the water reaches the phreatic zone where the only sources of additional CO_2, apart from a possible endogenous supply, is from the oxidation of minor amounts of transported organic matter or bacterial activity [17]. However, in such conditions, the total amount of CO_2 may be considered practically constant, but the relative amounts of free CO_2 (equilibrium plus independent CO_2) and combined CO_2 (to form $CaCO_3$ and $Ca(HCO_3)_{2)}$ may change with variations of pressure and temperature. In a closed system, free CO_2 may also be derived from the mixture of solutions saturated with different concentrations of $CaCO_3$ [18].

Several factors may cause $CaCO_3$ precipitation [6][8]: Lower partial pressure of CO_2 at the groundwater emergence, increasing groundwater temperature at the emergence, consumption of CO_2 by aquatic plants, loss of dissolved CO_2 (degassing) induced by turbulence and pulverization of stream waters at waterfalls, breaks, and roughness reaches of the river profile, even at a great distance from the spring [19][20].

3. Types of Calcareous Tufa

Calcareous tufa may be divided into two main groups: autochthonous tufa, deriving from in situ encrusted organisms, and allochthonous tufa, consisting of phytoclasts (encrusted fragments of plants) arenitic (microdetrital facies) and ruditic (macrodetrital facies) in size [21][22][23][24][25]. Based on the sedimentary facies, autochthonous tufa may be distinguished:

- stromatolithic tufa, including sequences of laminae (usually 1–10 mm in thickness) formed during short depositional intervals characterized by the presence of particular encrusting microorganisms (**Figure 1**);
- microhermal tufa, consisting of strata lens whose fabric reveals the structure of constructing organisms (usually mosses or algae) encrusted in growth position;
- phytohermal tufa, exhibiting a layered/lensoid organization similar to microhermal tufa but larger and composed of large, encrusted plants, usually mosses, reeds, and other phanerogams (**Figure 2** and **Figure 3**).

Figure 1. Stratified stromatolithic tufa in the upper basin of the Esino River (Marche, Italy).

Figure 2. Plant remains encrusted in phytohermal tufa at the Romanatt dam (Tigray, Ethiopia).

Figure 3. Phytohermal tufa at Romanatt Dam (Tigray, Ethiopia).

Allochthonous tufa deposits have a typical clastic texture with fragments of incrustations on vegetal organisms sometimes providing information (e.g., clast orientation, imbrication, etc.) about their transporting flow. Fragments with an irregularly laminated cortex of calcium carbonate, often characterized by a spheroidal to oblate shape and usually referred to as oncoids [26], are common components of allochthonous tufa deposited in streams, rivers, and lakes. Pedley [24] attributes the spheroid shapes of grains to high competence flow, the elongated shapes to slow flow, and the irregular shapes to calm waters.

Clastic fragments cemented by calcareous tufa are sometimes found inside terraced alluvial or slope deposits. They form mainly in the first stages of tufa deposition [27].

Following Choquette and Pray [28], the porosity of calcareous tufa limestone may be distinguished into non-fabric porosity (produced by fracturing, karstic dissolution, and burrowing invertebrates) and fabric porosity.

Depending upon the cohesion between the constituting crystals, calcareous tufa deposits range from soft and chalky to dense and highly indurated [6].

Tufa deposits are affected by meteoric diagenesis soon after deposition when exposed at the surface and by burial diagenesis when overlain by more recent thick sediments [6][25][29].

The principal changes caused by meteoric diagenesis are related to the dissolution/precipitation of calcium carbonate (void filling, cementation) induced by percolating rainwater or groundwater; other diagenetic effects are recrystallization, microbial micritization, bioturbation, oxidation of organic matter and sparmicritization, a term introduced by Kahle [30] to describe the etching action of microorganisms at or near the tufa surface [6]. Burial diagenetic effects resulting from increased lithostatic and hydrostatic pressure, heating, and the ingress of mineral-enriched solutions include compaction and porosity reduction resulting from further cementation, dissolution of the original fabric, sometimes with replacement by other minerals, and reactions between the original carbonate component and accessory minerals [6].

The original differences in porosity combined with those due to diagenesis make the permeability of tufa deposits extremely variable.

4. Calcareous Tufa Deposits and Landforms

The deposition of calcareous tufa may give rise to construction landforms such as small mounds at springs and dams across the riverbeds or coatings of steep slopes, rough river beds, or swamp/lake bottoms generally lacking a recognizable shape [6][31][32]. These features are geologically not durable as the construction process can be interrupted, and landforms can be destroyed, in whole or in part, by erosion [6]. Bedding within the deposit, where present, is usually inclined and undulated and rarely horizontal; thin laminations resulting from daily/seasonal variations are often recognizable [6].

Slope deposits essentially consist of wedge-shaped, layered bodies of microhermal tufa locally passing to stromatolithic tufa with minor intercalations of phytoclastic tufa. Calcareous tufa systems may develop either along slopes forming wedge-shaped sedimentary bodies with the thickest accumulation downstream and transforming the original water flow into a system of hanging channels, low barrages, ponds, and terraces, or across rivers giving rise to dams with pools or larger basins on their backside [6][22].

Dams are the showiest construction bodies of calcareous tufa (**Figure 4**). They may reach heights up to several tens of meters in correspondence with breaks or obstructions of riverbeds that reduce erosion by flowing water, thus allowing $CaCO_3$ precipitation [6][33][34][35]. These features mainly consist of massive phytohermal tufa encrusted on a skeleton made of remnants of vegetal organisms. In addition to growing upward, the aggradation of tufa progrades onward, forming sub-vertical layers unconformably covering the earlier deposits, including those of the basin down valley (**Figure 4**) [21][24][36]. On the backside of dams, water basins form (ranging in size from small pools to vast lacustrine basins) whose bottom hosts tufa sands (deriving from dismantling tufa deposits upstream), phytoclastic tufa, and stromatolithic tufa, interspersed with clayey sediments and peaty layers (**Figure 5**) [1][21][24][33][34][37].

Figure 4. The imposing Holocene tufa dam of May Makden in Tigray (northern Ethiopian Highlands).

Figure 5. The backfill deposits of the May Makden tufa dam: a complex sequence of stromatolithic tufa levels, lacustrine clay, peat, alluvial gravels, and buried soils testifying repeated aggradation/erosion phases.

Dams and backside pools usually follow one another along the watercourse forming characteristic depositional systems (**Figure 6**) [6][21][24].

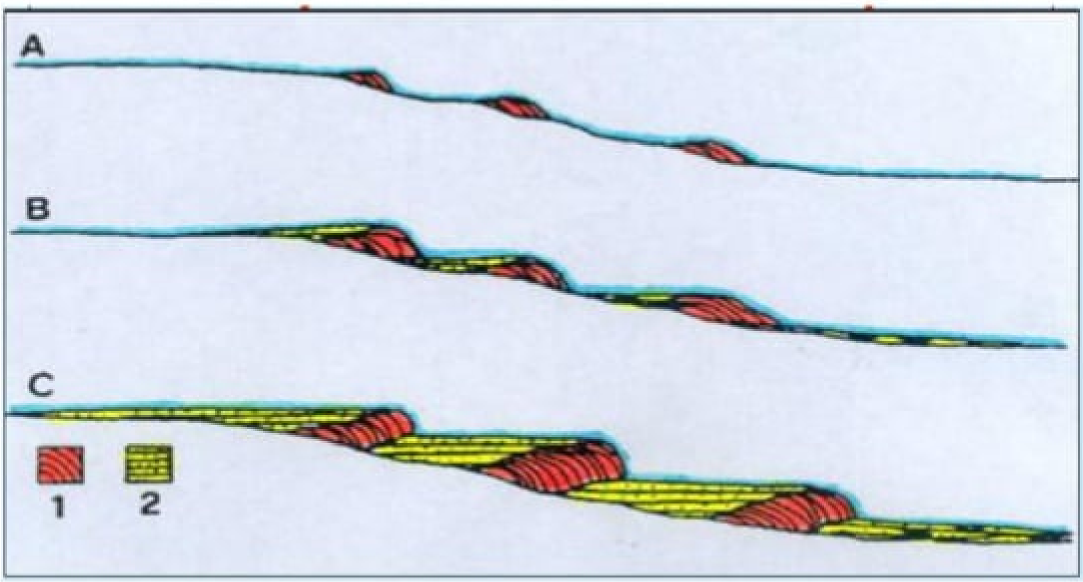

Figure 6. Evolutionary scheme (from initial phase A to final phase C) of tufa dams and backside pools along a watercourse: 1. phytohermal tufa; 2. stromatolithic and phytoclastic tufa.

The growth of tufa dams occurs where the deposition rate of calcium carbonate from water is high enough to balance the streamflow erosion [38].

In correspondence with significantly high steps in the riverbed profile, dams often fail to grow due to the erosion exerted by rapid water flow, and the deposition of tufa mainly progresses downstream from the tufa dam, giving rise to a “cascade tufa” deposits (**Figure 7**) [6].

Figure 7. Cascade tufa overlying Mesozoic limestone in the upper Esino River basin (Central Italy).

5. Factors Controlling Calcareous Tufa Deposition/Erosion

There is general agreement in referring the development of calcareous tufa to climatic causes [6][8][39][40][41].

Warm climates are believed to favor calcareous tufa formation due to higher concentrations of biogenic CO_2 in soils [6][8][14][39][40][41][42][43][44][45] enhancing the dissolution rates of $CaCO_3$ [12] and increasing photosynthetic activity by aquatic plants [1][8][25][46]. Conversely, cold climates are considered less favorable because of the reduced biological activity of soils and the lesser development of aquatic plants [6][45].

Humid climates are generally considered favorable for tufa deposition by allowing abundant water infiltration and emergence, enhancing the development of vegetation covers and related biogenic processes in the soils, and promoting the growth of aquatic plants. This is contrary to dry climates where there is a scarcity of rainwater and a consequent general reduction in water circulating in the ground and discharging at springs. However, delayed responses to climate aridification of deep aquifers reached by river incision may locally result in tufa deposition, even during dry periods [47][48].

An explanatory model for the alternating periods of tufa deposition/erosion during geological times refers to the variations of thermal gradient induced in the bedrock by significant climate changes [56 (https://www.mdpi.com/2076-3417/13/7/4410#B49- applsci-13-04410)]. Due to the low thermal conductivity of bedrock [57], major climatic changes to warmer conditions, such as the rapid increase in air temperature at the Late Pleistocene-Holocene transition, induce significant thermal contrasts between the surface and the ground and reverse thermal gradients in the deep limestone aquifers. With climate warming, the infiltration water, made highly acidic when crossing the soil due to the elevated partial pressure of biogenic CO_2 present therein, percolating through the progressively colder levels of the aquifer, causes relevant dissolution of $CaCO_3$ [14], higher than in normal conditions. At the emergence, because of the higher surface temperatures, the groundwater loses CO_2, becomes oversaturated with $CaCO_3$ and produces tufa deposition, even at a great distance from the spring, favored by the running water turbulence, photosynthetic activity of mosses and algae, and evaporation of spray droplets. Opposite effects, such as deposition of dissolved carbonate in the upper bedrock layers and the emergence of aggressive spring waters undersaturated with $CaCO_3$, are expected to occur with major climatic changes to cold conditions [11].

In all conditions, tectonics strongly influences tufa deposition by opening waterways in fractured rocks and giving rise to fault steps across rivers, thus favoring the growth of tufa dams [49].

References

1. Hynes, H.B.N. The Ecology of Running Waters; University Press: Liverpool, UK, 1978; p. 378.
2. Chafetz, H.S.; Folk, R.L. Travertines: Depositional morphology and bacterial constructed constituents. J. Sediment. Petrol. 1984, 54, 289–316.
3. Pentecost, A. Moss growth and travertine deposition: The significance of photosynthesis, evaporation and degassing of carbon dioxide. J. Bryol. 1996, 19, 229–234.
4. Preece, R.C.; Robinson, J.E. Molluscan and ostracod faunas from Post-glacial tufaceous deposits in County Offaly. Proc. R. Ir. Acad. Sect. B Biol. Geol. Chem. Sci. 1982, 82B, 115–131.
5. Krolopp, E. The importance of mollusc fauna in the study of travertine deposits. Földtany Közlöny 2003, 134, 219–225.
6. Pentecost, A. Travertine; Springer-Verlag: Berlin, Germany, 2005; p. 445.
7. Gandin, A.; Capezzuoli, E. Travertine versus calcareous tufa: Distinctive petrologic features and stable isotopes analysis. Alp. Mediterr. Quat. 2008, 21, 2125–2136.
8. Gullentops, F.; Mullenders, W. Age et formation de dépôts de tuf calcaire Holocène en Belgique. In Proceedings of the Symposium International de Géomorphologie, Liège, Belgium, 29 June–4 July 1969.
9. Goudie, A.S.; Viles, H.A.; Pentecost, A. The late-Holocene tufa decline in Europe. Holocene 1993, 3, 181–186.

10. Frank, N.; Braum, M.; Hambach, U.; Mangini, A.; Wagner, G. Warm period growth of travertine during last Interglaciation in Southern Germany. Quat. Res. 2000, 54, 38–48.
11. Fubelli, G.; Soligo, M.; Tuccimei, P.; Bonasera, M.; Dramis, F. Calcareous tufa deposition in connection with Late Pleistocene abrupt warming events. J. Ecol. Nat. Resour. 2021, 5, 000236.
12. Schoeller, H. Les Eaux Souterraines; Masson and Cie: Paris, France, 1962; p. 642.
13. Tillmans, J. Die Chemische Untersuchung von Wasser und Abwasser, 2nd ed.; Wilhelm Knapp: Halle, Germany, 1932; Volume 1, p. 252.
14. Atkinson, T.C. Carbon dioxide in the atmosphere of the unsaturated zone: An important control of hardness in limestones. J. Hydrol. 1977, 35, 111–123.
15. Drake, J.J. The effect of soil activity on the chemistry of carbonate groundwaters. Water Resour. Res. 1980, 16, 381–386.
16. Roques, H. Observations physico-chemiques sur les eaux d alimentation de quelques concretions. Ann. Speleol. 1963, 18, 377–404.
17. Moore, G.W. Introduction to the origin of limestone caves. Natl. Speleol. Soc. Bull. 1960, 22, 3–4.
18. Bőgli, A. Mischungskorrosion-ein Beitrag zum Verkarstungs-problem. Erdlcunde 1964, 18, 83–92.
19. Merz-Preiss, M.; Riding, R. Cyanobacterial tufa calcification in two freshwater streams: Ambient environment, chemicalthresholds and biological processes. Sediment. Geol. 1999, 126, 103–124.
20. Dramis, F.; Fubelli, G.; Calderoni, G.; Esu, D. Holocene aggradation/degradation of tufa dams in northern Ethiopia and central Italy: A paleoclimatic comparison between East Africa and Mediterranean Europe. Z. Geomorphol. 2014, 58, 419–434.
21. Buccino, G.; D’Argenio, B.; Ferreri, B.; Brancaccio, L.; Ferreri, M.; Panichi CStanzione, D. I travertini della bassa valle del Tanagro (Campania). Studio geomorfologico, sedimentologico e geochimico. Boll. Della Soc. Geol. Ital. 1978, 97, 617–646.
22. D’Argenio, B.; Ferreri, V.; Stanzione, D.; Brancaccio, L.; Ferreri, M. I travertini di Pontecagnano (Campania) geomorfologia, sedimentologia, geochimica. Boll. Della Soc. Geol. Ital. 1983, 102, 123–136.
23. Ferreri, M. Criteri di analisi di facies e classificazione dei travertini pleistocenici dell’Italia meriodionale. Rend. Acc. Scienze. Fis. Mat. 1985, 52, 121–147.
24. Pedley, H.M. Classification and environmental models of cool fresh-water tufas. Sediment. Geol. 1990, 68, 143–154.
25. Golubic, S.; Violante, C.; Ferreri, V.; D’Argenio, B. Algal control and early diagenesis in Quaternary travertine formation (Rocchetta a Volturno, Central Apennines). Boll. Della Soc. Paleontol. Ital. 1993, 1, 231–247.

26. Riding, R. Classification of microbial carbonates. In Calcareous Algae and Stromatolites; Riding, R., Ed.; Springer: Berlin, Germany, 1991; pp. 21–51.
27. Gradzinski, M.; Jach, R.; Stworzewicz, E. Origin of calcite-cemented Holocene slope breccias from the Dluga Valley (the Western Tatra Mountains). Ann. Soc. Geol. Pol. 2001, 71, 105–113.
28. Choquette, P.N.; Pray, C. Geologic nomenclature and classification of porosity in sedimentary carbonates. Am. Assoc. Pet. Geol. Bull. 1970, 54, 207–250.
29. Rodríguez-Berriguete, A.; Alonso-Zarza, A.M.; Martín-García, R. Diagenesis of continental carbonate country rocks underlying surficial travertine spring deposits. Quat. Int. 2017, 437, 4–14.
30. Kahle, C.F. Origin of subaerial Holocene calcareous crusts: Role of algae, fungi and sparmicritization. Sedimentology 1977, 24, 413–435.
31. Julia, R. Travertines. In Carbonate Depositional Environments; Scholle, P.A., Bebout, D.G., Moore, C.H., Eds.; AAPG: Tulsa, OK, USA, 1983; pp. 64–72.
32. Viles, H.A.; Goudie, A.S. Tufas, travertines and allied carbonate deposits. Prog. Phys. Geogr. 1990, 14, 19–41.
33. Berakhi, O.; Brancaccio, L.; Calderoni, G.; Coltorti, M.; Dramis, F.; Umer, M. The Mai Maikden sedimentary sequence: A reference point for the environmental evolution of the Highlands of Northern Ethiopia. Geomorphology 1998, 23, 127–138.
34. Dramis, F.; Fubelli, G. Tufa dams in Tigray (Northern Ethiopia) as Late Pleistocene -Holocene climate proxies. In Landscapes and Landforms of Ethiopia; Billi, P., Ed.; Springer: Dordrecht, The Netherlands, 2015; pp. 201–211.
35. Golubic, S. Cyclic and non cyclic mechanism in the formation of travertine. Verh. Int. Ver. Limnol. 1969, 17, 956–961.
36. Calderoni, G.; Cilla, G.; Dramis, F.; Esu, D.; Magnatti, M.; Materazzi, M. La deposizione di travertino nelle aree prossimali dei fiumi Esino, Potenza e Chienti durante l’Olocene antico (Appennino Centrale Marchigiano). Quaternario 1996, 9, 481–492.
37. Dramis, F.; Mohamed, U.; Calderoni, G.; Mitiku, H. Holocene climate phases from buried soils in Tigray (northern Ethiopia): Comparison with lake level fluctuations in the Main Ethiopian Rift. Quat. Res. 2003, 60, 274–283.
38. Fubelli, G.; Dramis, F.; Calderoni, G.; Cilla, G.; Materazzi, M.; Mazzini, I.; Soligo, M. Holocene aggradation/erosion of a tufa dam at Triponzo (Central Italy). Geogr. Fis. Din. Quat. 2013, 36, 259–266.
39. Nicod, J. Facteurs physico-chimiques de 1’accumulation des formation travertineuses. Méditerranée 1986, 57, 161–164.

40. Weisrock, A. Variations climatiques et périodes de sédimentation carbonatée à l’holocène. L’âge des dépôts. Méditerranée 1986, 57, 165–167.
41. Pazdur, A.; Pazdur, M.F.; Starkel, L.; Szulc, J. Stable isotopes of Holocene calcareous tufa in southern Poland as paleoclimatic indicators. Quat. Res. 1988, 30, 177–189.
42. Brook, G.A.; Folkoff, M.E.; Box, E.O. A world model of soil carbon dioxide. Earh Surf. Processes Landf. 1983, 8, 79–88.
43. Hennig, G.J.; Grun, R.; Brunnacker, K. Speleothems, travertines and paleoclimates. Quat. Res. 1983, 20, 1–29.
44. Bonifay, E. Origine et age des formations travertineuses de la Vallee de l’Huveaune entre Roquevaire et Auriol (Bouches du Rhone). Méditerranée 1986, 57, 101–104.
45. Vaudour, J. Travertins holocenes et pression anthropique. Méditerranée 1986, 57, 165–167.
46. Allen, E.T. The agency of algae in the deposition of travertine and silica from thermal waters. Am. J. Sci. 1934, 28, 373–389.
47. Ordonez, S.; Gonzalez Martin, J.A.; Garda del Cura, M.A.; Pedley, H.M. Temperate and semi-arid tufas in the Pleistocene to recent fluvial barrage system in the Mediterranean area: The Ruidera Lakes Natural Park (Central Spain). Geomorphology 2005, 69, 332–350.
48. Viles, H.A.; Taylor, M.P.; Nicoll, K.; Neumann, S. Facies evidence of hydroclimatic regime shifts in tufa depositional sequences from the arid Naukluft Mountains, Namibia. Sediment. Geol. 2007, 195, 39–53.
49. Camuera, J.; Alonso-Zarza, A.M.; Rodriguez-Berriguete, A.; Melendez, A. Variations of fluvial tufa sub-environments in a tectonically active basin, Pleistocene Teruel Basin, NE Spain. Sedimentology 2012, 59, 502–526.