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# Geomicrobiological Properties and Processes of Travertine

With a Focus on Japanese Sites

 Springer

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# Preface

The best thing about being geologist is facing mysteries of nature during fieldwork. It is something like treasure hunting. That was 20 years ago when I saw a valley filled with light-yellow-colored sediments beside a hot spring. For a common Japanese geologist, I learned taking a bath after hard fieldwork. I was tired for serious mapping of carbonate rocks on a steep mountain slope and could enjoy the water with rich mineral precipitates and bubbling. This mysterious valley made me a deep impression, but it was 5 years later that I chose the travertine as my study subject. I needed time to grow my basic knowledge on chemistry and microbiology, which is necessary to unlock the mysteries of travertine. Also, I needed to find collaborators.

My fortune was to have three capable young researchers who contributed to this book as coauthors, namely, Tomoyo Okumura, Chizuru Takashima, and Fumito Shiraishi. Our research was somewhat abstruse but a motivational practice. We realized that it opens the door to a long road eventually to the birth of life and our planet. Travertine research is a practice of a new science that integrates geology, geochemistry, and microbiology. Travertine is a product from the interaction among activity in the Earth interior, material exchange in the surface environment, and metabolisms of primitive microbes.

We started our travertine research from the “yellow valley” and extended it to a number of intriguing travertine sites in Japan, and later in Indonesia. The results from fieldwork and laboratory work were already published in several papers that unlocked some of the mysteries of travertine. But it is only partly. Experiences and findings that we obtained through our 15-year research should be shared with scientists working with travertines and other related subjects. This is the motivation for writing this book.

Our study has been supported by a number of people. Seeking travertines across the Japanese Islands with Masako Hori is an unforgettable experience. Kouya Ito is the owner of Satono-yu who provided a perfect environment for our continuous observation in Nagayu Hot Spring. Harijoko Agun and Akmaluddin organized everything for fieldwork in Indonesia. Chiya Sugihara and Katsunori Yanagawa

also contributed to successful research in Indonesia. Yasuhiro Shibata and Hayami Ishisako provided technical supports that improve visualization of our research objectives. Our science was largely improved through the discussion with Gernot Arp, Brian Jones, Zaihua Liu, Kazue Tazaki, Yoshio Takahashi, Kiyotaka Ishida, Takeshi Naganuma, and Ken Takai. In addition, we deeply appreciate many students who joined the research on travertines.

We wish that this book can give a tip to young readers dealing with earth sciences and stimulate the research of travertines. We would continue our treasure hunting in *onsens*.

Bunkyo-ku, Japan

Akihiro Kano  
On behalf of the authors

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# Chapter 1

## Introduction



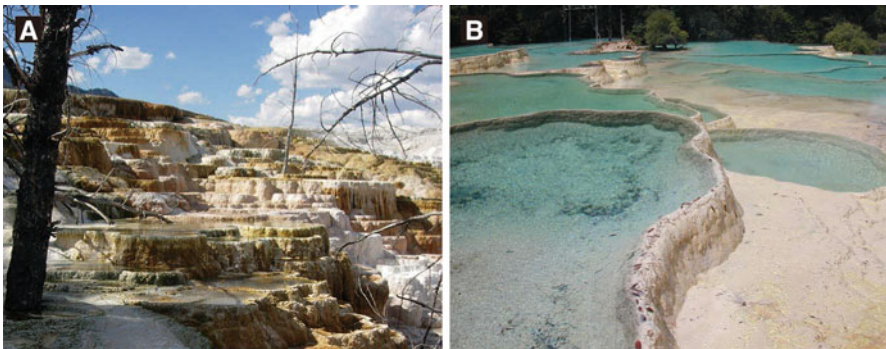
Stone of light yellow color, sometimes laminated and porous, is often found on wall material. The word travertine in general means such kind of limestone material. It was derived from *lapis tiburtinus* that means stone of Tivoli, an Italian town located 30 km east from Rome. Since Roman times, travertine has been used for popular stone material of buildings (e.g., *Colosseum*), sculpture, and tombs because the stone is relatively light, massive, and easy for cutting work. The stone material is still actively produced in many countries such as Italy and Slovenia and exported all over the world. Almost everybody has seen the travertine. However, it is much less known what the origin and formational processes are of this particular kind of stone.

In the central lobby of the Japanese Diet Building, we can find pinkish carbonate rock called “Onyx Marble” that was mined from Toyama Prefecture in central Japan. The building was completed in 1936, using a number of stone materials that were collected from different places within the Japanese islands. The Onyx Marble was selected as material of main columns of elevator hall (Fig. 1.1a). In petrologic definition, it is not marble, i.e., metamorphosed limestone. Its mesoscopic lamination (Fig. 1.1b) and its microscopic fabrics, such as a cedar-tree structure, are indicative for travertine as its origin. However, nobody has cared about the origin of the Onyx Marble until recently. It was in 2016 when the first scientific investigation with supportive isotopic data was done for the Onyx Marble. Kubo (2016) demonstrated that it was a travertine. The Onyx Marble has been consolidated to dense stone material through cementation and compaction for millions of years.

People can witness what a travertine is through tourism. Some modern travertine localities are attractive scenic sites, such as the World Heritage Sites at Pamukkale in Turkey, Mammoth hot springs in the United States of America (USA), and Huanglong in southwestern China where extensive and long-term formation of travertine develops beautiful terraced landscapes (Fig. 1.2). These scenic sites occurring in deep forests are currently prepared for tourists to access easily. Millions of people visit these sites every year and enjoy sharp contrasts between pure white of the travertine deposits, sky blue of the water pools, and green of the forests. These travertine scenic sites are tremendous features resulted from interaction among



**Fig. 1.1** “Onyx Marble” in the Japanese Diet Building. (a) Elevator hall. (b) Closeup image of a column showing laminated texture. (Image was provided by Kitaniippon Newspaper Co. Ltd.)



**Fig. 1.2** Two representative travertine sites. (a) Mammoth hot springs in Yellowstone National Park, USA. (b) Huanglong in Sichuan province, southwestern China

geochemical, physical, and microbial processes in a unique hydrochemistry of water that is highly supersaturated with respect to calcium carbonate. However, only few people visiting there really know how such scenic site has been developed.

In our definition, the term travertine is the calcium carbonate deposit formed from spring water in hydrothermal settings, which is similar with one of Ford and Pedley (1996). However, several definitions for the term *travertine* can be found in the literature. Travertine, tufa, and calcareous sinter were used for describing the hydrothermal carbonate precipitates of a similar origin. Although Pia (1933) advocated the use of the term sinter for all abiotic hydrothermal deposits, sinter has been usually restricted for the spring deposits consisting of silica (e.g., Ford 1989). Therefore, using of calcareous sinter for carbonate deposit is not recommended to avoid confusion (Jones and Renaut 2010).

Differentiation between *travertine* and *tufa* is more problematic. The term, *tufa*, was derived from *tophus* in Roman language describing crumbly whitish deposit and has been preferably used by British scientists, in a wider term of calcareous nonmarine deposits of various origins. In contrast, *travertine* has been used in central-southern European and the United States and often extended to non-hydrothermal carbonates (Pentecost 1995). Therefore, attention should be paid for terminology when we read the papers referring terrestrial carbonate deposits. At present, there is no absolute consensus on the usage of these terms, but some scientists become advocated to the definition of Ford and Pedley (1996) and Pedley et al. (2003); the precipitates from cool (in ambient temperature) water are defined as *tufas*, while ones from hot spring water (above ambient temperature) are defined as *travertines*. Following these studies, we use the term *tufa* for carbonate deposit formed from non-thermogenic water in riverine, lacustrine, and spring settings.

There has been the long historical identification of travertine over 2000 years, and geologists in the early nineteenth century have already mentioned the hydrothermal origin for travertine. However, scientific investigation has started much later because theoretical understanding for the travertine process postdated to the establishment of chemical principle for the carbonate reaction in the 1950s. In this sense, one of the leading countries for the travertine study is Japan where the hydrothermal settings are extensively developed. Travertine is called *Sekkai-ka* in Japanese, which means flower (or coloring) made of calcium carbonate. Studies of mineralogy and chemical systems of *Sekkai-ka* have been reported since the 1960s. Yasushi Kitano (1962, 1963) in Nagoya University was a pioneer. His geochemical works demonstrated basic processes and factors controlling the precipitation of calcium carbonate and travertine mineralogy, which are still valid in many recent studies. Kitano's works that stimulated studies of the Japanese *Sekkai-ka* have been studied with various scopes such as chemistry (Kitano et al. 1971; Ichikuni and Kikuchi 1972; Ichikuni 1973; Sakai et al. 1983; Furuhashi et al. 2008), biomineralization (e.g., Tazaki 1995; Tashiro and Tazaki 1999; Yasuda et al. 2000; Kawano and Obokata 2007), mineralogy (Nakadate and Fujita 1984; Nakadate 1986; Ito 1993; Ueno et al. 2008; Hirano et al. 2009), and analog for CO<sub>2</sub> underground sequestration (Sasaki et al. 2009).

Following the pioneer studies in Japan, Italy (Folk et al. 1985), and the United States (Friedman 1970), researches on travertine have expanded in many fields including isotopic chemistry, kinetics of carbonate chemistry, mineralogy, sedimentology, tectonic chronology, paleoclimatology, and geomicrobiology. In Chap. 2, we explain the basic geochemical principles of travertine formation, along the route of hydrothermal water, from the volcanic heat source to the site of active travertine formation. Explanation is extended to stable isotope and mineralogical polymorphism, two long-standing subjects that have not fully understood. Relatively high  $\delta^{13}\text{C}$  and low  $\delta^{18}\text{O}$  signatures can differentiate the travertines from the other terrestrial carbonate deposits, such as tufas. These characteristics fit well to the basic processes noted in Chap. 2. Despite the rapid precipitation of carbonate, travertine and water hold nearly equilibrate relationship in both  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$ . In this context, the isotopic compositions of travertine can be signatures indicating paleoenvironments. However, some travertines clearly bring non-equilibrium

isotopic signature. We note brief consideration for a possible interpretation for this isotopic non-equilibrium. Travertine study seems to have a suitable objective which is to specify the controlling factor for  $\text{CaCO}_3$  polymorphs (calcite and aragonite) because the travertine environment covers a wide range of water temperature,  $\text{Mg}^{2+}/\text{Ca}^{2+}$  ratio, and  $p\text{CO}_2$ . However, this problem is not straightforward (Jones 2017).

As products of carbonate mineral, travertines often show particular morphologies and fabrics. In Chap. 3, we describe these unique fabrics with terms, such as paper-thin rafts, coated bubbles (Guo and Riding 1998), shrubs, dendrites (Jones and Renaut 2008), and spherulites (Verrecchia et al. 1995). Because of the common occurrence of some of these fabrics, microbial carbonate including travertines can be a modern analog for the extensive reservoir rock of the Presalt oil field in deep below the seafloor of the Brazilian offshore (Wright 2012). Increasing energy demand encouraged researchers to identify geological, textural, and geochemical characteristics of travertines (Pedley and Rogerson 2010; Brasier 2011; Capezzuoli et al. 2014; Pola et al. 2014; Gradzinski et al. 2014; Croci et al. 2016; Claes et al. 2017).

In the later part of this book, we present important outcomes from what we have investigated in our laboratories in the last two decades. Because we recognize that travertines are products from interaction of geological, physical, chemical, and microbiological processes, comprehensive understanding of its formational processes requires a wide range of analyses with different scales of viewpoints. We briefly review analytical methods of travertine studies adopted in our research group in Chap. 4. Scientific understanding and knowledge on travertine has improved rapidly as reviewed by Pentecost (2005), and the improvement has been accelerated in the last decades owing to development of analytical methods.

Some travertines show regular lamination that is visible on a hand specimen. The laminations are often daily associated with daily metabolic cycle of biofilm developed on the travertine surface (e.g., Takashima and Kano 2008; Okumura et al. 2013). This is the topic presented in Chap. 5 and probably the most important result from our own works. The laminations of travertine show different types of texture likely due to hydrological, mineralogical, and microbiological properties. These travertines can be regarded as a laminated type of microbialites, i.e., stromatolites. Modern stromatolites and travertines are largely different in depositional textures and processes; however, some laminations in the modern travertines resemble the fabrics observed in geological material including the Archean-Proterozoic stromatolites that are significant archives of microbial communities and seawater chemistry in the early Earth. We here raise a question, “are they modern analogs for the ancient stromatolites?”

In our studies of the laminated travertine, we made substantial analyses for microbes that form biofilm on the travertine surface. Microbial communities developed on the travertine surface are highly variable due to the geochemical conditions (pH, Eh, and  $\text{Ca}^{2+}$  concentration) along the water pathway where the travertine is

deposited (Fouke 2011; Sugihara et al. 2016). This is the consequence of travertine-forming hot spring water that is initially high in partial  $\text{CO}_2$  pressure and almost deficient in dissolved oxygen and of gas exchange with the atmosphere after the spring water discharge. The rapid precipitation of carbonate crystals rapidly renews the travertine surface, on which a biofilm-forming microbial community adapts to the specific conditions. Therefore, travertine can be regarded as a natural culture substratum that preserves the relation among the environment, the biofilm-forming microbes, and the sedimentary textures. Colors of the travertine surface in many cases reflect the dominant microbe in the biofilm. Chemical gradient from the upstream anoxic conditions to the downstream oxic conditions appears an epitome of environmental evolution of the Earth's surface. Microbiological study of travertine is an attempt to find clues for understanding the evolution of early biosphere.

Second, travertines generally have the very large growth rate basically by quick mineral precipitation at travertine/water interface. We focus on this topic in Chap. 6. Growth or precipitation rate was accurately quantified for the daily-laminated travertines, and the quantified rate (up to 1 mm/day) was much larger than other carbonate deposits. In addition, such high rate was hardly accommodated into any of the previous models of the carbonate precipitation. We assume that  $\text{CO}_2$  degassing induced carbonate precipitation; based on this assumption, we propose a geochemical model that is somehow consistent with the actual precipitation rate of travertine. Our models still include uncertainty, but may help to reduce inconsistency between the actual phenomena and the previous models. Here we represent our own interpretations that include some simplification and therefore can be modified in the future studies.

Statements, discussions, and conclusions in this book are largely based on our research results of the Japanese travertines. In Chap. 7, we introduce a variety of key features observed in the Japanese travertine sites. Most of these sites are used for *onsen*, a public bathing facility using natural hot spring water. Japanese people (and monkeys) believe that taking *onsen* is good for healing both our mind and body, and it is a popular destination for spending holidays. Onsen sometimes activate the economy in less-populated rural areas, and landowners of a potential hydrothermal area drill a well of hundreds of meters deep. Onsen water comes from a wide range of drilled depths and geothermal, hydrological, and geological conditions, which reflect a variety in physicochemical and environmental properties of water. The official definition of *onsen* requires a certain level concentration of some chemical components, including sulfur, iron, calcium, and carbon dioxide, and/or the discharged temperature above 25 °C. Thousands of *onsens* on the Japanese islands are categorized into several types according to water chemistry. Travertine develops mainly into two types of *onsens* (sodium bicarbonate saline spring and carbon dioxide spring) that satisfy geochemical requirements. Areal expansion of the Japanese travertine sites is generally much smaller than the famous World Heritage Sites; however their coverage in environmental conditions is wide.

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# Chapter 2

## Basic Knowledge of Geochemical Processes



### 2.1 Subsurface Processes and Basic Requirement for Travertine Formation

Travertines (or thermogene travertines in Pentecost 2005) are formed from hydrothermal water with an initial high concentration of  $\text{Ca}^{2+}$  and  $\text{CO}_2$  partial pressure (Ford and Pedley 1996; Gandin and Capezzuoli 2008, 2014; Capezzuoli et al. 2014). In this type of water, the active  $\text{CO}_2$  degassing immediately after discharging on the ground increases pH and saturation state with respect to  $\text{CaCO}_3$  of the water. Precipitation (and dissolution) of  $\text{CaCO}_3$ , which is associated with  $\text{CO}_2$  degassing (and uptake), is often simply represented in the following reaction 2.1:



This is also applicable to a karst/cave system where limestone is dissolved by high  $\text{CO}_2$  partial pressure of a soil layer in ambient temperature and pressure (Fig. 2.1). When the water dissolving  $\text{CaCO}_3$  percolates through the limestone bedrock and eventually seeps out to the cave space, the water degasses  $\text{CO}_2$  to the cave air of lower  $p\text{CO}_2$  and precipitates calcium carbonate, called speleothems. In this case, the reaction 2.1 is generated by the difference in  $p\text{CO}_2$  between the soil layer and the cave air. Precipitation of  $\text{CaCO}_3$  often sustains after the water discharges from a limestone cave because further  $\text{CO}_2$  degassing is generated by lowered  $p\text{CO}_2$  of the atmosphere. Carbonate precipitate in such riverine settings is called *tufa*, for which the water is not originated from hydrothermal processes.

In comparison with the water in a karst system, the travertine-forming water gains two requirements, higher  $\text{Ca}^{2+}$  and  $\text{CO}_2$  partial pressure, through different processes and sources and in a certain depth. Origin of carbon dioxide in the travertine system is endogenic. The water often contains  $\text{Ca}^{2+}$  concentration more than 20 mM ( $10^{-3}$  mol/L) and  $p\text{CO}_2$  nearly 1 atm. Although the origin of such high  $\text{Ca}^{2+}$  and  $\text{CO}_2$  in hydrothermal water has not been systematically understood and proven, a series of

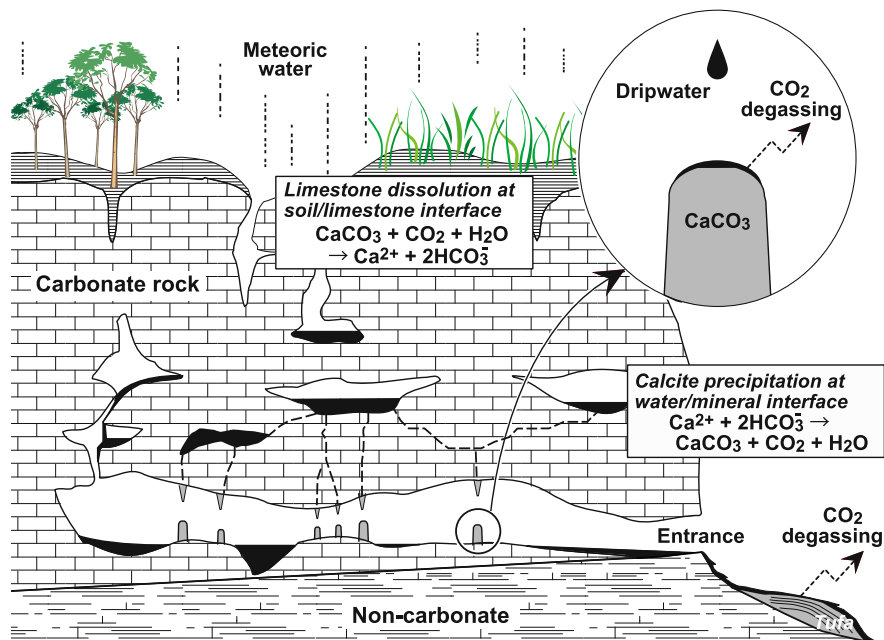


Fig. 2.1 Dissolution and precipitation in a limestone cave system. (Modified after Kano 2012)

research by Giggenbach (1980, 1984, 1988, 1995) proposed reasonable and useful processes to understand what happens in underground.

The first step is generation of carbon dioxide that has lower critical P/T point (Angus et al. 1976). The hydrothermal or endogenic carbon dioxide is originated from thermal degradation of two major crustal sinks of carbon; carbonate, and organic carbon (Berner 1991). In a tectonically active area like the Japanese islands, heat source can be a subducting plate, fault movement, and magmatic activity. It is known that carbon isotope of the endogenic  $\text{CO}_2$  is around  $-6\text{‰}$  (vs. VPDB; Des Marias and Moore 1984) reflected from a particular proportion of inorganic (around  $0\text{‰}$ ) and organic carbon (around  $-25\text{‰}$ ) in the source. This value implies that more  $\text{CO}_2$  was degenerated by carbonate degradation than by degradation of organic matter (inorganic: organic =  $\sim 3$ ). There are cases in which the carbon dioxide was originated mainly from decarbonation of carbonate rock (Turi 1986; Pentecost 1995).

Carbon dioxide, which is supercritical in high P/T conditions, becomes aqueous or gaseous in shallow aquifer having lowered P/T conditions (Fig. 2.2). Solubility of carbon dioxide increases with decreasing temperature (Giggenbach 1984). Gaseous portion of the carbon dioxide in a high-temperature condition near a heat source migrates to the surrounding aquifer of a lower temperature. This mechanism may control the distribution of high  $\text{CO}_2$  hot springs. In many of the active volcanic areas in Japan, such as Aso, Kujyu, Garandake, and Towada, the high  $\text{CO}_2$  springs are