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Travertine

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With 102 Figures and 22 Photoplates, some in color

 Springer

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Preface

During the spring of 1960, an uncle showed me a ‘petrifying spring’ near Plaxtol in Kent where twigs had been encased in a calcareous jacket. A twig was collected and having recently been given I. Evan’s *Observer’s Book of Geology* by my parents, I found a photograph of another petrifying spring and an explanation of its origin. In those days, Derbyshire was too far for a holiday destination, and I took little further interest until a research studentship with Professor G. E. Fogg became available in 1971. Tony Fogg had recently moved to the University College of North Wales, Bangor and the research was to be into cyanobacterium mats, with fieldwork along the Red Sea coast. The fieldwork never materialised but my interest in algal mats had been aroused. A chance stroll along the Bangor shore revealed beautifully calcified cyanobacterium mats, and Tony generously allowed me to investigate these instead. The old Plaxtol collection was retrieved and yielded abundant cyanobacteria. It became apparent that here was a wealth of information about a rock whose formation was so rapid, that the process could be studied in days rather than years – an exceptional state of affairs. A search of the literature also revealed that the rock, a form of travertine, had other unusual features. The decision to bring this information together in a book was soon made, but it was to be many years before time allowed its initiation. Progress was sometimes slow, when heavy German tomes had to be translated, and obscure publications had to be found. This was punctuated by amusing encounters such as Weed’s description of the cowboy who bathed in the waters of Mammoth Hot Springs, only to find that he was becoming ‘petrified’, no doubt making a rapid retreat! The literature on travertine is widely scattered and references are encountered in a surprising number of disciplines. Indeed, travertine has played an important but neglected role in our understanding of nature. Not only does it continue to inspire millions of visitors to caves and travertine dammed-lakes – it was also the careful observation on the growth of travertine in the 19th Century that led to an appreciation of the true age of the Earth, and the foundation of the science of geology.

Many travertines develop at the Earth’s surface where they were often covered in plants, while others form in caves where they form flowstone, stalactite and stalagmite. In a work of this kind it is impossible to ignore cave deposits and they are widely referred to, although the original intent was to concentrate on the surface forms. It was soon apparent that the definitions of these forms were often vague and confusing and were badly in need of clarification. In the cool British climate, travertine formation has not occurred on a large scale, but in warmer latitudes, travertines can be extensive and of considerable economic value. Most of the largest deposits are formed around hot springs, in which Britain is impoverished. Despite this, British deposits are of great variety and have taught us much about biogeochemical processes and of the organisms that once inhabited them, and it is within this region that the author began his interest before venturing to warmer climes.

To my family

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Contents

1	Introduction	1
1.1	Definition of Travertine	2
1.2	Travertine Compared with Other Non-marine Carbonates	4
1.3	Etymology	5
1.4	History of the Science of Travertine Formation	7
2	Origins of the Components	11
2.1	Travertine Precipitation	11
2.2	Classification on Carrier CO ₂	12
2.2.1	Meteogene Travertines	12
2.2.2	Thermogene Travertines	13
2.2.3	'Orgamox' Waters and Other CO ₂ Sources	16
2.3	Other Classifications	16
2.4	Sources of Bedrock Carbonate and Calcium	17
3	The Travertine Fabric	19
3.1	The Microfabric	19
3.1.1	Calcite Fabrics: Micrite and Sparite	22
3.1.2	Calcite Fabrics: Dendritic and Similar Forms	25
3.1.3	Calcite Fabrics: Shrubs and Bushes	27
3.1.4	Aragonite Fabrics	29
3.2	Mesofabrics	30
3.2.1	Porosity	30
3.2.2	Bedding and Jointing	32
3.2.3	Floe, Nodules and Thinolite	32
3.2.4	Biofabrics	33
3.2.5	Coated Grains: Ooids and Oncoids	34
3.2.6	Lamination	37
3.3	Diagenesis	41
3.3.1	Primary Fabric and Cement	42
3.3.2	Meteoric Diagenesis	42
3.3.3	Burial Diagenesis	48
4	Morphology and Facies	49
4.1	Autochthonous Travertines	52
4.1.1	Spring Mounds	52
4.1.2	Fissure Ridges	55

4.1.3	Cascades	56
4.1.4	Dams	59
4.1.5	Fluvial Crusts	67
4.1.6	Lake Deposits	67
4.1.7	Paludal Deposits	68
4.1.8	Cemented Rudites and Clasts	69
4.1.9	Speleothems	69
4.2	Allochthonous (Clastic) Travertines	73
4.3	Travertine Caves	73
4.4	Postdepositional Effects On Morphology	74
4.4.1	Karstification	74
4.4.2	Soils	75
4.4.3	Mass Movement	75
4.4.4	Effects on Fluvial Systems	76
5	Limestone Solution, Groundwater and Spring Emergence	77
5.1	Limestone Solution and Groundwater	77
5.1.1	Meteogene Source Waters	77
5.1.2	Thermogene and Superambient Meteogene Source Waters	79
5.2	Spring Emergence – Structural Controls	81
6	Chemical Composition of Source Waters	85
6.1	Meteogene Source Waters	85
6.1.1	The CO ₂ -Ca-H System	86
6.1.2	Magnesium, Sodium, Sulphate and Chloride	91
6.1.3	Calcium Hydroxide Source Waters (Invasive Meteogenes)	93
6.1.4	Superambient Meteogene Source Waters	93
6.1.5	'ORGAMOX' Waters	94
6.2	Thermogene Source Waters	94
6.2.1	THE CO ₂ -Ca-H System	94
6.2.2	Magnesium, Sodium, Sulphate and Chloride	95
6.3	Minor Components of Source Waters	96
6.4	Saline Waters	99
7	Mineralogy and Elemental Composition	101
7.1	Calcite and Aragonite Mineralogy	101
7.2	Occurrence of Calcite and Aragonite in Travertine	103
7.3	Autochthonous Carbonate Minerals Excluding CaCO ₃	106
7.4	Calcite and Aragonite Crystal Habit	107
7.4.1	Calcite	107
7.4.2	Aragonite and Vaterite	110
7.5	The Calcium Carbonate Content of Travertine	110
7.6	Trace Constituents of Calcite and Aragonite	111
7.6.1	Strontium	112
7.6.2	Magnesium	113
7.6.3	The Alkali Metals	116
7.6.4	Iron and Manganese	116
7.6.5	Phosphorus	117

7.6.6	Other Elements	119
7.7	Autochthonous Non-carbonate Minerals	121
7.7.1	Gypsum	121
7.7.2	Barytes	121
7.7.3	Manganese and Iron Minerals	122
7.7.4	Sulphur	122
7.7.5	Silica	123
7.7.6	Other Minerals	124
7.8	Allochthonous Components	124
7.9	Fluid Inclusions	126
7.10	Organic Matter	127
7.11	Fluorescence and Phosphorescence	127
8	Stable Isotopes	129
8.1	Oxygen	130
8.1.1	The Hydrological Cycle	130
8.1.2	Oxygen Isotopes in Travertine	132
8.1.3	Oxygen Isotopic Equilibrium	135
8.1.4	Oxygen Isotopes and Evaporation	139
8.2	Carbon	139
8.2.1	Meteogene Travertine	140
8.2.2	Thermogene Travertine	143
8.2.3	Modelling Downstream Changes	143
8.2.4	Disequilibrium and the 'Metabolic Shift'	144
8.3	Sulphur, Strontium, Lead and Lithium	146
8.3.1	Sulphur	146
8.3.2	Lead, Strontium and Lithium	146
9	Organisms Associated with Travertine	149
9.1	Prokaryotes	149
9.1.1	Photosynthetic Bacteria	150
9.1.2	Non-photosynthetic Bacteria	151
9.1.3	Cyanobacteria	155
9.2	Eukaryotic Algae	162
9.2.1	Chlorophyta (Green Algae)	162
9.2.2	Diatoms	166
9.2.3	Other Eukaryotic Algae	169
9.3	Fungi and Lichens	170
9.4	Bryophytes	171
9.4.1	Mosses	171
9.4.2	Liverworts	175
9.5	Tracheophytes	176
9.5.1	Lycopods, Horsetails and Ferns	176
9.5.2	Gymnosperms and Angiosperms	176
9.6	Travertine Plant Ecology	177
9.6.1	Plant Communities and Water Relations	178
9.6.2	Diversity	181
9.6.3	Light, Water Chemistry, Temperature and Pollution	182

9.6.4	Succession and Seasonality	183
9.6.5	Biomass and Growth	185
9.7	Fauna	186
9.7.1	Protozoa	186
9.7.2	Metazoa	187
9.7.3	Ecology of Animals	193
10	Deposition Processes	197
10.1	Travertine Deposition Rates	197
10.1.1	Meteogene Rates	198
10.1.2	Thermogene Rates	200
10.1.3	Temporal Variation	201
10.1.4	Lateral Variation	203
10.1.5	Amounts Deposited over Time	204
10.2	Carbon Dioxide Loss from Emerging Groundwaters	204
10.3	Saturation Indices and Nucleation	212
10.3.1	Calcium Carbonate Saturation Indices	213
10.3.2	Calcite Saturation Indices for Travertine-depositing Waters	214
10.3.3	Heterogeneous Nucleation and Crystal-Trapping	217
10.3.4	Apparent Onset of Nucleation in Streams	220
10.4	Crystal Growth	221
10.4.1	Models of Crystal Growth and Precipitation Rate	223
10.5	Travertine Deposition and Discharge	227
10.6	Inhibitory Effects	228
10.7	Biological Processes	228
10.7.1	Non-photosynthetic Bacteria	230
10.7.2	Photosynthetic Microbes	232
10.7.3	Bryophytes and Higher Plants	237
10.7.4	Photosynthesis and Respiration	240
11	Travertine Dating	243
11.1	Radioisotopes	243
11.1.1	Radiocarbon	243
11.1.2	Uranium Series	249
11.1.3	Other Radioisotopes	250
11.2	ESR and TL Dating	250
11.3	Palaeomagnetism	250
11.4	Amino Acid Racemisation	251
11.5	Seasonal Lamination	251
11.6	Chronostratigraphy	251
12	Palaeobiology and Biostratigraphy of Quaternary Travertines	253
12.1	Fossil Flora	254
12.1.1	Pleistocene Flora	255
12.1.2	Holocene Flora	256
12.2	Fossil Faunas	258
12.2.1	Invertebrates Excluding Mollusca	258
12.2.2	Mollusca	259

12.2.3 Vertebrate Faunas Excluding Primates	268
12.2.4 Primates	270
13 Climate, Man and Travertine	275
13.1 Travertine Deposition in the Quaternary	275
13.2 Climate and Travertine Deposition	279
13.3 Human Influence	283
13.4 The Conservation of Travertine	287
14 Travertines and Their Fossils: Archaean to Pliocene	289
14.1 Archaean and Proterozoic Travertines	290
14.2 Palaeozoic and Mesozoic	292
14.3 Paleocene to Oligocene	293
14.4 Miocene and Pliocene	296
15 Related Sediments and Industrial Deposits	299
15.1 Lacustrine Marl	299
15.1.1 Biogenic Marls	300
15.1.2 Abiogenic Marls	300
15.1.3 Clastic Marls	302
15.1.4 Other Marls	302
15.2 Calcrete	302
15.3 Coast Deposits	305
15.4 Industrial Deposits of Calcium Carbonate	306
15.4.1 Deposits in Wells, Pipes and Boilers	307
15.4.2 Quarrying and Construction	308
15.4.3 Remedies	308
15.5 Siliceous Sinter	311
16 Extraterrestrial Travertine	313
16.1 Vulcanism	314
16.2 Meteor Impacts	315
17 Utilisation of Travertine	319
17.1 Quarrying Methods	319
17.2 Mechanical and Physical Properties	321
17.3 Building and Exterior Decoration	321
17.3.1 Pre-Roman Use	321
17.3.2 Roman Buildings 200 B.C.–A.D. 455	323
17.3.3 The Dark Ages to the Renaissance, A.D. 455–1550	327
17.3.4 Europe 1551–2000	328
17.3.5 A Case Study in English Travertine Use: The North Kent Churches	331
17.4 Travertine in Art	335
17.4.1 Sculpture and Internal Decoration	336
17.4.2 Garden Decoration	337
17.4.3 Petrifying Springs	338
17.4.4 Graphic Art and Tourism	342
17.5 Agriculture and Industry	343

17.6 Medicinal	344
17.7 Economics and Tonnage	344
References	345
Photoplates	385
Index	431

Introduction

The work is divided into 17 chapters covering, it is hoped, most of the accumulated knowledge of this unusual stone. The first chapter provides definitions and looks at the history of our understanding of travertine formation. The second deals mainly with the properties of active travertines and begins with their classification using a broad range of criteria, from their geochemical origins to their gross morphology. In Chapter 3, hydrogeological processes leading to the formation of travertine-depositing waters are considered, including the role of the soil-atmosphere and factors controlling spring emergence. The chemical properties of travertine-depositing water are considered next according to the groundwater source. The range of springwater compositions is explored in Chapter 6 and compared with non-depositing waters. In Chapter 7, the mineralogy and gross composition of travertines is examined. The two common polymorphs of calcium carbonate, aragonite and calcite both form travertines and during their growth, trap other atoms, ions and molecules. These trace constituents together with other precipitating and trapped minerals can provide useful environmental and historical evidence in older travertines. Of equal significance are the stable isotope compositions of carbon and oxygen in the travertine carbonate. The ratios of the two stable isotopes of oxygen, ^{16}O and ^{18}O for example, are capable of providing valuable information on the conditions under which travertines were deposited in the past. Cave travertines in particular have been useful in unravelling climate change in the Quaternary. This topic is addressed in Chapter 8.

The flora and fauna of actively-depositing travertines has fascinated biologists for more than two hundred years. It was soon established that the specialised physico-chemical environment was home to a great diversity of plants and animals with some peculiar adaptations to a rapidly depositing environment. In Chapter 9, this diversity is explored with reference to the ecology and biology of the organisms involved. The process of travertine formation is arguably the most revealing and important aspect of any book devoted to a freshwater carbonate. The chemical changes leading to calcium carbonate deposition are considered in Chapter 10 and include the important of carbon dioxide evasion, the nucleation and growth of calcite crystals and the significance of the associated organisms. The chemical dynamics of travertine-depositing systems are described and processes ranging from carbonate nucleation to crystal cohesion investigated. The next four chapters deal with organic remains of travertines and their use as biostratigraphic markers and indicators of past climates. Chapters 11 and 12 concentrate on the Quaternary and its numerous and important interglacial travertines. Their floras and faunas are described, methods of dating are elaborated and the impacts on travertine formation by man are described. With the recent interest in climate change, interest in the recent past, as revealed by the Quaternary sediments has increased, leading to advances in our understanding of climate variation over the past two million years. Epigeal (surface) travertine formation is both sensitive to climate and replete with terres-

trial fossils, providing valuable evidence of local and regional climates. The effects of climate and man on travertine formation is taken up in Chapter 13. Travertines cannot form in organically polluted waters and are sensitive to catchment interference by man. As a result, the recent history of travertine formation can often be linked directly to human activity. The remaining chapters cover topics mainly relevant to inactive travertines and related deposits. Travertine is but one of a wide variety of Earth's continental limestones and in Chapter 14, the older deposits, dating from Archaean to Pliocene are considered. Marls, calcretes and beachrocks – other forms of continental carbonate, are often associated with travertine and are sometimes confused with them. They are described briefly in Chapter 15 along with industrial deposits of calcium carbonate. The latter are responsible for much of the scaling of industrial and domestic pipework, and the use of inhibitors and other forms of remediation are also described here. Some consideration is given to the likely occurrence of extraterrestrial travertines in Chapter 16. Such deposits almost certainly exist on other planets of the Solar System. Since microbes are frequently found entombed within travertine, they could provide a focus for the search of microbial activity on other planets.

While travertine-like deposits can be a nuisance in industry, the 'natural' travertines can be financially rewarding. Some are renowned for their visual impact and used extensively in art and architecture. The topic has a long and interesting history. In addition, many of the world's most scenic spots are travertine locations, bringing huge sums of money to those countries fortunate enough to possess them. They too are the subject of Chapter 17.

1.1 Definition of Travertine

Several recent definitions of travertine can be found in the literature. They vary from a single phrase to a short paragraph in length. Some emphasise temperature while others point to hydrologic setting or process. The latter is emphasised throughout this book. Process of formation should be of fundamental significance in the definition of all limestones. Among the more brief though not particularly concise definitions of travertine is that of Mitchell (1985): 'formed by evaporation of spring and river waters' while Whitten and Brooks (1972) define it as a 'kind of calc-tufa deposited by certain hot-springs'. Temperature also enters into the definitions of Riding (1991) who defined travertine as

... a product of warm carbonate springs where the elevated temperatures, together with the dissolved materials present in these warm waters, excluding most eukaryotic organisms.

He also lists them as one of five forms of microbial carbonate: 'a layered benthic microbial deposit with a dendritic microfabric', while Glover and Robertson (2003) define travertine simply as 'hot spring deposits (>20 °C)'.

Emig (1917) wrote one the best early 20th Century accounts of travertine formation and defined it as 'deposition from the water of springs or streams holding calcium bicarbonate in solution'. Fouke et al. (2000) apply a broader definition:

All non-marine carbonate precipitates in or near terrestrial springs, rivers, lakes and caves.

Although some the above definitions pay attention to process, they are insufficiently precise. For example, evaporation is not normally considered to be an important process in travertine formation, and all natural waters contain at least traces of calcium and bicarbonate. Restricting a definition on temperature alone would lead to difficulties with old, inactive deposits, while lake and playa deposits are varied and include the lake marls, not normally equated with travertine.

Of interest is the proposal of Koban and Schweigert (1993) who provide definitions based on the mode of precipitation (organic/inorganic), the hydrological setting (vadose/phreatic), and the porosity, on a triangular diagram distinguishing lacustrine limestones, sinters, travertines and tufas. The diagram is conceptually appealing and in placing emphasis on the hydrology, makes an important contribution. However, it would be difficult to apply in most situations. Bates and Jackson (1987) provide three definitions:

- a a dense finely crystalline, massive or concretionary limestone, of white, tan or cream, often having a fibrous or concentric structure and splintery fracture formed by rapid chemical precipitation of calcium carbonate from solution in surface and groundwater, as by agitation of stream water or by evaporation around the mouth or in the conduit of a spring, especially a hot spring. It also occurs in limestone caves where it forms stalactites, stalagmites and other deposits; and as a vein filling, along faults, and in soil crusts. The spongy or less compact variety is *tufa*. Synonym *calcareous sinter*.
- b a term sometimes applied to any cave deposit of calcium carbonate.
- c a term used inappropriately as a synonym of *kankar* (a type of calcrete).

Definition a) is more informative than most, but fails to clearly identify the main process leading to travertine formation, namely the degassing of aqueous carbon dioxide, although this is implied, along with evaporation. Deposits associated with soils are normally referred to as calcretes.

Travertine is defined here as:

A chemically-precipitated continental limestone formed around seepages, springs and along streams and rivers, occasionally in lakes and consisting of calcite or aragonite, of low to moderate intercrystalline porosity and often high mouldic or framework porosity within a vadose or occasionally shallow phreatic environment. Precipitation results primarily through the transfer (evasion or invasion) of carbon dioxide from or to a groundwater source leading to calcium carbonate supersaturation, with nucleation/crystal growth occurring upon a submerged surface.

This definition attempts to emphasize inorganic processes, namely reactions involving gaseous carbon dioxide and a calcium bicarbonate solution leading to the precipitation of calcium carbonate in a non-marine setting. It does not preclude biological processes nor evaporation, but regards them as subsidiary. The principal reaction involves the loss of carbon dioxide gas from a calcium bicarbonate solution leading to calcium carbonate deposition. Most definitions fail to cover all cases of a particular process and the above is no exception. For example, on rare occasions, travertine is formed under the influence of seawater, while algal and bryophyte photosynthesis is locally important. These processes are detailed below, but it should be emphasized that they remain exceptional and apply to few deposits considered here as travertines.

Travertine deposition frequently occurs on steep slopes, and bedding within the deposit, where present, is usually inclined and undulatory. Travertines formed *in situ* are rarely horizontally bedded. Laminations on a millimetre to centimetre scale are common and often the result of daily/seasonal growth rhythms. Bacteria, algae, bryophytes and reeds are frequently encrusted with travertine and photosynthetic activity will enhance calcium carbonate precipitation. In caves, these fabrics are normally absent. Most frequent morphologies are mounds, pendants and terraces associated with dams. Key travertine

features are lack of horizontal bedding and formation by chemical precipitation. Clastic travertines resulting from autochthonous travertine erosion are common and often occur as terraces and fans. These deposits often show horizontal bedding but their clastic nature is usually obvious. Deposits formed by the common ion effect would not be classed as travertines, although in practice, some of the resulting forms would be difficult to distinguish from them and they are considered here along with the travertines as defined above.

1.2 Travertine Compared with Other Non-marine Carbonates

Travertine is distinguished from:

- *lake marl* which is deposited on the beds of lakes and results largely from the precipitation of calcium carbonate through phytoplankton /macrophyte photosynthesis augmented by CO₂ evasion and evaporation. Precipitation occurs either within the lake water and subsequently deposited as a calcareous mud, or upon submerged benthic macrophytes such as *Chara* that become incorporated into a fine, weakly laminated sediment in a fully phreatic environment. Lake travertines are normally more localised, being deposited at the emergence points of submerged springs by *in situ* precipitation to form mounds, and also as travertine dams at the lower end of a lake in a vadose/phreatic setting. Littoral deposits associated with microalgae may also occur. Deposition is focussed and horizontal bedding is lacking. Where travertine forms into dams across rivers and streams, impounded lakes or ponds usually form into which marls accumulate. In these cases, the marl contains a significant amount of clastic travertine and is best regarded as part of a 'travertine-depositing system'.
- *lake reef*: Occasionally, reefs form at calcareous lake margins which appear to result from the coagulation of fine planktonic carbonates (e.g. Green Lake, N.Y.). The deposits may result from precipitation in the lake water as a combined result of degassing of CO₂ and photosynthesis. They may not be deposited *in situ* but consolidated in the lake littoral as carbonate reefs. Their fabrics can be travertine-like but they cannot be strictly classified as travertine and they are referred to here as lake-reef carbonates. The mechanism of reef formation is uncertain and they will be referred to briefly in Chapter 15.
- *calcrete* (caliche), a subaerial deposit formed by evaporation and CO₂ evasion of water at the moist soil surface. These deposits are typically laterally extensive and usually no more than a few metres in thickness and of low porosity. They reach their maximum development in warm, arid climates. Travertines may become 'calcretised' during periods of aridity but this is a secondary process, and evaporation is rarely an important factor in travertine formation.

In modern settings, travertines are usually readily separated from marine limestones, lake marls and calcretes as the process of formation is easy to recognise. Travertine deposition tends to be localised around points of spring emergence, or associated with calcium-rich river systems. Bedding, if present, is often irregular. Cave travertines contain little or no mouldic porosity but form characteristic pendants, pillars and curtains, often with bizarre shapes. Old inactive travertines may be more difficult to recognise. Their hydrological settings may be obscure and their morphologies much modified by erosion and diagenesis. Examination of thin sections is normally required where characteristic microfabrics are often revealed.

1.3 Etymology

The word travertine is thought to originate from the *lapis Travertinus* used for the volcanic spring deposits of Bagni di Tivoli in Lazio, Italy. Other spellings are sometimes encountered in the early literature, notably *trevertine* and *travertin*. In Italian it is *travertino*. Travertinus was originally *tiburtinus* or *Tivertino*, from the Roman name of Tivoli, a town 26 km east of Rome. There are several references to travertine in the classical literature. Vitruvius noted its strength; '*Tiburtina vero et quae eodum genere sunt omnia, sufferunt et ab oneribus et a tempestibus iniuria*', and it is mentioned in Plinius' *Natural History*; '*lapides Tiburtini ad reliqua fortes, vapore dissiliunt*'. Travertine was quarried near Bagni di Tivoli to provide building materials during the Roman period, but these sites have been largely if not entirely destroyed by more recent excavations. During the Roman Empire, the rock was probably won from many quarries in the vicinity of important towns, but those near Tivoli were likely to be among the most important as it could be sent directly to Rome by barge. Bagni di Tivoli should therefore be regarded as the type locality for travertine.

Several other names have been applied to travertine and are in common use. In English-speaking lands, *calcareous tufa* is used, often reduced simply to *tufa*. Barker (1785) used the term *tuft*. These terms apply to soft, poorly consolidated deposits that abound in the British Isles. The French use *le tuf calcaire*, and occasionally *touviere* or *tout* (Blot 1986). In Germany, *Kalktuff* is often used, with *alm* to distinguish the soft, unconsolidated forms (Jerz 1983). More rarely it was called *Duckstein* (Damm 1968), and occasionally *Sprudelstein* or *Quellekalk*. The travertine of Cannstatt was referred to specifically as *Sauerwasserkalk*. Many of these words are derived from the Latin *tofus*, and in early English writings, *tofw* or *tophus* can be found (Leland c. 1538 in Hearne 1711; Rudder 1779). Townson (1797) distinguished 'the common calcareous Tophus, (*tophus communis*)' from both volcanic tufa and the travertino, along with other writers such as Baier (1708) and Naumann (1850).

Tofus is an ambiguous term which seems to have been applied to a range of soft rocks. Ovid compared it with pumice, as a material unsuitable for building and Plinius wrote; '*reliqua multitudine lapidum tofus aedificis inutilis est mortatilate, mollitia*'.

Stattius observed its use in road building but the identity of the material is uncertain. However, *tofus rubrum* has been equated with 'lithoidal tufa', a term applied to pyroclastic deposits erupted from the Colli Albani volcanoes, southeast of Rome (Platner 1830). Vitruvius states; '*sunt etiam alia genera plura, uti in Campania rubrum e nigrum tofum*', though Virgil considered *tophus scaber* a general term. In modern Italian, *tufo* is used for pyroclastic deposits consisting of volcanic ash, lapilli and pumice fragments found in great quantity in the vicinity of Naples, Rome and elsewhere. This description extends to ash sufficiently consolidated to be cut for building stone and has been used widely since the Roman period. Poorly consolidated deposits of travertine, which many would call calcareous tufa, are uncommon in this region, and it is unlikely that such deposits represent the original tufo. Blake (1947) clearly distinguishes between this tufa, with its variable colour and strength, and travertine.

The term *algal tufa* has been used in the early 20th Century literature for a range of algae-associated intertidal and evaporite carbonates (Warren 1982). Intertidal carbonates are outside the scope of this work and will be only briefly referred to. There is in fact a much earlier reference to this form of sediment. According to Agricola (1546), Theophrastus (c. 370–287 B.C.) used *poros* for such deposits, but this was not taken up by later writers.

Another term occasionally used to describe travertine is *sinter*, which originated in Germany for the dross formed during the smelting of iron (Damm 1968). *Sprudelsinter* is still used for hot spring deposits formed at spas, such as Carlsbad (Karlovy Vary) in the Czech

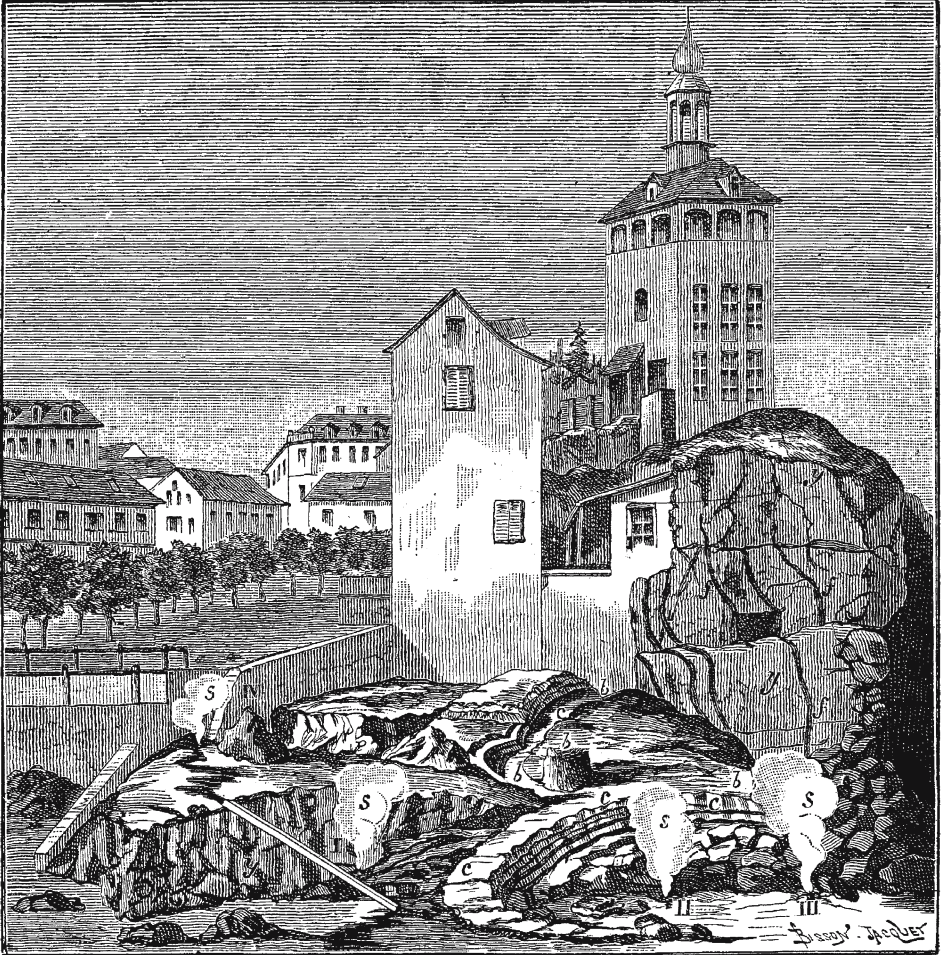


Fig. 1. The hot spring of Carlsbad, Czech Republic where many early observations of travertine formation (c) were undertaken. From Daubrée (1887)

Republic (Fig. 1). Walch (1773) considered sinter 'feiner und kompakter als die Tophstein'. Sinter could apply to the travertine of Bagni di Tivoli, though it would then be confused with siliceous sinter, used for the opaline silica deposits of hot springs. Sinter, according to Pia (1933) should be applied to inorganically formed deposits, whereas the Bagni travertine contains layers of 'shrubs' thought to have formed through bacterial activity (Chafetz and Folk 1984). A more accurate term *calc sinter* has found occasional use. Hubbard and Herman (1990) revived the term *travertine-marl* as an alternative, including the softer clastic sediments.

Ought these terms be distinguished in the light of current knowledge? Recent research has revealed a rich microbial flora in many modern hot spring travertines, but their role in its formation remains equivocal and it is clear that at Bagni di Tivoli, shrubs occur only in discrete layers. Not only would it be impracticable to distinguish layers and give them separate names, but it is difficult, if not impossible to determine the precise origins of many ancient travertines.

Should the term *calcareous (calc) tufa* be encouraged as an alternative to travertine? It is well enough understood in much of Europe, and Blot (1986) coined the term *tufologie* for the study of such deposits, but it might be misunderstood in Italy. It could be argued that the softer, poorly consolidated varieties should be so described, as indeed they are in numerous publications (e.g. Pedley 1990). The problem here is one of definition. There is no practical way of unambiguously setting a degree of strength or consolidation to these deposits. Julia (1983) recognised this and used travertine for all carbonate encrustations on plants without reference to pore volume or density. While admitting the impracticability of porosity measurements during field surveys, a classification into tufa and travertine is difficult to apply in cases where deposition is not obviously associated with plants. There are therefore good reasons in the author's view for reassessing these terms, and in this work, the term *tufa* will not be used, though its use will no doubt continue, and be reasonably well understood in most parts of the world.

1.4 History of the Science of Travertine Formation

Travertine has been exploited as a building material for at least two thousand years but is mentioned little in classical texts, and an understanding of travertine formation has come to us only recently. That certain springs could deposit a stony material on submerged objects has been known since the first century B.C. Strabo (c. 20 B.C.) mentions the petrifying waters of the hot springs at Hierapolis, Turkey and recounts a legend concerning a bird overflying them. In China, cave travertines were described as early as the 4th Century B.C. in the Chi Ni Tzu (Needham 1959) and epigeal travertine has been recognised since the Thang dynasty (A.D. 618–907). According to Yao Yuan-Chih (c. 1650), 'not only wood, but also herbs can change into stone when this happens to plants and the water-absorbing stone (*shang shui shih*) is produced'. The term *han shui shih* is applied to plant encrustations, and *chiang shih*, a more general term, aptly translated as the 'ginger stone'. An illustrated Chinese account is provided by Chang (1927).

After the collapse of the Roman Empire, nothing seems to have been written on the subject in the 'Dark Ages' that followed. However, the terms were known in the German area as early as A.D. 750. In the Middle Ages references are also sparse. Cohn (1876) recalled the hymn of Boleslau von Lobkowitz, c. 1500, where the algal colours of Carlsbad are described and Agricola (1546) notes a *tofus*, providing a brief description. 'Petrifying springs' were objects of curiosity in Europe and received passing reference in alchemical works such as Libavius (1597). Hot springs have always attracted interest and use made of their supposed medicinal qualities, but their calcareous and siliceous deposits passed by almost without comment. The travertine springs of Zerka Ma'in, Jordan once famous for their cures, were visited by Herod the Great (*Genesis* 36; 24). The encrustation of Rome's aqueducts, and doubtless the city's plumbing could hardly have gone unnoticed, but no written records have come to light.

Our current understanding of travertine formation can be traced back as far as the 11th Century but sound principles could not be formulated until the overturn of the 'Phlogiston Theory' late in the 18th Century when the true nature of matter began to unfold. The properties of calcium bicarbonate solutions were studied throughout the 19th Century when empirical formulae were superseded by equilibrium constants at the start of the 20th Century. This allowed chemists to determine the ionic constitution of natural waters and obtain predictions of the chemical changes occurring when temperature, pressure and composition was altered. Today we have a reasonably good understanding of travertine formation, but it would be a mistake to believe that our understanding is complete. Much remains to be done.

The precipitation of calcium carbonate at the Earth's surface is a major geochemical process that has played a significant part in the history of inorganic chemistry. The discovery and chemical properties of carbon dioxide are central to an understanding of the mechanism. Before the 17th Century, little was known of the nature of matter and its chemical transformation. Plinius (c. A.D. 70) mentions types of vapours that probably included carbon dioxide and also the speleothems of Mount Corycus, Greece. During the 11th–17th centuries, travertine is mentioned as speleothem in several influential works and three classes of mechanisms proposed to account for them (Shaw 1997). The first regarded speleothem as a plant-like growth and this is easy to understand in structures such as stalagmites with their root-like bases and concentric layers when seen in cross section. The second held that the deposits resulted from vapours rising from the depths of the Earth. The third maintained that some process of solidification from water occurred and this eventually led to our current understanding of the process. An important early development was the observation of dissolution and precipitation of salts. Experiments with the poorly soluble potassium nitrate led Palissy (1564) to conclude that speleothems formed by deposition of a salt taken up by water. The role of carbon dioxide in the process was not revealed until much later although the gas was known in other contexts. Helmont (1648) described *spiritus sylvestris* through the action of vinegar on limestone and the same gas was recognised in mineral springs. Later, Cavendish (1767) undertook experiments on the lime scale ('fur') forming on cooking utensils in London and found that the fur was held in solution by 'fixed air' but did not explain the process further. In 1770, Scheele recognised that carbonates and bicarbonates were different salts and noted the solvent action of carbon dioxide on limestone, and Black (1757) undertook experiments on the burning of lime and magnesia which were found to release carbon dioxide. Once Lavoisier (1780–90) overthrew the confusing 'Phlogiston theory' and deduced the proportion of carbon and oxygen in carbon dioxide, the correct formula was soon discovered. Not long after, Cuvier (1812) pronounced that water dissolves carbonates by means of abundant carbonic acid, allowing them to later crystallise after the acid has evaporated. This provided the correct solution, but did not explain where the carbonic acid came from. Bourguet (1742) proposed much the same mechanism but failed to mention the part played by 'fixed air' (CO₂). More detailed accounts of the early history of speleothem research may be found in Shaw (1997).

Geologists and botanists have long recognised epigeal travertine as spring-deposited limestone and speculated upon its origin. Leopold von Buch (1774–1853) a German geologist and pupil of Werner travelled to Italy in 1799 and described the deposits at Tivoli, distinguishing several forms (Buch 1809), noting their association with plants. Joseph Priestley discovered photosynthesis in 1776 and its formulation (CO₂ + H₂O + light = O₂ + organic matter) was given by Ingen-Housz (1796). Charles Lyell (1829) described some British travertines remarking that:

the water of the springs ... must also contain lime, since oxalate of ammonia renders the water turbid ... and carbonic acid is very evident.

Raspail (1833) is attributed by Julius Pia as the first to recognise that CO₂ uptake by plants could result in calcium carbonate precipitation. Agardh (1827) visited the travertine-depositing hot springs of Carlsbad and prepared the first list of algae from such deposits. Ferdinand Cohn, Professor of Botany at Breslau (now Wrocław, Poland) made detailed studies of travertine and their associated algae. At Carlsbad he collected and described the cyanobacterium *Fischerella thermalis (laminosus)*, observing that 'presst man die Polster dieser Alge aus, so fühlt man zwischen den Fingern einen äusserst feinen Sand zurückbleiben'. The 'sand' was found to be calcium carbonate and Cohn describes the close association

between algae and the travertine deposits. Cohn supported Raspail's view that plant metabolism could result in the precipitation of calcium carbonate, but did not cite his work. He also observed that not all plant species deposit carbonates in otherwise favourable circumstances and that CO_2 loss to the atmosphere was responsible for some travertine formation (Cohn 1862). He later turned his attention to the travertines of Italy, making a study of samples collected at the 'Cascatelle' of Tivoli, a series of travertine-encrusted waterfalls on the Anio River (Cohn 1864). He found further support for his plant hypothesis and also visited the springs at Bagni di Tivoli containing the 'volcanic' travertines used by the Romans. He distinguished, as had Buch, between the Cascatelle and Bagni travertines and described their algal flora in detail. One of his significant observations, for long overlooked, is the distinction between intracellular and extracellular biomineralization based in part on his observations of travertine.

Advances in carbonate chemistry were few in the first half of the 19th Century and awaited an understanding of the nature of ions and chemical equilibrium. Measurements by Schloesing (1872) showed that the amount of calcium carbonate dissolved by carbon dioxide could be expressed as a simple empirical equation and in the same decade it was found that for dilute solutions, the quotient $[\text{base}][\text{acid}]/[\text{salt}]$ was constant at a given temperature and pressure. A few years later the ionic product of water was obtained. Hassack (1888) confirmed Cohn's views that aquatic plants could precipitate calcium carbonate by performing laboratory experiments, and the great deposits of travertine and siliceous sinter at Yellowstone were described in detail by Weed (1889a). Walter Harvey Weed provided a review of the algae of hot springs, noting the preponderance of cyanobacteria and showed that the amount of calcium carbonate held in solution greatly exceeded that held by water in contact with the epigeal atmosphere.

By the end of the 19th Century, chemists were able to obtain equilibrium constants for some of the carbonate system reactions and these were essential if the dissolution and precipitation of carbonates were to be understood. Equations relating the activity of the $\text{Ca}^{2+}\text{-HCO}_3^-$ system to dissociation constants were standardised by Johnston (1915) and the combined equations used to predict solution composition as a function of the CO_2 partial pressure, although it would be some years before biologists recognised their importance. One of the first influential works on travertine written in English was that of the American W. H. Emig who worked for a while as a biologist for the Oklahoma Geological Survey. He provided a well-informed account of the travertines of the Arbuckle Mountains (Emig 1917) that included speculation regarding their recent history, an account of their flora and some early chemical analyses of the waters. Emig was born at Coulterville, Ill. and graduated from the University of St. Louis in 1911.

Julius Pia reviewed the earlier work relating plant metabolism to calcium carbonate deposition (Pia 1933, 1934) and described eight theories to explain the precipitation process. These included the 'Water loss theory' whereby plants take up water, concentrating the calcium bicarbonate remaining in the water, and the 'Carbon dioxide loss theory' which is essentially calcium carbonate precipitation brought about by photosynthesis. During the past 50 years knowledge of travertine has increased rapidly and papers on travertine now appear regularly in many fields of science, as well as in the arts. Influential post-war developments include the application of stable and radioactive isotope measurements, the latter permitting dating, advancing studies of palaeoclimatology and palaeobiology. Further progress arose through the advent of the electron microscope, computers and more refined methods of chemical analysis plus a realisation of the environmental significance of many deposits and their relationships with plants. More recently, the possibility of travertine deposits on other planets has been given serious attention in relation to the discipline of exobiology. These and other uses of this remarkable rock are described in the following chapters.

Origins of the Components

Travertines exist in a variety of forms and are classifiable on a range of criteria. A review of the literature by Pentecost and Viles (1994) identified four salient features; the precipitation process, carbon dioxide geochemistry, the travertine fabric and its morphology. The first two are considered below along with schemes applied to limestone in general. Chapters 3 and 4 consider the travertine fabric and morphology and their use in classification. Travertines may also be classified according to their hydrological setting and this is also referred to in Chapter 4.

2.1 Travertine Precipitation

Four chemical processes are responsible for almost all travertine formation on Earth. Most travertines form from the degassing of surfacing carbon dioxide-rich groundwaters containing $>2 \text{ mmol L}^{-1}$ (c. 80 ppm) calcium. A groundwater capable of depositing travertine is produced when dissolved carbon dioxide ('carbonic acid') attacks carbonate rocks to form a solution containing calcium and bicarbonate ions ('calcium bicarbonate') (Eq. 2.1):



Travertine deposition is the reverse of reaction (1). Carbon dioxide is lost from solution on contact with an atmosphere whose CO_2 concentration is lower than that in equilibrium with the 'attacking' below-ground solution. The sources of underground carbon dioxide capable of contacting and dissolving carbonate rocks (hence termed the carrier CO_2 or 'carrier') are manifold but two are of particular importance, the respired soil-zone CO_2 and thermally-generated CO_2 . Where the evasion of carbon dioxide occurs to the epigeal (i.e. above-ground and illuminated) atmosphere, additional CO_2 loss frequently occurs through the photosynthesis of aquatic plants and evaporation.

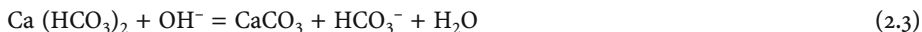
A few travertines are formed by the reaction between atmospheric carbon dioxide and hyperalkaline groundwater (Eq. 2.2):



These groundwaters most frequently occur in regions undergoing serpentinization (O'Neil and Barnes 1971) or those in contact with natural or industrially produced calcium hydroxide. This process may be considered *invasive* rather than *evasive* with respect to the carrier.

Travertines arising from (Eq. 2.2) are widely distributed but uncommon. Another process may be described as groundwater alkalinisation and is observed when groundwaters rich in

calcium mix with alkaline surface water. Hydroxyl ions in the lake water react with bicarbonate (HCO_3^-) to form carbonate (CO_3^{2-}) followed by precipitation of calcium carbonate (Eq. 2.3).



This reaction is mainly confined to a class of saline lakes where the OH^- concentration is elevated as a result of geochemical processes. These carbonates do not form through a direct transfer of carbon dioxide to or from the atmosphere and are not strictly travertines. However, they may be described as 'travertine-related' and are included in this book.

Another travertine-related process is the 'common ion effect'. The best known example is provided by the reaction of groundwaters infiltrating evaporites that become saturated with gypsum or anhydrite (CaSO_4). Gypsum-saturated waters contain high concentrations of CaSO_4 , approaching 2 g L^{-1} . When mixed with a Ca-bicarbonate water, Ca is sufficiently elevated to exceed the solubility product of calcite and precipitation follows. In this case, precipitation may be subsurface and within stratified sediments when mixing occurs underground. Again, the resulting deposits are not strictly travertines as described in Section 1.1.

To summarise, precipitation of calcium carbonate results from: evasion/invasion of CO_2 ; reactions involving OH^- ; and increase in Ca. Deposits resulting from these five processes often appear similar both in their microfabric and gross morphology.

2.2 Classification on Carrier CO_2

In this section, consideration will be given to the reactions which give rise to the carrier CO_2 . It will be seen again that a small number of independent processes are involved in the majority of cases, but as some of them are believed to originate deep in the Earth's crust, a number rely on indirect evidence or are merely speculative. However, useful classifications can result which have implications for the prospecting of travertines, and impinge upon some aspects of their morphology, fabric and biota. In the majority of cases the carrier originates either from the soil (meteogene) or from more deeply seated thermal processes (thermogene) providing a primary subdivision into two categories. This classification has the value of being independent of scale but is more difficult to apply to ancient travertines since it is ultimately dependent upon source water composition. As Riding (1999) and others have pointed out, purely descriptive definitions, irrespective of their origin, may be so broad as to have little value.

2.2.1 Meteogene Travertines

Soil-zone and atmospheric carbon dioxide may be regarded as meteoric in origin, since the terrestrial vegetation and associated soil contains carbon fixed from the atmosphere. Travertines formed from groundwaters charged with a meteoric carrier are termed meteogene (Pentecost and Viles 1994). They form typically in cold-water springs in regions underlain by carbonates, or occasionally evaporites (gypsum). Their dissolved inorganic carbon content (DIC) and dissolved calcium rarely exceeds 8 mmol L^{-1} (480 ppm as HCO_3^-) and 4 mmol L^{-1} (160 ppm as Ca) respectively and the stable carbon isotope composition averages around -10‰ (see 8.2). Occasionally, such waters circulate deep beneath the ground where they become heated and rise as hot springs, but contain only the meteoric carrier. These travertines, often the result of artesian flow, have been described as thermometeogene

(Pentecost 1995a). This is probably not the most suitable term because the name suggests that thermal water issues from the source. While the water is indeed warm or even hot in most of these springs this not always so. For example at high latitudes, where the mean air temperature is close to 0 °C, the groundwater temperature may be 10 °C higher due to deep circulation, but water at 10 °C is hardly 'thermal' (a term usually associated with 'hot'). The problem is discussed in more detail by Pentecost et al. (2003) and a better term for these waters is *superambient*. This implies that the groundwater issues significantly above the ambient temperature (the mean annual air temperature). *Invasive meteogenes* include those formed through the reaction of atmospheric CO₂ with hyperalkaline groundwater as described in (Eq. 2.2) above.

The soil atmosphere is by far the most important contributor of carbonic acid leading to limestone dissolution and the CO₂ enrichment of groundwaters. Concentrations of carbon dioxide gas in the soil air vary from about 0.2–10% (Jakucs 1977; Brook et al. 1983; Ford and Williams 1989) and a large proportion is dissolved by percolating rainwater. The epigeal atmospheric CO₂ concentration of 0.03% is too low to contribute significantly to direct carbonate dissolution where soils are present.

Thus the meteogene travertines are divided into two categories; the *evasive meteogenes* where carbon dioxide evasion leads to travertine deposition and the *invasive meteogenes* where the reverse process leads to deposition. Both may be further subdivided into the *ambient meteogenes*, the most frequently encountered where waters rise at ambient temperature, and the *superambient meteogenes* where, through deep circulation, the waters rise at a temperature above ambient and often as hot springs (>37 °C). Since all invasive meteogenes so far investigated are ambient, the terms *ambient* and *superambient* may be used without qualification as 'evasive' or 'invasive'.

2.2.2 Thermogene Travertines

The second group usually contains some meteoric carrier, but the bulk of the carbon dioxide originates from thermal processes within or even below the Earth's crust. Thermally generated carbon dioxide dissolves in groundwater, often under considerable pressure and the resulting high concentrations of CO₂ are capable of dissolving large volumes of rock, the solutions rising as hot, bubbling springs, forming a hydrothermal circuit (see 5.1.2). Typical dissolved inorganic carbon (DIC) and Ca levels are 10–100 mmol L⁻¹ (400–4000 ppm as HCO₃) and 2–20 mmol L⁻¹ (80–800 ppm as Ca) respectively, two to ten times higher than most meteogene sources. Rates of degassing and precipitation are correspondingly higher, providing distinctive fabrics and the travertine stable carbon isotope composition is generally heavier than meteogene waters (typically -3 to +8‰). Thermogene deposits have a more localised distribution than meteogenes and are often associated with regions of recent volcanic or tectonic activity. For example, the waters giving rise to Mammoth Hot Springs in the USA are heated by magma chambers close to the surface and the extensive deposits of Central Italy are associated with a number of Quaternary volcanic centres. High geothermal gradients may also exist locally in areas containing large blocks of radioactive igneous intrusions resulting in hydrothermal activity.

It is important to note that thermogene source waters are not necessarily hot, although this is frequently the case, the term applying to the source rather than the exit temperature of the water. Hot springs, with exit temperatures of 37 °C or above, are likewise not necessarily of thermogene character as noted above.

2.2.2.1 Magmatic Generation of Carrier

Deep sources of carbon dioxide have long been suspected to occur in thermal discharges of spring-water as they are often accompanied by ^3He , thought to be present in the upper mantle (Piperov et al. 1988). Carbon dioxide is a common magma constituent and significantly affects its melting point (Deines 1992). In fact the amount of CO_2 within the Earth is now thought to far exceed that at the surface. As magma rises toward the Earth's surface, pressure reduction leads to outgassing, with the vertical migration and eventual release of carbon dioxide to the epigean atmosphere. This may be encouraged by the presence of deep faults in regions of crustal tension. Circulating groundwaters are capable of dissolving large quantities of gas under high hydrostatic pressures. The resulting solutions dissolve calcium carbonate at depth, providing highly concentrated bicarbonate solutions that begin degassing as the waters rise. Hydrothermal solutions often ascend along fractures and Khoury et al. (1984) noted that within a region of Jordan with an elevated geothermal gradient, basalt was releasing CO_2 into deep faults and precipitating travertine at the surface. In the Carpathian Mountains, Dowgiallo (1976) provides evidence for the magmatic origin of some high- CO_2 springs on isotopic evidence while conceding that the bitumen oxidation hypothesis of Nowack (1938) may account for some of the CO_2 . In a Japanese site, helium isotope studies suggest that decarbonation was responsible for up to 90% of the deep carbon source (Sano 1996) while at Huanglong, China, Yoshimura et al. (2004) suggest that most of the CO_2 originates in the upper mantle. Some mantle-derived carbon dioxide could be juvenile as carbon compounds occur frequently in meteorites, though a proportion may also come from sediments having entered the upper mantle via subduction. This probably explains at least in part the wide range of $\delta^{13}\text{C}$ values reported from travertines and their associated waters (Barnes et al. 1984; Allard 1988; Deines 1992). The topic will be considered further in Chapter 8.

2.2.2.2 Decarbonation

Baking of carbonate sediments in the presence of clay and other minerals leads to the formation of carbon dioxide gas. The importance of these processes has been advocated by Germann and Ayres (1941), White (1957), Hurley et al. (1966), Muffler and White (1968), Panichi and Tongiorgi (1976), Barnes et al. (1984), Amundson and Kelly (1987), D'Amore (1989) and Cathelineau et al. (1989). Both contact- and regional metamorphism provide sufficiently high temperatures to release carbon dioxide from carbonate-silicate rock. Reactions proceed at temperatures ranging from 100–800 °C (Cathelineau et al. 1989; D'Amore 1989) and at depths of up to 5 km. The mineral products include chlorite, epidote, forsterite, wollastonite and more rarely portlandite, $\text{Ca}(\text{OH})_2$ dependent upon the composition of the associated country rocks, limestone impurities and fluid compositions. Portlandite may itself produce hyperalkaline groundwaters as noted above (Saines et al. 1980; Barnes et al. 1982). Some relevant reactions are shown in Table 1. Many of these reactions are easily reversible and some (e.g. iv) occur at moderate temperatures (100–150 °C) producing thermogene carrier within regions of average geothermal gradients and shallow depths. Such reactions are thought to occur in oil fields (Hutcheon and Abercrombie 1989) but their overall significance in travertine formation and CO_2 evasion in general is unknown.

While the reactions in Table 1 may proceed to the right, liberating gaseous CO_2 , the associated pressure-temperature field and activities/fugacities of the species involved are conjectural. Where geothermal gradients are high, such as regions of active vulcanism, or in mountain-building areas where hot radioactive rock underthrusts limestone, decarbonation could proceed at a low lithostatic pressure close to the surface. The overall significance of decar-

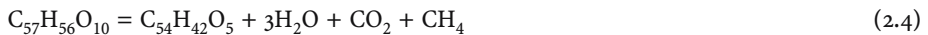
Table 1. Carbon dioxide generation by subsurface thermal processes. From Germann and Ayres (1941); Barnes et al. (1982, 1984) and Hutcheon and Abercrombie (1989)

A) Reactions between silicate minerals and carbonates	
i)	$2\text{CaMg}(\text{CO}_3)_2 + \text{SiO}_2 = \text{Mg}_2\text{SiO}_4$ (forsterite) + $2\text{CaCO}_3 + 2\text{CO}_2$
ii)	$\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3$ (wollastonite) + CO_2
iii)	$7\text{CaMg}(\text{CO}_3)_2 + 2.5\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite) + $3\text{H}_2\text{O} + 3\text{Fe}^{2+} + 3.5\text{O}_2 =$ $\text{Mg}_7\text{Al}_2\text{Fe}_3\text{Si}_5\text{Al}_3\text{O}_{20}(\text{OH})_{16}$ (chlorite) + $7\text{CaCO}_3 + 7\text{CO}_2$
iv)	$5\text{FeCO}_3 + \text{SiO}_2 + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (kaolinite) + $2\text{H}_2\text{O} = \text{Fe}_5\text{Al}_2\text{Si}_{13}\text{O}_{10}(\text{OH})_8$ (chlorite) + 5CO_2
v)	$4\text{CaCO}_3 + \text{K}_2\text{Al}_4\text{Si}_6\text{Al}_2\text{O}_{20}(\text{OH})_4$ (mica) + $6\text{SiO}_2 + 2\text{Fe}^{2+} + \text{O}_2 =$ $2\text{Ca}_2\text{Al}_2\text{FeSi}_3\text{O}_{12}(\text{OH})$ (epidote) + $2\text{KAlSi}_3\text{O}_8$ (feldspar) + $\text{H}_2\text{O} + 4\text{CO}_2$
vi)	$\text{CaCO}_3 + \text{H}_2\text{O} = \text{Ca}(\text{OH})_2$ (portlandite) + CO_2
B) Reactions of carbon and some of its non-carbonate compounds	
vii)	$\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$
viii)	$\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2$
ix)	$\text{CH}_4 + 2\text{H}_2\text{O} = 4\text{H}_2 + \text{CO}_2$
x)	$(\text{COOH})_2$ (oxalic acid) = HCOOH (formic acid) + CO_2 (decarboxylation)

bonation is disputed by some geochemists because of the relative ease of reaction reversal and restricted access to carbonates of hydrothermal fluids.

2.2.2.3 CO₂ from Heated Organic Matter

Most oil fields possess a cap of gas containing 1–5 vol-% carbon dioxide. Its origin is unclear but may include thermally-generated sources (Tiratsoo 1972; Hutcheon and Abercrombie 1989). Oil is also accompanied by large volumes of interstitial and ‘bottom’ connate water, often with a high alkalinity, though this may be due to the presence of organic acids rather than CO₂. Carbon dioxide also occurs with methane in coal and other carbonaceous deposits resulting from a low temperature reaction (Eq. 2.4; Tiratsoo 1972):



A significant source of CO₂ may be the reaction between methane and ferric oxide (haematite) and could account for some gas field CO₂ (Eq. 2.5; W. F. Giggenback, *pers comm.*)



Few travertines seem to be associated with such processes. One example may be the Colusa Oil Spring, in California (Feth and Barnes 1979). Bituminous limestones in Greece also give rise to travertines containing hydrocarbons (de Boer et al. 2001) and others probably occur in the Pannonian Basin of central Europe.

Decarboxylation of organic acids occurs between 200–300 °C, but can begin as low as 100 °C due to cleavage of the weak C-COOH bond. The extent of decarboxylation is also dependent upon pressure and its geochemical significance is unclear at present.

2.2.3 'Orgamox' Waters and Other CO₂ Sources

Significant oxidation of buried (non-soil) organic matter can occur at low temperatures (0–30 °C) and it is conceivable that large quantities of carbon dioxide could be released by this process and dissolve in groundwater. This is clearly not a case of thermally-generated carbon dioxide but is likely to occur where there are shallow organic-rich sediments.

Deposits of peat have been suggested as a possible CO₂ source for the Plitvice travertines (Srdoc et al. 1983). Carbon dioxide is also formed in anaerobic waters and sediments by bacteria, particularly sulphate-reducers (Eq. 2.6):



Sulphate reduction may occur deep underground providing a suitable organic substrate is available, and may become a significant CO₂ source (Chapelle and McMahon 1991). Acetate fermentation by methanogenic bacteria may also produce carbon dioxide.

These processes could not be readily distinguished from the organic oxidation processes above using standard analyses of groundwaters but are included for the sake of completion. At least one minor travertine deposit probably results from this kind of process, namely the Harrogate Sulphur Springs of the UK. It has been classified as a 'cool orgamox' (cool non-soil organic matter oxidation) travertine (Pentecost 1996a).

Another uncommon but well-known process of CO₂ formation is by near-surface spontaneous combustion. This occurs within bituminous carbonates in Jordan, and also forms portlandite leading to extensive travertine deposition (Clark et al. 1991).

Carbon dioxide generation is also possible by the oxidation of pyrite. The resulting sulphuric acid could then react with carbonate to produce CO₂. Some Chinese caves have high CO₂ atmospheres as a result of this process which could lead to increased limestone solution (Waltham et al. 1993). Its relevance to carbonate deposition is unknown.

Thus three geochemical types of travertine, meteogene, thermogene and 'cool orgamox' may be distinguished. While the distinction can often be made on the basis of source water chemistry, intermingling of thermogene and meteogene waters can occur (Boni et al. 1980; Scheuer and Schweitzer 1981; Yoshimura et al. 2004), and a mixed water will result. A summary of the distinguishing features of meteogene and thermogene source waters is shown in Table 2. Cool orgamox waters have been excluded since too few have been recognised and investigated.

2.3 Other Classifications

Mention must be made of other limestone classifications since they may be applied to the travertines. Folk (1962) recognised three main limestone constituents: allochem (=grain); matrix (micrite) and sparite (cement). He also described four families of allochems; peloid, ooid, bioclast and intraclast. Using these, four families of limestone, capable of further subdivision were obtained, namely: 1) allochem cemented by sparry calcite; 2) allochem with micrite matrix; 3) microcrystalline limestone lacking allochems and 4) limestone with *in situ* organic remains – biolithites. Most travertines would fall under groups 3 and 4.

Another scheme was devised by Dunham (1962). Three subdivisions are made between limestones which are: 1) matrix-supported (lime mudstones and wackestones and micrite taken as <20 µm by Dunham); 2) grain-supported limestones (packstones and grainstones) and 3) biologically bound (boundstones) with a further category for crystalline limestones.

Table 2. Geochemical characters of the autochthonous travertines and associated waters

Origin		Carrier	DIC mmol L ⁻¹	pCO ₂ vol-%	δ ¹³ C (PDB‰) of travertine	pH	Typical morphology	Typical fabrics
Metegenene								
Evasive	Ambient	soil	2–8	1–10	–12 to –3	7–8.1	Stream crust, cascade, river dam, oncooids, stalagmites	Algal bushes and laminae, bryophy- tes and phytoclasts. Mouldic porosity
	Super- ambient	soil	2–8	1–10	–12 to +2	7–8.1	Stream crust, cascade, river dam	Algal bushes and laminae, bryophytes and phytoclasts. Mouldic porosity
Invasive		atmos- phere	<1	<0.03	–20 to –9	9–11	Stream crust, river dam	Limited biofabric, usually sinter-like
Thermogene								
		mantle, magma, decarbon- ation	12–50	20–70	–1 to +10	6–7	Mounds and fissure ridges	Bacterial and cyano- bacterial shrubs and laminae, abiogenic shrubs. Fenestral porosity.

Some travertines belong to this fourth category, whilst others may be described as lime mudstones and boundstones. Neither scheme is closely related to a particular depositional environment or origin and all schemes are complicated by post depositional change. However, they have found use in the description of travertine deposits, particularly where a range of different limestones need to be distinguished.

2.4 Sources of Bedrock Carbonate and Calcium

It is impracticable to classify travertines according to the source of bedrock carbonate mineral or calcium but these sources require consideration as they influence the distribution of travertine deposits. Most travertines originate from calcium bicarbonate waters, and these have been shown to arise, in most cases, from the reaction between dissolved carbon dioxide and a carbonate rock. The marine carbonates (calcite, dolomite) are the most abundant carbonate source in the Earth's crust. Of these, calcite is more rapidly dissolved by CO₂ solutions and travertines are often uncommon in regions underlain entirely by dolostones. Continental carbonates such as older travertines, calcretes and lake marls may themselves provide a carbonate source for further travertine deposition but this has been little documented. Another source is carbonatite, an uncommon igneous rock containing a high proportion of calcite and/or dolomite (Deines 1989). Carbonatites are widespread along the African Rift where they have been identified with at least two travertines (Holmes 1965; Casanova and Hillaire-Marcel 1992). Another calcium-containing carbonate, ankerite (Ca,Fe,Mg)CO₃ occurs in metamorphic rocks and occasionally provides the calcium source for travertine (Spötl et al. 2002). Other carbonates include magnesite (MgCO₃), siderite (FeCO₃), natron (Na₂CO₃ · 10H₂O) and trona (Na₂CO₃ · NaHCO₃ · 2H₂O). It is not known to what extent, if any, they serve as a CO₂ source.

Calcium enters solution mainly from limestones of varying purity. Gypsum can be a significant source in some regions leading to common-ion precipitation. Thermogene waters may undergo bedrock reactions allowing calcium to enter from other sources. For example it can be removed from the biotite of gneisses and from anorthite during kaolinisation (Yoshimura et al. 2004). There are several stable isotopes of calcium but no attempts have yet been made to use them as tracers.

The Travertine Fabric

This chapter describes the fabric of travertine under two main headings, the microfabric and the mesofabric. The former relates to mainly microscopic characters identifiable in thin section and the scanning electron microscope (SEM), and the latter to characters visible mainly in hand specimens visible to the naked eye. Microscopic characters are by far the most important and lead to an understanding of travertine formation, its subsequent mineralogical history (diagenesis) and provide explanations for many of its physical characteristics. Meso-fabrics merge with microfabrics but permit discussion of travertine porosity and banding, both of which provide characteristic features of the rock, and are normally evident in polished hand specimens. They also include descriptions of small mobile forms of travertine known as ooids and oncoids.

Many factors are responsible for the fabric of travertines. In speleothems, Frisia et al. (2000) list seven: kinetics of growth processes, discharge, carbonate mineral supersaturation, CO₂ evasion rate, presence of growth inhibitors, ion transport mechanism and temperature. For the epigeal travertines there are additional factors such as plant growth characteristics and animal burrows. In addition, most of these factors have multiple effects and are interdependent. For example, discharge affects the hydrodynamics at the travertine surface (laminar or turbulent flow) influencing the CO₂ evasion rate, as well as providing energy which can be used to build oncoids and form clastic travertines. These factors will be discussed more fully in Section 10.5. Here, the emphasis will be upon structural features of the fabric, rather than its genesis.

3.1 The Microfabric

Fabric refers to the textural and structural features of a rock on a range of scales, including spatial relationships between the constituent mineral grains to the degree of lamination and the jointing system, where present. Important textural features are grain size, grain shape and the relationships between adjacent mineral grains. As a limestone, the great majority of travertine grains are of calcium carbonate, either as calcite or aragonite. Individual calcite grains, often consisting of single crystals, vary greatly in size, from submicroscopic (<0.2 μm) to macroscopic (>10 mm), while aragonite usually occurs as microscopic acicular crystals. The term *micrite* is commonly used for the fine-grained calcite <5 μm in diameter, and is the major constituent of many limestone matrices, with *microspar* used for crystals in the range 5–15 μm (Folk 1959). Unfortunately, these definitions have not been adhered to universally. Special terms are also used for grain shape. Equant crystals are approximately equidimensional and are common in travertine. Grains without distinguishable crystal faces are termed *anhedral*, those showing at least one plane crystal face are *subhedral*, while grains showing well developed rational faces throughout are termed *euhedral* (Bates and Jackson 1987). Micrite is normally equant and