Roman aqueducts and Calcareous sinter deposits as a proxy for

environmental changes

Dissertation

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Abstract

The ancient cities of Aspendos and Patara, located in southern Turkey, were two very important trade centers for Roman era with a dense population. Aqueducts supplied both cities with water that deposited calcium carbonate in their channels, here referred to as calcareous sinter. In this study, laminated sinter deposits from the water channels are investigated by geochemical and petrographical analysis to determine the nature of laminae couplets and to try and correlate them with seasonal environmental changes.

Along both aqueduct lines, samples were taken from several locations to see if there was any variation in the nature of sinter due to changes in slope of the water channel or channel type. Laminated calcareous sinter deposits were examined by optical microscopy and EBSD (Electron Backscatter Diffraction) analysis to investigate crystal shape and orientation in different laminae couplets. EPMA (Electron Probe Micro-Analyzer) analysis was used to determine major element distribution and stable isotope analysis showed the seasonal temperature variations in the water. LA-ICP-MS (Laser Ablation- Inductively Coupled Plasma-Mass Spectrometry) trace element analysis was implemented to find small changes in minor elements. Based on these analyses, it was concluded that laminated calcareous sinter deposition can record seasonal changes in water chemistry, temperature and degassing rate during the year, besides lateral changes due to aqueduct structure and slope. Calcareous sinter deposits show a noticeable lamination of fine-grained, porous and coarse-grained, dense layers, which were shown to correspond to dry and wet seasons respectively. Fine-grained layers show high epifluorescence due to an organic rich content, which may be a result of bacterial activity during the dry, warm season. Stable oxygen and carbon isotope curves also correspond to seasonal variations in different laminae couplets; especially δ^{18} O curves reflect annual changes in temperature and seasonal changes in discharge. The most important result is that periodicity in δ^{18} O is caused by warming of water in the aqueduct channel, and not due to evaporation or source water characteristics. Periodicity in δ^{13} C is of a more complex nature, but mostly, δ^{-18} O and δ^{-13} C have anti-correlation along the laminae couplets. This is probably mainly due to degassing inside the aqueduct channel. Trace element results are mostly inconsistent and do not show significant and repeated changes through the different laminae couplets, although Magnesium, Strontium and Barium isotopes have positive correlation with each other in some samples and reach highest values within fine-grained, porous layers. In addition to this, major element results show that Iron, Potassium, Silicium and similar detrital elements reach relatively higher values inside the fine-grained, porous layers.

Precise dating of calcareous sinter deposits is desirable, but should be very precise since the age of the aqueducts is already fixed by archaeological constraints within 200-300 years. Paleomagnetic and ¹⁴C dating has not given satisfactory results, and U/Th is hampered by high initial Th in the samples; however dating of a test sample from the Béziers aqueduct gave promising results.

Deposition mechanisms and geochemical evolution of laminated sinter can be better understood if modern analogues of sinter deposition in water channels can be investigated. Another on-going project of this PhD work is the monitoring of sinter deposition and seasonal water composition changes in some still working aqueduct sites. The aim is to investigate recent environmental conditions that generate calcium carbonate deposition in aqueduct channels. First results show that few regular seasonal changes exist in the isotopic composition of the source water, and that observed periodicity in stable isotopes must be due to changes in the channel itself.

In conclusion, calcareous sinter deposits from Roman aqueducts show promising results for practical use as environmental and archaeological proxies, especially for the Roman Era. This study only gives first results on two aqueducts. Further study of more aqueducts, combined with dating and more monitoring on still functioning aqueducts will give more precise results, and can lead to exploration of a new proxy for ancient climate, archaeology, and possibly archaeoseismology.

Zusammenfassung

Die, im Süden der Türkei gelegen, antiken Städte Aspendos und Patara, waren in der Römerzeit zwei bedeutende Handelszentren mit hoher Bevölkerungsdichte. Aquädukte versorgten beide Städte mit carbonathaltigem Wasser, wobei sich Kalksinter (Calciumcarbonat) in der Kanalrinne ablagerte. Dabei lagern sich im Wechsel eine hellere und dunklere Kalksinterlage ab, die als Sinterpaar bezeichnet wird. Um die Entstehung dieser Sinterpaare besser zu verstehen, und die beteiligten Prozesse mit saisonalen Veränderungen der Umwelt zu korrelieren, werden in der vorliegenden Arbeit laminierten Sinterablagerungen mit geochemischen und petrographischen Methoden untersucht. Entlang der Kanalrinne beider Aquädukte wurden an mehreren Stellen Proben entnommen. Es wurde untersucht in wieweit sich die Sinterstruktur aufgrund von Änderungen in der Neigung des Wasserkanals oder des Kanaltyps ändert. Um die Kristallform und die kristallografische Orientierung der Kristalle innerhalb der verschiedenen Sinterpaare zu untersuchen, wurden die entnommenen laminierten Kalksinterablagerungen mit Hilfe optischer Mikroskopie und EBSD (Electron Backscatter Diffraction) analysiert. Der Electron Probe Micro-Analyzer (EPMA) wurde verwendet, um saisonale Schwankungen der Hauptelementverteilung und den Anteil der stabilen Isotope im Wasser zu bestimmen. Die LA-ICP-MS (Laser Ablation-induktiv gekoppeltem Plasma-Massenspektrometrie) Spurenelementanalyse wurde durchgeführt, um kleinste Schwankungen der Spurenelemente zu finden. Basierend auf diesen Analysen wurde festgestellt, dass laminierten Kalksinterablagerungen laterale Änderungen in der Aquäduktstruktur und -neigung, jahreszeitliche Änderungen der Wasserchemie, der Temperatur sowie der Entgasungsrate während eines Jahres widerspiegeln. Die Kalksinterablagerungen zeigen eine deutliche Laminierung in Form von feinkörnig-porösen und grobkörnig-dichten Schichten, die trockene und nasse Jahreszeiten anzeigen. Feinkörnige Schichten zeigen eine hohe Epifluoreszenz aufgrund reichhaltiger organischer Inhalte, die vermutlich eine Folge der bakteriellen Aktivität während der warmen und trockenen Jahreszeit sind. Stabile Sauerstoff und Kohlenstoff-Isotop-Kurven entsprechen auch den jahreszeitlichen Schwankungen der verschiedenen Schichtenpaare. Vor allem δ¹⁸O spiegelt jährliche Veränderungen in der Temperatur und jahreszeitliche Veränderungen des Abflusses wieder. Das wichtigste Ergebnis ist, dass die Periodizität von 8¹⁸O durch Erwärmen des Wassers im Wasserkanal und nicht durch die Verdunstung oder der Brunnenwasser-Charakteristik verursacht wird. Die Periodizität von δ^{13} C ist komplexer Natur, vor allem zeigen δ^{18} O und δ^{13} C eine Antikorrelation entlang der Lamellenpaare. Dies wird wohl vor allem durch Entgasungsprozesse im Aquädukt verursacht. Die Ergebnisse der Spurenelemente sind meist inkonsistent und zeigen keine signifikanten Veränderungen in den verschiedenen Lamellenpaaren. Die Isotope Mg, Sr und Ba zeigen hingegen bei einigen Proben eine positive Korrelation und erreichen Höchstwerte innerhalb feinkörnig-poröser Schichten. Auch sind die Hauptelementwerte von Fe, K, Si und anderer detritischer Elemente innerhalb der feinkörnige-porösen Schichten maximal. Eine genaue Datierung der Kalksinterablagerungen ist wünschenswert, da der Zeitraum, in dem die Aquädukte aktiv waren, bereits archäologisch auf 200-300 Jahre festgelegt wurde. Paläomagnetische und ¹⁴C-Datierung geben keine brauchbare Ergebnisse. Die U/Th Isotopie wird durch eine hohe Anfangskonzentration von Th in den Proben behindert. Trotz dieser Schwierigkeiten war eine U/Th Datierung an einem Testbeispiel des Béziers Aquädukt erfolgreich. Mit Hilfe von analogen Untersuchungen an aktiven Wasserkanälen der heutigen Zeit, werden die Ablagerungsmechanismen und die geochemische Entwicklung der laminierten Sinterschichten besser verstanden.

Ein weiteres laufendes Projekt dieser Doktorarbeit ist die Überwachung von Sinterabscheidungen und der saisonale Zusammensetzung des Wassers an einigen heute noch aktiven Aquädukten. Das Ziel ist die Untersuchung der jetzigen Calciumcarbonatabscheidungen in Aquäduktkanälen unter den heutigen Umgebungsbedingungen. Erste Ergebnisse zeigen, dass kleine regelmäßige jahreszeitliche Veränderungen in der Isotopenzusammensetzung des Wassers vorliegen, und dass die beobachtete Periodizität der stabilen Isotope aufgrund von Änderungen im eigentlichen Kanal entstanden ist. Die Untersuchung von Kalksinterablagerungen in römischen Aquädukten liefern vielversprechende Ergebnisse, für die Untersuchung des Paläöklimas, der Archaeoseismologie und anderer Umweltbedingungen in der Römerzeit. Diese Studie beschränkt sich auf zwei Aquädukte. Die Untersuchungen weiterer Aquädukte und einer Überwachung, der noch in Betrieb stehenden Aquädukte werden genauere Ergebnisse liefern.

Özet

Türkiye'nin güneyinde yer alan Aspendos ve Patara, özellikle Roma döneminde yoğun bir nüfusa sahip olan, ticaret merkezleri olup, bugün ise çok sayıda turistin ziyaret ettiği antik şehirlerdir. Antik Roma döneminde her iki şehrinde, kalabalık nüfusuna yetecek miktarda su temin edebilmek icin Romalı mühendisler uzun ve inşaası oldukça zor, bugün bile zihinlerde o dönemde, kısıtlı teknolojik imkanlarla, nasıl yapıldığına dair soru işaretleri barındıran, su kemerleri inşaa etmişlerdir. Bu doktora çalışmasının temelini oluşturan karbonat çökelleri bir başka deyişle sinter çökelleri ise, bu su kemerlerinin üzerindeki su kanalları içerisinde, ya da, toprağa gömülü, aynı su yolunun parçası olan kiremit su boruları içerisinde, muhtemelen antik Helenistik ve Roma döneminden bu yana taşınan su vasıtasıyla biriken tortu çökellerdir.

Bu doktora çalışmasının esas amacı, çeşitli arazi çalışmalarıyla Patara ve Aspendos antik kentlerinde konumlanan su kemerlerinden elde edilen söz konusu laminalı karbonat çökellerinin doğal yapısını, jeokimyasını araştırarak, antik çağlardaki çevre ve iklim koşullarına ışık tutmaktır. Bununla birlikte, bugün halen başka amaçlarla da olsa kullanılmakta olan, antik döneme ait su yollarının çalışma prensiplerini inceleyip, gözlemleyerek, bugünkü iklim ve çevre koşulları büyüteci altında, fosil sinter oluşumuna yorum getirebilmek ve bu sinter çökellerinin oluştukları dönemlere ait iklim ve çevre koşullarını ortaya koyabilmektir. Bu amaçla, söz konusu sinter ya da diğer bir deyişle karbonat çökelleri, çeşitli jeokimyasal ve petrografik analizlere tabii tutulmuştur. Optik mikroskopi ile ince kesitlerin yorumlanmasının ardından, duraylı oksijen (δ¹⁸O) ve karbon (δ¹³C) izotop analizleri ile, izotopların, farklı laminalı çökeller içerisinde gösterdiği mevsimsel ve yıllık değişimleri, yani salınımlarına bakılmış; esas (EPMA, elektron-prob mikroanalizör) ve iz element (LA-ICP-MS, laser ablasyon indüktif eşleşmiş plazma kütle spektrometresi) analizleri ile ise çökel içerisindeki her iki element grubunun dağılımı incelenmiş; Raman spektrometri yöntemi ile kristal çeşitliliği ve EBSD analizi (elekron geri saçılım kırınımı) ile kristallerin şekli ve farklı lamina çiftleri içerisindeki oryantasyonu incelenmiştir.

Tüm analiz calışmalarının sonucu ortaya koymuştur ki, sinter çökelleri, su kimyası, sıcaklık ve gaz çıkısında meydana gelen yıllık değişimleri muhafaza etmekte olup, ince-taneli, poroz ve iri-taneli, sık lamina çiftlerinin ardalanması sonucu oluştuğu ve bu lamina çiftlerinin anılan sıraya göre, kurak ve yağışlı iklimsel koşulları temsil ettiği sonucuna varılmıştır. İnce-taneli, poroz tabakalar, nispeten yüksek epifloresans özellik göstermekte olup, bu durumun, kurak ve sıcak koşullardaki artan bakteri aktivitesiyle alakalı oldugu düşünülmektedir.

 δ^{18} O e ğisinde görülen periyodik salınımların, muhtemelen sıcaklık ve su akışında meydana gelen mevsimsel değişimleri yansıttığı sonucuna varılmıştır. δ^{13} C eğrisindeki salınımların izahi ise çok daha komplike olup, daha çok su kemeri farklı noktaları boyunca ve özellikle mevsimsel olarak değişen gaz çıkışlarıyla direkt bağlantılı olduğu düşünülmektedir. Genel olarak δ^{-18} O ve δ^{-13} C eğrileri farklı lamina çiftleri boyunca negatif korelasyon göstermektedir. Ana element analizleri sonuçları göstermiştir ki; demir (Fe); silisyum (Si) ve potasyum (K) gibi kırıntılı malzemeler, ince taneli tabakalar içerisinde zenginlik göstermektedir. İz element analiz sonuçları ise, maalesef çalışmaya fazla yarar getirmemekle beraber; magnezyum (Mg), stronsium (Sr) ve baryum (Ba) genel anlamda, göreceli bir şekilde yine ince-taneli ve poroz laminalar içerisinde zenginleşmektedir. Sinter çökellerinin yaşlandırılması hususunda maalesef yine birçok problemle karşılaşılmış ve henüz devam etmekte olan çalışmalardan sadece bir tanesinden, yaş verisi elde edilmiştir; Béziers (Güney Fransa) su kemerine ait sinter örnekleri U/Th (Uranium/Toryum) ile yaşlandırılmıştır ve elde edilen sonuç, daha önceki yaşlandırma sonuçlarına oldukça yakın bir yaş elde edilmiştir. Paleomanyetik yaşlandırma ise tatmin edici sonuçlar vermemiştir.

Günümüzde halen aktif olarak çalışan, çok az sayıdaki su kemerlerinin gözlemleme çalışması, hem sinter birikimine neden olan, bugünkü çökelme koşullarının incelenmesi, hem de antik döneme ait iklimsel ve çevresel koşulların ortaya konması bakımından çalışmamızın oldukça önemli bir parçasıdır. Bu çalışma kapsamında, hem *in-situ*; pH, su sertliği, elektrik iletkenliği gibi su özellikleri, hem de laboratuar ortamında su analizleri üzerinde duraylı isotop ve iz element analizleri yapılmaktadır. Bununla birlikte modern koşullarda oluşan, günümüze ait sinterlerin incelenmesi icin, hazırlanılan metal ekipman, sinter çökelinin üzerinde birikmesi için, kanal boyunca çesitli bölgelere yerleştirilmiştir.

Sonuç olarak, Roma dönemine ait su kemerleri içerisinde biriken karbonat (sinter) çökelleri, hem çevresel koşulların çalışılması, hem de arkeolojik çalışmalara destek olması bakımından oldukça önemli ve umut veren bir ajan malzemedir. Diğer, benzer özelliklerdeki su kemerlerinde yapılacak ayrıntılı çalışmaların yanı sıra, yaşlandırma ve gözlemleme calışmalarının birlikte değerlendirilmesi, bu yeni proksi, sinterin daha iyi anlaşılmasında ve daha faydalı bir şekilde kullanılması bakımından önemli bir hedef calışmadır.



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

Charles Lyell, 1829

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Goal and development of this PhD study

This thesis is the first extensive and multidisciplinary work on calcareous sinter deposits from Roman aqueducts.

The main aim of this study was to investigate the nature of calcium carbonate deposits from different Roman aqueduct sites to compare them with other terrestrial carbonate examples from similar settings and to try and see whether these deposits can be used for palaeo-environmental studies, and for applications to reconstruct climatic conditions during Roman times. Another objective was to contribute useful information to archeology by investigation of calcareous sinter samples. Important topics are the age of aqueduct construction and use; the history of their functioning; data on water quality and its history by means of geochemical analysis; identification of the water source if various possibilities exist; and data on the transported water volume from sinter thickness using flow quantity equations such as the Manning-Stricker equation (Chapter 3 and 5). These data can indirectly shed light on the population and economic prosperity of ancient cities. Quantitative data from the Roman epoch are scarce and it would be undoubtedly useful to obtain new data about this time of world history from a sedimentary deposit that we see today as just a nuisance in our water taps, a potential treat of blocked water pipes. On that score, this work is a contribution to several branches of science by highlighting one of the more rarely studied materials in the world.

Although the main subject of this study was to investigate Roman aqueducts and their calcareous sinter deposits in general, the work mostly concentrated on sites in Turkey because numerous well-exposed aqueducts on which archaeological work was already done are available here. The results of this study are presented here as two papers, one in print, the other is submitted (Chapters 2, 3). The main results of this study are from the ancient cities of Patara and Aspendos on the south coast of Turkey, which were chosen for their relevance, their sinter quality and sampling convenience. The focus was to investigate lamination in these selected aqueducts and to investigate their suitability as a data source. The work focused on the alternating laminae couplets and origin of calcareous sinter deposits from the Roman aqueduct channel, and on factors that play a role in laminae coupling using careful field and laboratory analysis.

Originally, the idea was to work on the deposits of a number of neighboring aqueducts using geochemical analysis, in order to reconstruct climate changes during the Roman Period in the study area. The reason to limit and focus our aim further was that calcareous sinter deposition in Roman aqueducts is more complicated than was expected initially, and no other systematic studies have yet been published on the subject. In order to understand the aqueduct systems and the calcareous deposits in them, intensive fieldwork was carried out on the selected aqueducts, and *in-situ* observations were made on different part of the water ways such as channel sections on slopes, channel sections in plains, bridges, tunnels and inverted siphons. As many samples as possible were obtained, within the limits set by archaeological permits, in order to make a comparison amongst them in terms of response to external factors. All conceivable factors that can cause different laminae coupling in channel deposits were considered, even in terms of their microbiology. Several other aqueduct sites in Turkey and Greece were visited for comparison, considering their possible different response to different local weather and geological properties. Comparison of calcareous sinter in Roman aqueducts and other terrestrial carbonate deposits allowed to determine their discrepancies by considering the different processes that played a role in their formation.

In addition to studies of fossil calcareous sinter deposits and aqueducts, the first monitoring studies on still functioning ancient aqueducts were set up with the aim to study modern conditions of calcium carbonate deposition in the channels, to sample modern sinter deposits and compare them with the results of the fossil deposits. Today, one of sites in Galermi, Sicily, has been an ongoing monitoring project since November 2010. Ultimately, the whole work, by synergy of different disciplines such as geology, archeology, geochemistry, hydrology and freshwater biology creates the first multi-disciplinary study of an ancient system to understand climatic conditions of the Roman Era. So far, present publications on this subject did not receive much attention. In this thesis, several themes are treated, from principles of taking sinter samples to factors that we should consider to understand the ancient water systems. Comprehensive work on calcareous sinter geochemistry has shown that there are still a lot of questions that need to be answered by observing the nature of the deposits and the surrounding geological and climatological settings.

Terminology

Since this thesis deals with a multidisciplinary subject, some terminology will crop up, which might not be understood by readership of one of the relevant disciplines. The most important terms used in this thesis are:

- * Aqueduct a water transportation system, including water channel, bridges, tunnels and other elements
- Inverted siphon a closed water pipe under pressure that transports water across a valley at a lower level than the rest of the water transport system (in Chapter 1, *Figure-20*)
- Venter bridge a low and usually wide bridge built to carry water pipes of a pressure line or an inverted siphon across the deepest part of a valley (in Chapter 1, *Figure-20*)
- * Castellum aquae the final distribution installation that is present at the end of a Roman aqueduct as a transition to the urban water distribution system (in Chapter 1, *Figure-18*)
- * Specus the channel of an aqueduct (in Chapter 1, Figure-14)
- Opus signinum a red, cement containing crushed tiles, used by the Romans to waterproof the inside of a water channel



Cross section through the aqueduct of Cologne showing the concrete base of the channel (grey), a layer of opus signinum with fragments of red crushed tile in cement, and on top a thick package of calcareous sinter deposited by the aqueduct water.

* Cyclopic wall – wall built of large polygonal stones



Cyclopean wall of the Delikkemer inverted siphon of Patara, Turkey. A cyclopic wall is composed of large, polygonal stones.

- * Drop-shaft shaft in the aqueduct channel where its level drops abrubtly. This installation is meant to reduce the slope of the main channel (in Chapter 1, *Figure-15*)
- * Manhole access shaft to a buried aqueduct channel for maintenance and inspection. These shaft were the main source of ventilation for aqueduct channels (in Chapter 1, *Figure-14*)
- * Half-rounds –quarter-circular ridges of opus signinum inserted in the bottom corners of many aqueduct channels: it was probably done to avoid leakage (in Chapter 1, *Figure-11*)
- * Sicker gallery subterranean channel section at the head of an aqueduct with porous walls, that serves to capture ground

Chapter 1- Introduction

Terrestrial carbonates

Today, non-marine carbonate deposits are significant proxies which researchers use for paleoenvironmental studies by applying high-tech geochemistry methods. Classification of carbonates, however, has always been a problem, especially for non-marine carbonate deposits. There are many different deposits, but a discussion should be started with a treatment of the best-known and studied example, travertine deposits and especially concerning the difficulties which most of researchers faced to describe them in a consistent way.

Strabo (c. 20 B.C) is known as the first person to mentioned calcium carbonate deposition (encrustation) from hot springs at the ancient city of Hierapolis, Turkey, well known as Pamukkale (*Figure-1*). He writes:

"Near the Mesogis, opposite Laodicea is Hierapolis where are hot springs, and the Plutonium, both of which have some singular properties. The water of the springs is so easily consolidated and becomes stone that if it is conducted through water-courses, dams are formed consisting of a single piece of stone"..... "The conversion of water into stone is said to be the property of certain rivers in Laodiceia although the water is fit for the purpose of drinking" (Strabo Geography, Book 13).



Figure-1 A tomb at Hierapolis embedded in travertine, looking over the Denizli plain.

The Roman author Vitruvius (De Architectura) also remarks on carbonate deposits:

"In the same manner, at Hierapolis, in Phrygia, a large head of hot water boils up, and is conducted by ditches round the gardens and vineyards. At the end of a year the ditches become incrusted with stone; and hence, making yearly cuts to the right and left, they carry off the incrustations, and use them for building field walls." (*De Architectura* VIII, 3-10)

Although today we know that most terrestrial carbonate deposits form by degassing of surfacing carbon-dioxide rich groundwater, several publications considered temperature as the main factor for calcium carbonate

deposition, while others pointed out the importance of hydrological setting or the deposition process. Emig (1917) made one of the best early definitions by saying that depositions from streams and springs carry calcium bicarbonate in solution. Bates & Jackson (1987) defined travertine as "dense, finely crystalline, massive, with whitish color, having fibrous or concentric structure and formed by rapid chemical precipitation of calcium carbonate from surface and groundwater, by water turbulence or evaporation around the mouth or the conduit of a spring, in particular hot spring". Riding (1991) elaborated on the importance of high temperature for travertine deposition together with the dissolved materials in the warm water besides eukaryotic organisms.

One of the most recent and effective definitions for non-marine carbonate was given by Pentecost (2005), who put emphasis on chemical processes of carbon dioxide degassing from calcium bicarbonate solution leading to depositions of calcite or aragonite, located mostly around seepages, springs, streams and rivers. Porosity is variable in different types of deposits, from moderate, intercrystalline porosity, often highly mouldic (with secondary porosity) to framework porosity inside a vadose or rarely shallow phreatic environment. Evaporation and biological processes remain as minor factors.

Besides this terminology discussion, the classification of different type of terrestrial carbonate deposits should be discussed. The terminology for "tufa" and "travertine" has been used since Medieval times, but can lead to confusion, since there are transitions between both, and to other less common types of terrestrial carbonate deposits.

Koban & Schweigert (1993) classified terrestrial carbonate deposits depending on their origin, setting and visible porosity as shown in *Figure-2*. However, the diagram does not include all possible carbonate types nor all the factors of importance to be considered (Pentecost, 2005).



Figure-2 Diagram of terrestrial carbonates classification by Koban & Schweigert (1993)

Travertine is usually a warm water deposit with limited porosity, and it occurs in huge masses. Its name derives from the Latin "*lapis tiburtinus*", stone of Tibur (modern Tivoli), from the type locality of this deposit where it was quarried in large quantities close to Bagni di Tivoli for use as a building material because of its strength despite its porosity, and the ease by which it could be worked. Travertine was used to construct the Coliseum, the Trevi Fountain and many other buildings in the city of Rome and was mentioned by Vitruvius and Plinius in their books (*Figure-3*). Even today travertine is still a common building material in Italy and many European cities.



Figure-3 The Coliseum in Rome, standing for many centuries with supporting walls made of travertine¹

Tufa is formed from freshwater with ambient temperature, usually a combination of biologically induced physicochemical processes. In English speaking countries, calcareous tufa was used as a general term for tufa (Pentecost, 2005). Tufa is usually more porous than travertine and is common in rivers saturated or supersaturated with calcium carbonate, and near springs or cave entrances with the same water properties. It normally forms growing between and over plants, thus creating a strong porosity when these decay. The growth pattern of the plants also gives many tufa deposits a grained, wood-like texture. Tufa contains both microphytes and macrophytes and notably mosses and remains of biofilms. At cave entrances, deposition is increased by evaporation (Ford & Williams, 2007) (Figure-4). Several invertebrates may also be present in the complex ecosystem formed where tufa is deposited. Consequently, tufa is more micritic and porous by comparison to travertine which is deposited from thermal water and has a dense, more crystalline fabric with shrub-like bacterial growth structures (Banks & Jones, 2012, Ford & Pedley, 1996). The biological content of travertine is limited to cyanobacteria and bacteria (Flügel, 2004). Both travertine and tufa are deposited under daylight conditions, and therefore contain abundant photosynthetic organisms (Flügel, 2004). This is important, since such organisms consume CO₂, and therefore can change the delicate balance of carbonate solutions in water (Flügel, 2004). Travertine and tufa can form from deep, meteoric water, but also from soil-derived meteoric water.

¹ "Quandiu stat Colisaeus, stat et Roma; quando cadet Colisaeus, cadet et Roma; quando cadet Roma, cadet et mundus (While stands the Coliseum, Rome shall stand; when falls the Coliseum, Rome shall fall; and when Rome falls--the World." - Venerable Bede & Lord Byron).



Figure-4 Development of different kinds of carbonate deposits in a cave environment. Travertine is not shown, since it forms around hot springs (Frisia & Borsato, 2010).

Speleothems are another type of terrestrial carbonate deposits that form in caves from a soil-derived meteoric water supply; they are the end member of a structural range of freshwater carbonate deposits.

Tufa - Travertine - Calcareous sinter - Speleothem

(biomediated)

(inorganic end member)

Scheme of the different types of non-marine carbonate deposits and the influence of biomediation

Speleothems have a dense and laminated fabric due to a general lack of biological features formed by bacteria and algae, in contrast to tufa (Pedley & Rogerson, 2010). Speleothems have been extensively studied as possible proxies for palaeoclimate and palaeoseismology, over periods of tens of thousands to millions of years. Since speleothems form in the dark, their biological content is limited and lacks active photosynthetic organisms. Since caves are deeply buried and poorly ventilated, they also form at near constant temperature and humidity, and at predictable levels of atmospheric CO_2 . These factors make speleothems more suitable as a long-term proxy for palaeoclimate than tufa or travertine.

The most common and studied examples of speleothems are stalagmites, formed by drip-water. A less commonly studied speleothem deposit is *flowstone (Figure-5*). Flowstone is formed by degassing of a thin, uniform sheet of water that flows over cave surfaces with little variation in water level. It is similar to the aqueduct deposits described in this thesis. There are two different types of flowstone; subaqueous flowstone formed in relatively deep water, and subaerial flowstone that forms below a thin film of moving water (Hill & Forti, 1997). Flowstone is mostly deposited on floors or gently sloping areas of the cave settings. These deposits are more common at karst springs where rapid growth occurs due to evaporation and where light is available, leading to vegetation coupling. Although deepwater flowstone can give rather continuous deposits, shallow water flowstone shows growth layering with extensive hiatuses (Ford & Williams, 2007). Flowstone can be used

to investigate dry and very cold periods by looking at the interruptions they show in the normal, continuous deposition (Spötl et al, 2002, Drysdale et al, 2007). *Moonmilk (Figure-4)* is another cave deposit that is essentially the result of abundant bacterial activity and has two different fabrics; while it is wet it is pasty or plastic and it is powdery and fragile in its dry state (Hill & Forti, 1997). There are some examples of moonmilk from cave deposits and some from tufa sites, which show that continuous water flow and important bacterial activity are essential for moonmilk formation. If photosynthetic processes play a role, the result is an increase in supersaturation rate of the water by other means than degassing (Frisia & Borsato, 2010). *Calcrete* (caliche) is another type of calcium carbonate deposit, which mostly occurs by evaporation and CO_2 degassing, seen in moist soil surfaces with variable porosity, from powdery to nodular to highly indurated (Wright & Tucker, 1991). Best examples can be seen in warm and arid climatic zones (*Figure-5*).



Figure-5 Examples of some different types of non- marine carbonate deposits: (a) Calcareous sinter: (b) Travertine: (c) Speleothem (d) Tufa; (e) Flowstone and (f) Calcrete (b- http://www.oum.ox.ac.uk/, c- Treble et al., 2008, e- wikipedia.org, f – example from W-Australia (Photo Passchier)

The scheme given below by Gascoyne (1992) shows potential climatic indicators from cave calcite deposits, modified by Pentecost (2005) for meteogene travertine deposits, as follows:

Indicator	Possible palaeoclimatic implication
Growth layers	low deposition rate; cool and arid conditions high deposition rate; moist and warm conditions
Internal stratigraphy	changes in fabric, color or growth hiatus indicator of possible abrupt climate change
Alteration in calcite ¹⁸ O	variation in water ¹⁸ O content and/or deposition temperature: rainfall; air temperature; evaporation
Alteration in calcite ¹³ C	variation in ¹³ C of source water content and/or calcite precipitation process; soil or plant flora change and/or productivity; evaporation; temperature
Alteration in trace elements	variation in water composition and/or deposition temperature

Calcareous sinter

The subject of this study, calcareous sinter deposits from Roman aqueducts, is a rather curious example of nonmarine carbonate deposits, with regular laminae couplets and occasionally distinct layers in this clear regularity.

Calcareous sinter has several similarities with other terrestrial deposits such as speleothem, flowstone, travertine or tufa deposits from comparable settings. The deposits were already described by Sextus Julius Frontinus in his first Century CE treatise on the aqueducts of the city of Rome: "...*limo concrescente, qui interdum in crustam indurescit, iter aquae coartatur* (the accumulation of a deposit, which sometimes hardens into a crust, contracts the channel of the water)" (Frontinus, Book II, 122). *Sinter*, a term originally from Germany, was also used to describe travertine deposits (Damm, 1968), although the travertine in Bagni contains shrubs structures that may have formed by bacterial activity (Chafetz & Folk, 1984). Originally, Pia (1933) suggested using sinter as a term to describe inorganically formed deposits that are denser and more compact than tufa. However, sinter is also used to describe silica deposits from water (Boudreau & Lynne, 2012). In order to avoid confusion to readers, here the term "calcareous sinter" or "aqueduct sinter" is used to describe the carbonate deposits from aqueducts.

As mentioned above, calcareous sinter differs especially from tufa and travertine deposits by its almost abiotic origin and low porosity. It mostly develops as a result of physico-chemical and less effective biological activities. On the other hand, calcareous sinter has the same type of source as other freshwater carbonate deposits and is also laminated. However, laminae couplets have a different fabric as in other carbonate types (Flügel, 2004; Pedley, 1990).

The lamination seen in most terrestrial carbonate is as a result of cyclic changes in growth rhythms during the sedimentation of the deposits. This is sometimes related with rhythms in biological activity, especially in tufa and travertine. These laminations can be daily or seasonal, or due to another external rhythm in the regional climate.

Detailed study of lamination in aqueduct sinter is of relatively recent date (Passchier & Sürmelihindi 2010; Carlut 2011; Sürmelihindi et al, submitted). Older, mostly German publications give the first interpretations and descriptions of layering in Roman aqueducts, mostly those of Cologne in Germany and Nîmes and Fréjus in Southern France (Eick, 1867; Schmitz 1978; Baatz, 1978; Gilly, 1971; Gilly et al., 1978; Adolphe, 1973; Brinker, 1986; Guendon & Voudoir, 1986; Hauck et al., 1987; Blackman & Grewe, 2001). Alternating laminae in calcareous sinter were for the first time investigated in detail by Fabré & Fiche (1986) with their work on sinter deposits from the Nîmes aqueduct where they counted laminae couplets as annual. Other work mainly focused on solving archaeological problems (Blanc, 2000; Gebara, 2002; Guendon & Leveau, 2005) and questions about the provenance of water in the Roman aqueducts of Nîmes (Gilly, 1986; Fabré et al., 2000; Joseph, 2000; Rodier, 2000; Carbon et al., 2005; Volant et al., 2009), Fréjus (Guendon et al., 1998; Dubar, 2006; Bobee et al., 2011), Pompeii (Ohlig, 2001; Matsui, 2009) and Ostia (Keenan-Jones et al., 2008; Carlut et al., 2009). Palaeoclimate data were recorded from calcareous sinter by Garczynski et al (2005) and Dubar (2006). Aqueducts damaged by earthquakes have been reported from Italy (Galli & Naso, 2009; Galli et al., 2010), Syria (Meghraoui et al., 2003; Sbeinati et al., 2010) and Nîmes in France (Levret et al., 2008; Volant et al., 2009), showing that aqueducts can provide information on seismic activity during the past 2000 years in the Mediterranean. However, none of these authors has so far systematically investigated the microstructure of aqueduct sinter. This is one of the reasons why we have chosen to study aqueduct sinter from the dual perspective of research in structural geology and palaeoenvironmental studies.



Figure-6 Two common types of calcareous sinter from Roman aqueducts: (a) Tufa-type deposit with a high organic component, Aristion aqueduct of Ephesus, Turkey; (b) Dense, crystalline speleothem-type sinter with low organic component, Patara aqueduct, Turkey.

Most terrestrial carbonates show a layering defined by variations in color, microstructure, or varying concentrations of trace elements or organic compounds (Ford & Williams, 2007). This layering is usually interpreted as an effect of changes in water composition, temperature and biological activity (Pentecost 2005; Pedley & Rogerson, 2010). In most deposits, part of the layering is regular with near constant thickness, and is therefore interpreted to be annual (*Figure-6*). However, in most cases, this is only an assumption and not proven by independent methods. Many other types and frequencies of laminae and layers may occur on shorter or longer time scales. The main difficulty in unraveling the nature and origin of layering in terrestrial carbonates is the complex environment in which it forms, and the many uncontrolled factors that can influence the microstructure and chemistry of the deposits. In this Thesis, layering in calcareous sinter was found to be an effect of different rates of accumulation, and different crystal morphology and porosity derived from organic content. Details are discussed in Chapters 2 and 3. The alteration that we can see in terrestrial carbonate deposits may give information about palaeohydrology of the setting area and seasonal changes in regional climate.

Calcareous sinter has some advantages in comparison to similar terrestrial carbonate deposits. Contrary to the hydrology of most natural terrestrial carbonate deposits, water flow in Roman aqueducts is easier to understand and model: the aqueduct channels are rectangular structures of constant shape, width and slope, covered to avoid contamination, while the water level was kept relatively constant. Water in the channels was flowing without interruption for many decades, in some cases up to 800 years (Sbeinati et al., 2010). These factors set aqueducts apart as "long-term man-made experiments" in carbonate deposition, a high-resolution archive of layered carbonate that formed under controlled conditions over several centuries. As such, aqueduct sinter can act as an interesting high-resolution benchmark for studies of natural terrestrial freshwater carbonates.

By using calcareous sinter, it is possible to see small scale alterations, seasonal or even daily variations in climatic factors which are difficult to see in other carbonate examples, especially from caves due to their long deposition process by drip water. Lamination types in Roman sinter can be subdivided into annual, sub-annual, multi-annual, and event horizons (*Figure-7*). Annual lamination may result from the regular annual cycle in temperature and rainfall, and its annual nature can be proven as explained below. Sub-annual lamination is

usually irregular and may indicate minor environmental changes due to sub-annual fluctuations in the biological activity in the channel, the composition of the source water, or the water temperature. Multi-annual laminations are possibly caused by longer-term fluctuations in climate or spring aquifer characteristics. Moreover, to see anthropological aspects from the Roman era is interesting, especially for archaeology. Examples of this are evidence for cleaning out of an aqueduct, evidence for interruptions of the water flow for an unknown reason, and evidence for repairs and structural changes.



Figure-7 (a) Calcareous sinter from a 30 cm-wide ceramic tube in the Patara aqueduct. Three different event horizons are marked by arrows. The thickness of the sample is 8 cm; (b) Enlargement of the layering in typical sinter (Roman aqueduct of Sikyon, Greece) showing annual, sub-annual and multi-annual lamination. The height of this sample is 3 cm: the complete section was 42 cm thick. The annual nature of the regular layering in both samples is indicated by cyclic changes in the O-isotope composition across the laminae (Sürmelihindi et al, 2012).

Event horizons are commonly visible in calcareous sinter as erosion surfaces and discontinuities. Event horizons (*Figure-7*) are a conspicuous and interesting layering type; they stand out because of their thickness, colour, porosity and/or composition and apparently formed because more gradual changes in water chemistry and temperature were interrupted by a sudden event. Event horizons in carbonate deposits can have several causes: (1) climatic, such as floods or periods of extreme drought; (2) tectonic, such as earthquakes and landslides; (3) biogenic, such as a sudden increase in the abundance of certain organisms; (4) sudden changes in spring aquifer discharge and compositional characteristics; (5) in the case of Roman aqueducts: anthropogenic causes such as building measures, restoration, maintenance, or wanton destruction. Hence, event horizons can provide important information about extreme events and other sudden changes in the depositional environment.

Sampling principles

In cave studies, scientists prefer to work on stalagmite and flowstones rather than stalactites because of advantages of their internal structure and manner of growth. Generally, by using X-ray tomography, scientists can decide the preeminent site for sampling. For this study, we usually tried to sample where the whole stratigraphy is exposed. As a rule samples from ceramic pipes, which were commonly used on steep slopes, are preferred due to their dense fabric and relatively complete stratigraphy, which gives a large amount of information on the deposition history in Roman times. In masonry channels, samples from the lower side-wall and bottom are preferred since they will have the most complete stratigraphy. Sampling from the channel floor is another possibility, although samples tend to contain more sediment. Tufa from the outside of the channels and pipes, though often layered and of spectacular thickness, is avoided since its stratigraphy is almost certainly incomplete.

Formation of Terrestrial Calcium Carbonate

The deposition of calcium carbonate from water is a complex process on which a large volume of literature exists. The chemical details of the process are treated in geochemical handbooks such as Stumm & Morgan, 1996; Flügel, 2004; Pentecost, 2005 and Ford & Williams, 2007 and need not be repeated here. In this section, only the main outline of the process as it proceeds in Roman aqueducts is treated in a simplified manner (*Figures-9* and *10*).

CO2 gas dissolves and dissociates in water by four reactions, each with its own equilibrium constant

1.	CO_2 (gas) \leftrightarrow CO_2 (aq)	$[CO_2 (aq)] / CO_2 (gas)$	= 0.034 (K _H)
2.	CO_2 (aq) +H ₂ O \leftrightarrow H ₂ CO ₃	[H ₂ CO ₃] / [CO ₂ (aq)]	$= 1.70 \text{ x} 10^{-3}$
3.	$H_2CO_3^* \leftrightarrow H^+ + HCO_3^-$	$[{\rm H}^+]$ $[{\rm HCO_3}^-] / [{\rm H_2CO_3}^*]$	$= 4.3 \text{ x} 10^{-7} (\text{K}_1)$
4.	$HCO_3 \leftrightarrow H^+ + CO_3^{2-}$	[H ⁺] [CO ₃ ²⁻] / [HCO ₃ ⁻]	$= 4.7 \text{ x} 10^{-11} \text{ (K}_2\text{)}$

Reaction (3) forms bicarbonate ions and reaction (4) carbonate ions, while both reactions produce H^+ and therefore decrease the pH of the water. All equilibrium constants are temperature dependent and are given in this chapter for 25°C. *Figure-8* presents two commonly used diagrams for the distribution of carbonate species in water as a function of pH. The *Bjerrum plot* is used for a closed system, with constant total carbon C_T :

5. $C_{\rm T} = [{\rm H}_2 {\rm CO}_3^*] + [{\rm HCO}_3^-] + [{\rm CO}_3^{2-}]$

 C_T is total carbonate, the sum of H₂CO₃* (carbonic acid + CO₂ (aq)), bicarbonate and carbonate ions. The Bjerrum plot shows how the carbonate species distribution changes with pH, and that in the pH range of most aqueduct water, bicarbonate is the dominant species (*Figure-8a*). More realistic for a Roman aqueduct, however, is the *speciation diagram* (*Figure-8b*) that shows an open system, in contact with the atmosphere. It is similar to the classical Bjerrum plot for closed systems, but shows how total carbon increases with increasing pH since more CO₂ will be taken up by the water. Rain water, with only dissolved carbon dioxide will plot at around pH 5.7.

When calcium carbonate comes into contact with water, it dissociates into Ca⁺⁺ and carbonate ions according to:

6.
$$CaCO_{3} \leftrightarrow Ca^{2^{+}} + CO_{3}^{2^{-}}$$
 [Ca²⁺][CO₃²⁻] = 4.8 x10⁻⁹ (K_{sp})

Carbonate ions capture H^+ ions to form bicarbonate (reaction 4), while the other reactions (1-3) between carbonate species are also set in motion until equilibrium is reached again. If the water has taken up CO₂, a significant amount of calcium carbonate can dissolve, depending on the amount of CO₂ dissolved in the water (*Figure-9*).

Normally, it is not common for running surface water to show carbonate deposition because of the low ion content of freshwater. If this water is in equilibrium with atmospheric CO_2 , even if it is saturated in $CaCO_3$, there is equilibrium and no deposition will occur: only if the water becomes supersaturated in $CaCO_3$, deposition can take place. This can happen where water is enriched in CO_2 , so that more carbonate can go into solution. If calcium carbonate would dissolve in rainwater and run down an aqueduct, there would be no reason to form deposits unless the water would evaporate or increase in temperature (*Figure-9*). It could never form the huge thickness of carbonate deposits seen in some aqueducts. However, when rainwater enters the soil, it can take up a lot of CO_2 , which is produced by organisms in the soil (*Figures-9 and 10*). CO_2 levels in the atmosphere are presently at a partial pressure of 0.0004 bar, but in the soil it can increase up to 0.2 bar. When such CO_2 enriched water enters limestone below, it can dissolve a lot of the rock (*Figures-9 and 10*). Moreover, more CO_2 can dissolve in water under pressure, so when the water runs through deep caves, even more calcium carbonate is dissolved.



Figure-8 (a) Bjerrum plot with a linear vertical scale, giving fractions of carbonate species between 0 and 1, with relative fraction distribution. In this distribution diagram, equal amounts of the species occur at pH= 6.3 and pH=10.3. This diagram is valid for any total CO₂ concentration in a closed system. (b) Speciation diagram for carbonates at atmospheric CO_2 levels in an open system.

When an aqueous solution that is in chemical equilibrium, containing both a high CO_2 content and a high dissolved calcium carbonate level comes to the Earth surface and in contacts with the air, degassing of CO_2 will start. The process is defined by reaction (7) given below. The equilibrium reaction will move to the right by losing CO_2 to the air. Meanwhile, dissolved calcium carbonate is deposited as solid matter (Hill & Forti, 1997).

7. $Ca^{2+}+2 HCO_3 \bigoplus CaCO_{3(solid)}+H_2O+CO_{2(gas)}$

This deposition process will start when water becomes saturated in $CaCO_3$ due to decompression or degassing (*Figures-9 and 10*). If it only happens by degassing, the first deposits may therefore occur some distance from the source (*Figure-10*). The process will continue until the CO_2 level in the water is in equilibrium with that of the atmosphere (reaction 1). After that, no further deposition is possible, so that also the last parts of an aqueduct are commonly free of deposits. However, everywhere along an aqueduct, even in sections without deposits, thick tufa masses can form on the outside of a leaking or overflowing channel: this happens because there evaporation and photosynthesis of plants enhance deposition. Photosynthesis causes removal of CO_2 from the water in the daytime and drives equation (7) to the right.

If water has a high concentration of calcium carbonate and high CO_2 levels, turbulence, which increases CO_2 degassing may start calcite precipitation (*Figure-11a*). Since CO_2 is a gas, calcium carbonate precipitation is also enhanced by an increase in temperature. Especially where water temperature increases due to solar radiation on an aqueduct, this may lead to calcite precipitation (Gischler, 2011). In this respect, travertine may seem unusual because it forms in cooling water, and calcium carbonate is more soluble in cold than in warm water. However, it is degassing and photosynthetic biochemical activity which is more important than cooling, and leads to deposition of travertine.

Formation of Calcareous sinter

In order to understand the deposition of calcareous sinter, consider *Figure-9*. For a certain amount of CO_2 dissolved in water as $H_2CO_3^*$ and its derived carbonate species, there is a maximum amount of calcium carbonate that can dissolve, given by the curves in *Figure-9a*. Three curves are shown for three different temperatures, illustrating the fact that calcium carbonate can dissolve better in cold than in warm water. The vertical black line illustrates the atmospheric CO_2 concentration. If $H_2CO_3^*$ in the water is in equilibrium with atmospheric CO_2 , about 57 mg of calcium carbonate can dissolve in one litre at 20 °C.

The coloured tracks in *Figure-9c* illustrate what can happen with water before and during its path to and through an aqueduct. Three possible scenarios are given, while many others are possible. In all cases, rainwater in equilibrium with atmospheric CO₂ pressure (R) passes through the soil where CO₂ partial pressure can be 500 times bigger than the partial pressure in the atmosphere. There the water absorbs large quantities of CO₂, which dissociates according to the reactions (1-4) given above. When the water enters limestone or marble (*Figure-9c -L*), it stops absorbing CO₂ and starts dissolving calcium carbonate according to reaction (6), leading to a sharp upwards turn of the graph; this may proceed until the water is saturated in carbonate (curve 1), but may also stop at a lower level (curve 2 and 3), especially if the rock is not pure limestone, or if water moves rapidly through the rock. When water exits from a spring (*Figure-9c - S*), it stops dissolving CaCO₃, and starts degassing CO₂ to get back to equilibrium with the atmospheric partial pressure of CO₂ that exists in the air over the aqueduct water. This is visible in the curves as a sharp turn to the left at S. As water is degassing CO₂, CaCO₃ will be deposited as sinter, and the path follows the carbonate saturation curve towards (T). If water is saturated in CaCO₃ where it enters the aqueduct (red curve), it can start depositing calcareous sinter immediately. If it is not completely saturated in CaCO₃ (curves 2 and 3), water will degas for some time until it is saturated in CaCO₃, and then calcareous sinter will start forming: this means that sinter deposition in the aqueduct will only start some distance from the source (*Figures-10 and 11a*). As a result, many aqueducts show no deposits for the first few km. Sinter deposition continues (*Figures-11b and c*) until atmospheric levels of CO_2 are reached at (T) in *Figure-9*. This can be upstream from the destination of the aqueduct such as a city, in which case no deposits will be found in the water pipe network of the city (*Figures-10 and 18b*). In some cases, some degree of supersaturation is possible (curve 2 in *Figure-9c*).

The amount of calcareous sinter that is deposited at any point in an aqueduct channel per year depends on the saturation of water in CaCO₃; water temperature; water turbulence and on the amount of water transported through the channel. Thickness of annual layers varies from submicroscopic to several mm in thickness, but is usually in the range of 1 mm per year. Thickness of sinter in a channel can increase dramatically behind an abrupt bend in the specus (*Figure-11a*), a drop shaft or any other feature that increases turbulence of the water. In turbulent water, degassing of excess CO_2 in the water proceeds rapidly, similar to shaking a bottle of soft drink. As a result, deposition of calcareous sinter will be much more rapid at or just downstream from a turbulence site (*Figure-11a*). For similar reasons, deposition of sinter is commonly less in a large basin where water flow is quiet and laminar.



Figure-9 (a) The amount of CaCO₃ that can be dissolved in water for different levels of CO₂ at three different temperatures. Since the pH of the water is directly dependent on the amount of CO₂ in water, water pH is shown at the top of the graph for saturation. Diagram after Bolt & Bruggenwert 1979 and Drever 1982; (b) Schematic diagram of the water cycle associated with an aqueduct, letters refer to the letters along the graph in (c); (c) illustration of the carbon cycle in the same graph. Explanation can be found in the text.

Saturation index

The process described above can be quantified using a saturation index. A saturation index (SI) can be used for measuring saturation condition of subject waters as;

8. SI=log ({
$$Ca^{2+}$$
} { CO_3^{2-} }/K_{sp})

 ${Ca^{2+}}$ ${CO_3}$ is the ion activity product whereas K_{sp} (equation 6) is the solubility product constant in the equation at the same temperature. At equilibrium condition, the saturation index (SI) value is = 0, and we expect neither precipitation nor dissolution. If the "SI" value is positive, it represents supersaturation and we can expect calcite precipitation. When the "SI" value is negative, it implies undersaturation of the water, and the water can dissolve and corrode carbonate. Generally, karstic waters, which are most commonly the source for Roman aqueducts are at or below the saturation value (Kempe, 1982).



Figure-10 Formation and dissolution of calcium carbonate in an aqueduct channel

Thickness and nature of layering

The amount of calcareous sinter that is deposited in an aqueduct per day depends on the saturation of the water and water temperature, but also on the discharge (Pentecost, 2005); a high discharge means that more water passes through an aqueduct section, and that more sinter can be deposited. This implies that it can be expected that winter laminae will be thicker than summer laminae. On the other hand, there are some publications that suggested an opposite opinion (Drysdale & Gillieson, 1997; Drysdale et al., 2003 and Ihlenfield et al., 2003). Periodical changes in crystal morphology and porosity also tend to be part of layering in Roman aqueduct sinter. As explained in Chapters 2 and 3, enhanced porosity coincides with micritic crystal shape, probably due to growth of biofilms, while non-porous, sparitic laminae are thicker, and formed by inorganic, chemical precipitation. As such, the nature of calcareous sinter fluctuates regularly between a fabric typical of tufa and a fabric more common in speleothems (see Chapter 2 and Chapter 3).



Figure-11. (a) Curve in the channel of the Nîmes aqueduct in a section close to the source, where water is subsaturated in $CaCO_3$ because of high dissolved CO_2 . The walls of the aqueduct are therefore clean, although this channel functioned for more than 400 years. However, in a bend in the channel (arrow), where water is turbulent and will degas CO_2 , some thin carbonate deposits are visible; (b) thick carbonate deposits in the aqueduct channel of Nîmes tapering upwards as explained in (c), halfway between the source and the city. (c) Calcareous sinter deposition on channel walls and floors gradually fill a channel and form a layered deposit that is most complete at the floors and lower parts of the walls. The result is a deposit that gradually tapers upward; (d) half-moon shaped calcareous sinter deposits from a roman ceramic water pipe, Hierapolis, Turkey. The pipe was 30 cm in diameter. The deposit was inserted in the wall of a house.

Calcareous sinter grows along the bottom and wetted wall sections of aqueduct channels as shown in *Figures-11b* and c. As calcareous sinter gradually fills a channel, the water level in the channel will rise and carbonate deposition will rise up the walls of the channel (*Figure-11c*). As a result, the deposits are normally tapering upwards (*Figure-11b, c*: Hauck & Novak, 1987). In water pipes that run full, sinter forms circular deposits that gradually close the pipe; in those that do not run full, they form half-moon shaped deposits (*Figure-11d*).

Stable Isotopes

The natural stable isotopes of oxygen and carbon play a major role in the investigation of carbonate deposits for several reasons, especially paleoclimate and environmental studies. Carbonate deposits can display a wide range of values of carbon isotopes (-25 to +15 % - per mil notation) and oxygen isotopes (0 to +35 %). The isotopic composition is usually expressed as δ^{13} C and δ^{18} O according to the equations;

$$\delta^{13}C = \frac{\binom{1^3}{C^{12}}}{\binom{1^3}{C^{12}}} *1000 \text{ [VPDB]}$$

$$\delta^{18} O = \frac{\binom{18}{O}}{\binom{18}{O}}_{sample}^{l6} * 1000 \text{ [VSMOW]}$$

(VSMOW) is the standard that is used for fractionation in water by the Atomic Energy Agency in Vienna and for calcite fractionation, a fossil belemnite (VPDB) is used for the standard. The relationship between these two standards is shown as:

$$\delta^{18}$$
O _{VSMOW}= 1.03091 * δ^{18} O _{VPDB}+30.91‰ and
 δ^{18} O _{VPDB}= 0.97002 * δ^{18} O _{VSMOW}-29.98‰

If the values are more positive, it means enrichment in ¹³C or ¹⁸O stable isotopes. The lighter isotopes; ¹²C and ¹⁶O, because of their weak bonds, are more easily depleted.

Isotopic Fractionation

As the fractionation of stable oxygen and carbon isotopes is relatively well understood, and subject to few possible sources of influence, it is a powerful tool to investigate carbonate deposition. In general, the heavier isotope tends to remain preferentially in the denser phase. This means that in evaporation or degassing, the lighter isotopes are preferentially lost, while in condensation, or crystal growth from water, the heavier isotope will move into the denser liquid or crystal being formed (gas-liquid-solid). These selective processes are known as fractionation. These fractionation processes are also temperature dependent (*Figure-12*).

For oxygen isotopes, during evaporation conditions, ¹⁶O moves preferentially to the vapor phase and water enriches in the heavy ¹⁸O isotope. The amount of fractionation during calcite deposition can be determined only by ambient temperature, called **equilibrium fractionation** or together with evaporation as well, in which case it is called **kinetic fractionation** (Ford & Williams, 2007). The same happens between calcium carbonate and water: the lighter isotope remains preferentially in the water and the heavier isotope moves into the precipitating carbonate. The principle is illustrated in *Figure-12*.



Figure-12 Isotope fractionation in an aqueduct channel. Fractionation between water and precipitating calcium carbonate is stronger at low water temperature in winter than at high temperature in summer. Ornamented blue circles at right represent schematic, enlarged volumes of material where dark blue dots represent ¹⁸O, and light blue dots ¹⁶O. The different amounts of ¹⁶O in the circles at right, indicate the fractionation process between water (blue rim) and calcium carbonate (yellow/orange rim)

In aqueduct sinter the situation is rather different from that in a cave because water temperature can fluctuate in an aqueduct channel. As a result, in Roman aqueducts, δ^{18} O can be influenced by water composition of the source, which is again dependent on the variable composition of rainwater; on evaporation in the channel; and on water temperature in the channel (*Figure-12*). Details are explained in Chapters 2 and 3.

The isotopic equilibrium conditions in Roman aqueducts have been investigated by a "Hendy test", which is most commonly used in cave studies (Hendy, 1971). For this test, one growth layer from the sample should be selected. As it can be expected that there are isotopic equilibrium conditions in one layer, there should be no variation in δ ¹⁸O and δ ¹³C, nor any cyclic changes from the symmetry axis of the selected layer to the edges (Hendy, 1971, Gascoyne, 1992). An example of a Hendy test is given in Chapter 2.

In most cases, it is hard to find speleothems at equilibrium conditions as a result of major evaporation and fast degassing. This difficulty leads scientists to try and find the best settings that come closest to equilibrium conditions in closed chambers, high humidity areas with lowest air flow and at a minimum distance for drip water falls (Ford & Williams, 2007). In Roman aqueducts the situation is very different. The deposition setting here consists of channels closed by a roof and buried under soil cover, or terracotta pipes and less commonly channels closed with stone slabs without soil-cover. Although most aqueducts are buried, they are more likely to show annual changes in temperature than caves. Regular manholes for inspection allow relatively free air

exchange with the atmosphere, so that there is no limit to CO_2 degassing. In terracotta pipes, however, degassing may be hampered (Chapter 3).

In a cave environment, cooling due to a decrease in the outside temperature will cause the δ^{18} O value of carbonate deposits to be enhanced and this is known as the **"cave temperature effect"**. In aqueducts, we also have this situation in the wet season, typically for winter times in Turkey, by having a drop in the outside temperature which leads to δ^{18} O to having more positive values (Ford & Williams, 2007).

In the case of equilibrium conditions, the data obtained from δ^{18} O can give information on palaeoclimate, past temperature and evaporation. Evaporation increases ¹⁸O in the water and also causes enrichment in ¹³C, as a result of degassing or short water residence time. Disequilibrium conditions, by an increase in CO₂ evasion, cause higher levels of heavy ¹³C and ¹⁸O isotopes in the water. A study on a travertine deposits from Güterstein, suggested that abrupt calcite precipitation can lead to a decrease in ¹³C values (Michaelis et al., 1985).

Trace Element Analysis

Trace element analysis is the most complicated part of the geochemical analysis of terrestrial carbonate deposits. The reason is that, contrary to stable isotopes, trace element composition in carbonates can be influenced by many factors. The most important trace elements in carbonate deposits are magnesium and strontium. Mg/Ca and Sr/Ca ratios have been applied as a paleoclimate indicator especially for speleothems and epigean travertine (Pentecost, 2005). This has mainly been done since Mg is an excellent geothermometer in marine environments. Unfortunately, the situation is less clear in fresh water deposits. In a marine environment, Mg content of the seawater is rather constant, but in lakes, rivers and springs the original levels can vary considerably. Interpretation of Mg-levels in carbonates is therefore very hard except in some special cases (Ihlenfeld, 2003).

Alteration of trace element chemistry with layering, particularly on Mg/Ca and Sr/Ca ratios that can be seen in most terrestrial carbonate deposits, and may provide information about paleohydrology of the setting area (Fairchild et al., 2000, 2001). Mg/Ca ratio may be temperature dependent; conversely Sr/Ca is not related with temperature at all.

A study of two caves in Australia has shown that relatively low average Mg/Ca ratios in drip waters correspond to the wet season and higher values to dry periods with long water residence time. Mg/Ca and Sr/Ca ratios showed a regular increase throughout drought times and had their highest values shortly before drought conditions were broken by rainfall (McDonald et al, 2004). Fairchild (2000) also observed the same situation for two European caves, Mg/Ca ratio in cave drip waters being reported as a proxy for water residence time changes.

A study on Italian travertine demonstrated a positive correlation between Sr content and porosity (Cipriani et al., 1972, 1977). There are several studies which report Sr enrichment in lighter bands and Fe, P and Zn enrichment in darker laminae of carbonate deposits (Huang et al, 2001; Ford & Williams, 2007).

Biological activity

Aqueduct lines composed of terra-cotta pipes, vaulted channels or stone covered channels have similar low-light conditions as caves, and water in the channels was mostly poorly lit, except occasionally below manholes or breaches in the cover. Therefore, in both aqueduct and cave deposits, there is no large population of photosynthetic organisms. The origin of carbonate deposits in caves and aqueducts can therefore be partly abiogenic. However, some studies in recent years from cave deposits demonstrated that photosynthetic microbes can be present in twilight zones in cave entrances (Jones, 2001).

Photosynthetic microorganisms such as cyanobacteria can be important for the deposition of calcium carbonate, for example in tufa deposits, since they consume CO_2 for their photosynthetic metabolism during the day, and can therefore shift the SI to positive values (Merz-Preib et al., 1999). Examples of cyanobacteria that are active in such environments and which form small reef-like carbonate deposits are *Rivularia haematites* and *Schizothrix Fasciculata*. The presence of other, non-photosynthetic microbes in a cave can also play a role in calcite deposition and erosion. Microbes can be constructive by trapping and binding of detrital particles to a substrate. Sticky surfaces of microbes help small detrital grains to adhere and stromatolites can form deposits in caves in this way. The type of microbes present at nucleation sites for calcite precipitation may control the types of crystals that form. Nevertheless, in fossil deposits, determination of microbe existence and their identification is only possible if mineralization took place while the microbes were alive or immediately after they died. In any case, it is always crucial to prove their role in the formation of carbonate deposits (Jones, 2001).

Besides their constructive role, microbes can also play a destructive role in calcite deposition. In speleothems, they can even cause substrate collapse. Etching of a substrate by microbes can produce etch patterns, pits, spiky and blocky calcite. Etching of a substrate may cause significant substrate modification, produce residue micrite and modification of the composition of the groundwater by delivering Ca and carbonate from the substrate (Jones, 2001). Kahle (1977) claimed that etching of calcite crystals might lead to sparmicritization. However, if microbes have not been mineralized, it is not easy to find any evidence for microbial activity.

In aqueducts, microorganisms are probably most important in the formation of biofilms, and may mainly play a role in the capturing of detrital particles, as explained in Chapter 2. This changes the trace element chemistry of deposits, while microorganisms may also play a role in the determination of crystal morphology, as in speleothems. As described in Chapter 2, micrite is mostly associated with bacterial biofilms. Water velocity and turbulence are two factors that mainly play a role in biofilm colonization (Pedley & Rogerson, 2010). Some sites along aqueducts may have high carbonate precipitation rates and less biofilm or even no biofilm community because of high turbulence in the channel. Sinter may have a structure similar to tufa deposits due to their deposition from a freshwater source with ambient temperature conditions; however biofilms are not very common in many types of calcareous sinter because they form inside a pipe or a vaulted channel. As a result, they have a more solid structure. However, some calcareous sinter types such as sinter found in Ephesus and Galermi, Syracuse is very porous throughout, probably due to abundant biofilm growth (*Figure-6*). Since these aqueducts are built in the same way and functioned in a similar way to the ones with dense sinter, it may be the water composition that is responsible: water in the aqueducts with porous sinter may be rich in trace elements that favor bacterial growth.

Dating of calcareous sinter

Several methods have been used or proposed to date terrestrial carbonates. These include radiometric methods using radiogene isotopes: biostratigraphy, and palaeomagnetic methods. The most common dating methods for non-marine carbonate deposits are decay of unstable isotopes and biostratigraphy. Especially radiogene isotopes such as Carbon-14 and Uranium series (²³⁰Th, ²³⁴U and ²³⁸U) are the best-known methods used, and can be applied to give ages up to 30 and 400 Ka respectively (Pentecost, 2005). Autochthonous deposits are preferable for such dating since they have less contamination and as a result give more reliable age results.

 14 C is formed by cosmic radiation in the Earth's upper atmosphere, and decays to 14 N with a half-life of 5730±40 years (Ford, 1997). This dating method will only work if no exchange of ¹⁴C took place between the dated material and the environment after it was formed. In order to apply the Carbon-14 dating method successfully, sources of carbon must therefore be known. In calcareous sinter, like in similar terrestrial carbonate deposits, carbon included in the carbonate minerals originates from diverse sources and therefore ¹⁴C dating is always problematic. In addition, the porous deposits can easily exchange carbon with the surroundings after their deposition. Instead, using organic matter that can be found in the deposits might seem a solution; however, using these can also be difficult if the material can originate from tree roots or other material that can give an age, which is older than the aqueduct. The biggest problem is re-equilibration and contamination with more recent material than the actual deposits. Therefore, in carbonate environments, the ¹⁴C method is problematic. In addition, rocks and soil contain ¹²C and ¹³C, and as a result can give underestimated results (Ford, 1997), ¹⁴C is not a common method in cave studies either. One reason is that there is a limit on the length of the dating interval by comparison with U series methods. Most speleothems are simply too old to be dated with ¹⁴C. In conclusion, ¹⁴C may only be used in carbonate deposits in Roman aqueducts if pieces of wood are preserved included in the sinter (Frumkin et al., 2003). So far, we have not found such material preserved, although imprints of tree roots are common in some deposits.

As the ¹⁴C method is not reliable as a dating tool for calcareous sinter due to the problems mentioned above, the decay of ²³⁴U is the more accurate method than ¹⁴C. An additional advantage is that it represents a longer time period. Two dating techniques are used, associated with the decay of ²³⁴U to Th or Pa respectively. The former method is the most useful and accurate for dating carbonates (Edward et al., 2003). Contrary to Th, U is soluble in water, and can therefore be included in the carbonate lattice directly from the water. Th has very low solubility, and any Th found should therefore be derived from U, and can be used for dating. Unfortunately, this only works well in deposits that lack any detrital materials such as clays, which usually contain some Th. Corals, for example, are excellent to date with this method since they mostly lack clay contamination. Most terrestrial carbonate deposits, however, do contain detrital material and therefore careful sample selection is needed. Especially dense, sparry deposits have less contamination and are therefore more suitable for the method. U series is mostly used in caves where the longest-lived components of terrestrial settings are deposited.

There are three important requirements that should be considered for using the U series method (Ford & Williams, 2007);

- 1. The deposit should contain enough U and its concentration must range between ≤ 0.01 ppm to 300 ppm.
- 2. Porosity in the deposits has to be avoided, if possible. Dense, crystalline samples are preferable.
- 3. The most important requirement is not to have inherited ²³⁰Th and ²³¹Pa as contaminations.

So far, two authors have claimed to have dated sinter associated with ancient water system with some success: Frank et al., (2002) dated water sources beneath the ancient city of Troy, but their conclusions are not generally accepted by archaeologists. Hostetter et al., (2008) dated calcareous sinter deposits from the Caracalla Baths, Rome, but the final publication of the results has not yet appeared. Moreover, Frumkin et al (2003) dated speleothems from an ancient aqueduct tunnel, but not the sinter itself.

The large amount of initial Thorium in carbonate deposits in aqueducts is a problem, and we are presently investigating a number of samples from different aqueducts to find selected ones with minimal initial Th. This work is done in cooperation with Warren Sharp (Berkeley Geochronology Center) and Dennis Scholz (Mainz). Since the work is not concluded, it could not be included in this thesis, but it has shown some initial success. Preliminary U-series dating results on four aliquots of calcareous sinter from a Roman aqueduct in Beziers, France, resulted in a mean age of 32 ± 46 years AD showing that aqueduct sinter can be accurately dated with a precision of a few decades (D. Scholz, unpublished result): the aqueduct was previously dated to between 40-100 AD based on archaeological arguments (Andrieu, 1990).

The paleomagnetic dating method uses the fact that the Earth's magnetic field changes continuously in its field declination, inclination and intensity by small amounts and at each location on a timescale of hundreds of years or even decades. This produces a characteristic pattern that could theoretically be recognized in the orientation of magnetite grains embedded in sediments. The method may be used also in carbonates since magnetite can be found in most carbonate rocks in small quantities as detrital grains, and in some cases in bigger amounts or as a precipitate (Ford, 1997). During their precipitation or deposition, these magnetite grains arrange their orientation in the Earth's magnetic field, which can subsequently be measured. Darker laminae couplets contain more magnetic material by comparison to light colored ones (Ford, 1997).

Relative dating of calcareous sinter, especially of the deposits that represent a shorter time period, is possible by counting their annual laminae couplets. One of the first attempts to count the annual layers was by Magdefrau (1956) on travertine deposits of Ehringsdorf, Germany. For these deposits, an accumulation period of 900 years was counted (Pentecost, 2005). Another example is from the Roman aqueduct of Nîmes, France (Fabré & Fiches, 1986; Guendon & Voudoir, 1986). Lastly, Sbeinati et al. (2010) dated calcareous sinter from a Roman aqueduct in Syria using some layer count in combination with trenching and ¹⁴C dating of material in the trench.

At the onset of this study, it became clear that optical microstructure and color are not a reliable basis for an annual layer counting method. The most important point, which should be considered, is that some laminae may reflect other (subannual) periodicities such as exceptionally rainy periods or even daily variations (*Figure-7a*; Pentecost, 2005). Based on this, several layer counts were carried out in Patara, Aspendos, Ephesus and Pergamon. Two studies, on the history of the aqueducts in Ephesus and Pergamon are based on the method

developed in this study (Passchier et al, in press). One of the main results of this thesis is, that detailed stable isotope analysis can be used as a basis to recognize annual layering. Further details of the method and results are given in Chapters 2 and 3.

Romans and water

The Roman Empire is mostly located in dry Mediterranean terrain where it was a real problem to find perennial water sources. The Romans needed water for numerous reasons; drinking; agriculture; luxury fountains; pools and most importantly for bathing. Usually, it was necessary to find a spring source in the mountains, and mostly in karst settings.



Figure-13 Distribution of 1400 long distance Roman Aqueducts in Europe and the Mediterranean area.

The Romans could also take the water from rivers and lakes but these were often polluted for several reasons. Capturing water from a stream or a lake is mainly a problem because of flood events with muddy and detritusladen water after storms and heavy rain or due to melting snow. Muddy water will block channels and water pipes with sediments, and although this can be filtered out, it makes regular cleaning of filter installations necessary. Another reason to avoid river water is the frequent water level change in a river, which makes it difficult to build an inlet for an aqueduct. Floating branches and leaves form another hazard, potentially clogging inlet systems. Therefore, the best locations were always springs at an altitude above the destination of an aqueduct.

If we imagine the densely populated Roman Empire during its hey-day, it must have been hard work for Roman engineers to find the best sources and bring them to the ancient cities. Hence Roman engineers took their time to

find the best, drinkable water. Vitruvius, a famous Roman engineer, gave some tips for engineers to find the best source; he suggests talking with local inhabitants around a water source and considering their skin color, whether they are healthy or not; if they were, this could mean that the water they used was pure and worth tapping.

The Romans did not treat water with any chemicals, but intelligently, built settling pools and basins where water could run slowly and drop down impurities, sand and clay particles. There is some evidence that they selected calcium carbonate saturated water not so much for its taste, but because it will not corrode the inside of masonry aqueduct channels: modern pH control of swimming pools is also mostly done for this same reason. Moreover most water pipes inside cities were made of lead: sinter growth inside these lead pipes, by coating the pipe's interior, did help to avoid lead poisoning, which is often given as a reason for health problems in Roman times.



Figure-14 (a) Typical masonry aqueduct channel with a manhole for maintenance; (b) Cross section of the channel showing 20 cm-thick carbonate deposits (sinter) representing approximately 170 years of water flow. (c) Basin at the junction of two aqueduct branches, entering from right and top, with the water leaving through the main channel at the left. Notice the absence of sinter here, close to the sources, while there is thick sinter at (b), 30 km from the sources. All photos are from the Roman aqueduct of Cologne.

Roman aqueducts

Aqueducts were known to the Etruscans and Greeks, but were especially favored and technically improved by the Romans (*Figure-13*: Hodge 1992; Wikander 2000). Roman public baths, like the Baths of Caracalla in Rome, were a very important part of the Roman culture in any population centre, and these needed large quantities of running water. Roman aqueducts were therefore mainly built for the purpose of providing water to the public baths. A second important reason, of course was the provision of cities with drinking water, but this could also be obtained from wells, and many sizeable cities such as Ampurias in Spain, seem to have done without an aqueduct. The eleven aqueducts of Rome provided the capital with over one million cubic metres of water per day.

Greek aqueducts were usually built in the form of ceramic pipes, and this could provide enough water for the purpose of small Greek settlements. For the large quantities that Roman public bath-houses needed, however, masonry channels were built (*Figures-11c and 14*). These had the added advantage that they could be tall enough to walk through, and could therefore easily be cleaned and inspected for leakage.



Figure-15 (a) Well house for the spring of the Roman aqueduct of Xanthos, Turkey. The structure protects the spring, which was carried from here in a closed masonry channel. (b) Typical Roman aqueduct channel, Martigny, Switzerland. The channel is built of masonry and buried in a trench. The channel is plastered on the inside with red "opus signinum" (red) with typical "quarter rounds" in the edges to protect from leakage. The well-like structure at the end is a roman drop-shaft, where the water dropped down under controlled conditions in order to maintain a gentle slope for the main channel. Such drop-shafts are common on steep slopes.

More than 1400 Roman aqueducts are presently known from the literature (*Figure-13:* ROMAQ 2012) and these show a large number of different types. First of all, a distinction can be made between industrial aqueducts and consumption aqueducts. Industrial aqueducts were mostly built for mining, especially for alluvial gold mining where large quantities of water were needed. Famous examples of such aqueduct systems are found in NW Spain (Las Medulas mines) and the Dolaucothi goldmines in Wales. In Las Medulas, seven large aqueducts with a total length exceeding 570 km brought water to the mining site where "hushing" was used to extract 1650 tons of gold in 250 years. To a lesser extent, aqueducts were built for irrigation, for example near Valencia in Spain, or for flushing sediment from harbor basins (Caesarea, Israel). Several settlements on the coast of the Mediterranean, especially in Spain and Morocco (Baelo Claudia, Almuñecar, Kouass) had large aqueducts to provide water for the production of fish-sauce. Most aqueducts, however, served cities or smaller settlements, and in some cases isolated villas and bathhouses. These aqueducts could also be impressive, with channels up to 1.2 m wide and 250 km long (Valens aqueduct of Constantinople). The 11 aqueducts that served the capital, Rome, had a total length of 515 km and provided the city with over one million cubic meters of water a day.

Each aqueduct has a number of characteristic elements such as a spring, the main channel, bridges, tunnels, inverted siphons, basins, and a terminal distribution station (castellum aquae), from where water was distributed to different parts of a city, and to different types of users (*Figures-14 and 18*). Springs were favored as a water source of aqueducts where these were available and provided enough water. In many cases, water from several springs was combined and led into one main channel, and the spring was usually protected by a well house (*Figure-15a*). In many cases, large springs far from the target city were chosen to build expensive, long distance water supply lines. Obviously, perennial springs with clean water are a great advantage in building a water supply. In some cases, rivers were directly tapped for aqueduct water, either through a weir (Segovia) if the water supply was constant over the year, or by means of dams (Emerita Augusta, Glanum, Toledo). Another option that was used when a phreatic nappe of groundwater was to be tapped was the construction of a sicker
gallery, usually a covered channel with permeable walls though which water could enter the channel (Cologne, Almuñecar, Windisch).

The main channel of an aqueduct was usually rectangular in cross-section, and covered by a vault or slabs (*Figure-14*). The inside of the channel was waterproofed with a special red-colored cement, opus signinum, to which roof tile fragments and squashed figs were added (*Figure-15*). The corners of a channel were protected by "quarter rounds" of opus signinum since these corners were potential leakage sites (*Figure-15*). The channel of the aqueduct was usually buried to protect it from frost and contamination, but access shafts were normally built at regular distances to allow cleaning and maintenance (*Figure-14a*).



Figure-16 (a) Perfectly preserved aqueduct bridge of Nîmes, well known as the Pont du Gard, crosses the Gardon River; (b) Bridge of the Madradağ aqueduct of Pergamon, Turkey, This bridge has a long history having been built as a three-story open channel bridge, like the Pont du Gard, that collapsed in an earthquake, was reused as a venter bridge of an inverted siphon, and then again as a one-story open channel bridge.

The Romans did know hand pumps and used Archimedean screws and pumps to drain mines. However, their pumps could not cope with the large volumes of water needed for an aqueduct, and therefore, means were normally found to transport water by gravity. Since aqueducts operated by gravity, they should have a low, regular slope from source to target, for example 12 meters for the 55 km long aqueduct of Nîmes. Steep slopes were avoided since the resulting rapid water flow is erosive and can destroy a channel rapidly. Sudden changes in slope from steep to shallow are also to be avoided, as they will cause overflow of the channel.

As aqueducts had to be built with a gradual slope along the shortest possible way to the target, they commonly passed along the contour lines of hills. Where needed, or where a channel had to make a long detour, bridges or tunnels were built to shorten the route. Bridges were also built where an aqueduct was crossing a stream, in order to avoid damage when the stream or drainage was in flood (*Figure-16*). Tunnels were usually built by sinking vertical shafts along the trajectory, and connecting them (*Figure-17a*). When the hill or mountain to be crossed was too high, the tunnel was driven from two sides, with obvious difficulty to meet in the middle. This type of deep tunnel could be up to 8 km long (Traconnade, Aix en Provence: Hodge, 1992). A special type of tunnel was built to pass steep vertical rock walls: this was done by opening windows in the rock



Figure-17 (a) Aqua Claudia aqueduct tunnel (Rome), nearly 120 cm wide; (b) The aqueduct channels of the Aqua Marcia, Aqua Tepula, Aqua Julia on top of each other. This is the cross section of an arcade at Porta Maggiore, Rome.

wall at regular intervals, and connecting these by a tunnel: examples are known from Syracuse, Italy; Elaioussa Sebaste (Turkey) and Chelva and Cella in Spain (Casado, 1972, Ezquerra, 2007). Tunnels were occasionally also built where the geology made a masonry channel vulnerable, for example in areas with soft rock or land sliding: the longest known aqueduct tunnel, 106 km (Gadara, Jordan) was built because of this reason (Döring, 2009). Where small rock spurs had to be passed, in some cases a trench was preferred: here, the rock mass is cut vertically to a deep enough level to allow the aqueduct channel passage (Fréjus, Chelva, Cahors).

Basins were built shortly after the source, before bridges in order to capture sediment: sand or gravel in the water could rapidly erode the cement lining of the channel, and had to be captured and removed. Where branches of an aqueduct join, or more rarely, where they split, basins are usually built to avoid damage by turbulence (*Figure-14*). In addition, such basins usually have structures to let out water or to be able to close of one of the branches.

Valleys were crossed by means of aqueduct bridges such as the Pont du Gard. These bridges could be one, two or three stories high, with the channel passing on top (*Figure-16*). If an aqueduct was to reach high parts of a city that was not on a slope, it was necessary to build the channel on arcades, such as those outside Rome (*Figure-18*). These arcades could carry the aqueduct in levels, with up to three channels being carried by the same arcade, one on top of the other (*Figures-17* and *18a*).



Figure-18 (a) Arcade of the Aqua Claudia and Aqua Anio Novus channels, Rome, stacked on top of each other. (b) Castellum aquae of the ancient city of Nîmes.

Roman bridges with a normal open channel were built up to 50 m high (Pont du Gard), but if the bridge had to be higher, or the valley was too wide for a stable bridge, another solution was found in the form of an inverted siphon: here, a water pipe was built and laid out on a system of slopes and a low bridge crossing the central valley, known as a venter bridge. Such inverted siphons were constructed by series of lead pipes (Lyon: Hodge, 1992) or rows of perforated blocks (e.g. Aspendos and Patara: *Figure-20*, Chapter III, *Figure-2b*). Where aqueduct channels had to accommodate a large difference in height, special adaptations had to be made: a normal masonry channel would have rapidly been damaged by fast flowing water. The most common adaptation in such cases is the building of drop shafts, where water can drop down in a well-like part of the aqueduct, to continue at a lower level (*Figure-15b*; Cordoba, Martigny, Cuicul, Autun: Hodge, 1992). Another solution was the use of ceramic pipes, which are less subject to damage as can be seen in Patara (Chapter III, *Figure-2c*). The final structure in all aqueducts is a basin with structures to subdivide the aqueduct water over several tubes or channels to its final users. This structure is called *castellum aquae*. In some cases, such as Pompeii and Nîmes, the structure can be very complex (*Figure-18b*), but in most cases it is a simple set of basins, filters and pipes (Hodge, 1992).

The ROMAQ database (<u>www.romaq.org</u>) presently contains more than 1400 Roman aqueducts of which literature exists (*Figure-13*). SW Turkey has a large concentration of Roman aqueducts since it was a rich, densely populated area in Roman times with many large harbours, and a typical Mediterranean climate with dry summers and most precipitation in winter. The map segment of *Figure-19* shows 82 Roman aqueducts, some of which are over 90 km long (Phocaea; Öziş, 1994). Several cities such as; Pergamon, Ephesus, Hierapolis and Aphrodisias had more than one aqueduct. Many of the aqueducts are simple structures of ceramic pipes, but the largest ones are built as masonry channels with the usual array of tunnels, bridges and basins. Some bridges, in the Kaikos aqueduct of Pergamon were larger as the Pont du Gard in France (Garbrecht, 2003). Notable ruins of aqueduct bridges can be seen in İzmir, Ephesus, Alinda, Alabanda, Iasos, Keramos, Andriake, Phaselis, Perge, Aspendos and Side. What is special for SW Turkey is the large number of inverted siphons, notably in the aqueducts of Aspendos, İzmir, Pergamon, Cibyra, Trapezopolis, Oinoanda, Patara, Ephesus, Alabanda and Laodicea. Such pressure channel bridges were more elaborate to build than normal bridges with an open

channel, but were also lower and more solid: the frequency of earthquakes in SW Turkey may be a reason for the frequency of inverted siphons. Most spectacular are the long siphon with two pressure towers in Aspendos (*Figure-20*) and the siphon of Pergamon, with 180 m the deepest of the ancient world (Garbrecht, 1992; Mays, 2010).



Figure-19 Presently known Roman aqueducts in SW Turkey. ROMAQ Database (www.romaq.org)

Few aqueducts in SW Turkey have been studied in detail, although for most, some general information is available (Tanriöver et al., 2006; Öziş, 1994, 1996, 2006). Detailed archaeological work was only on the aqueducts of Pergamon (Garbrecht, 2003), Ephesus (Wiplinger, 2008), Hierapolis (Scardozzi, 2007), Aspendos (Kessener, 2000) and some minor work on those of Iasos, Side, Andriake, Patara, Oinoanda, Sagalassos, Cremna, Arycanda, Xanthos, Keramos, Tralles, Miletus and Alinda (ROMAQ Database).



Figure-20 Inverted siphon bridge of the aqueduct of Aspendos, Turkey

In the course of this study, the following aqueducts in SW Turkey were visited and briefly investigated: Pergamon, Smyrna, Ephesus, Alabanda, Iasos, Keramos, Laodicaea, Cibyra, Oinoanda, Xanthos, Patara, Andraike, Myra, Arycanda, Phaselis, Perge, Side and Aspendos. Those of Pergamon, Smyrna, Ephesus, Iasos, Keramos, Laodicaea, Xanthos, Patara, Perge, Side and Aspendos contain carbonate deposits. We investigated the deposits in Pergamon, Ephesus, Patara and Aspendos more closely since here, abundant archaeological data were available, while the aqueducts of Patara and Ephesus are presently being studied by archaeological groups. Finally, Patara and Aspendos were selected as the most promising examples and investigated for this thesis, the results of which are given in Chapters 2 and 3.

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Chapter 2

Laminated carbonate deposits in Roman aqueducts: origin, processes and implications

TOT AQVARVM TAM MVLTIS NECESSARIIS MOLIBVS PYRAMIDAS VIDELECET OTIOSAS COMPARES AVT CETERA INERTIA SED FAMA CELEBRATA OPERA GRAECORVM - (With such an array of indispensable structures carrying so many waters, compare, if you will, the idle Pyramids or the useless, though famous, works of the Greeks - Sextus Iulius Frontinus, DE AQVIS VRBIS ROMAE)

Abstract

Carbonate deposits in Roman aqueducts of Patara and Aspendos (southern Turkey) were studied to analyze the nature of their regular layering. Optical microscopy and electron-backscattered diffraction results show an alternation of dense, coarsely crystalline, translucent laminae composed of bundles and fans of elongate calcite crystals with their c-axes parallel to the long axis, and porous, fine-grained laminae with crystals at near-random orientation. The δ^{18} O and δ^{13} C data show a strong cyclicity and anti-correlation, whereby high and low δ^{18} O values correspond to dense columnar and porous, fine-grained laminae, respectively. Geochemical analyses show similar cyclic changes in carbonate composition. Electron microprobe and laser ablation inductively coupled mass spectrometry analyses show that porous, fine-grained laminae are enriched in elements associated with detrital material (Fe, Mg, K, Al and Si), whereas the dense columnar laminae are nearly pure calcite. The gradient in major and trace-element distribution, regular changes in crystal type and in oxygen and carbonisotope composition from porous fine-grained to dense columnar laminae reflect changes in water chemistry, discharge, temperature and biological activity. Because of the strong bimodal cyclicity of the Mediterranean climate in southern Turkey, the observed laminae can be attributed to calcite deposition during the dry (porous fine grained) and wet season (dense columnar), respectively. This observation implies that, with proper geochemical and microstructural control, lamination in carbonate deposits in Roman aqueducts can be used for relative dating of aqueduct construction and maintenance, and to obtain data on external factors that influenced the aqueducts such as palaeoclimate and natural hazards. Carbonate deposits in Roman aqueducts show properties of both flowstone speleothems and riverine fresh water tufa. As many aqueducts of nearly identical channel geometry are present in different climate zones and with different source water characteristics, they can be used as natural experiment setups to test and improve existing models of how laminated fresh water carbonates record climate on time scales ranging from seasonal to millennial.

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INTRODUCTION

Drinking water has always been an essential commodity for all civilizations. In the Roman Empire, a large number of aqueducts were built that carried water to cities such as Rome, Constantinople, Athens and Carthage over distances of up to 250 km (Hodge, 1992; Wikander, 2000; ROMAQ Database). More than 1300 major Roman aqueducts are known presently, with a combined length of over 6000 km. These aqueducts usually are buried masonry channels or ceramic pipes that transported water by gravity from a source to a distribution station for a Roman villa or town. Bridges, tunnels, basins and inverted syphons are standard supporting structures in such aqueducts. Large karst springs were generally used as a source, and many aqueducts therefore carried water with dissolved calcium carbonate. Depending on the degree of calcite saturation, this was deposited in the channel as a layered sediment similar to travertine or tufa but with a different microstructure; for this reason, these aqueduct deposits are referred to in this article as calcareous sinter, after Grewe (1986, 1992). As most aqueducts carried water all the time, the deposits form a continuous record of water discharge, composition and temperature for the lifetime of the aqueduct (Passchier & Sürmelihindi, 2010). Many aqueducts operated for decades, and some deposits in aqueducts represent up to 800 years (Sbeinati *et al.*, 2010).

Terrestrial calcium carbonate deposits, such as speleothems in caves, travertine at springs and riverine tufa, are commonly characterized by regular dark and light layering couplets (Fouke *et al.*, 2000; Matsuoka et *al.*, 2001; Ihlenfeld *et al.*, 2003; Kano *et al.*, 2003; Andrews & Brasier, 2005; Pentecost, 2005, p47, 401; Andrews, 2006; Immenhauser *et al.*, 2007; Baker *et al.*, 2008; Pedley & Rogerson, 2010; Kele *et al.*, 2011). Such couplets have been interpreted as annual layering, formed by seasonal changes in water composition and depositional conditions, and have been used to study climatic processes (McDermott, 2004; Andrews, 2006; Boch *et al.*, 2011). Calcareous sinter in Roman aqueducts shows a similar type of layering.

Calcareous sinter forms in steady contact with running water, and has properties of both riverine tufa (Matsuoka *et al.*, 2001; Ihlenfeld *et al.*, 2003) and subaqueous flowstone in caves (Hill & Forti, 1997). Similar to subaqueous flowstone and other speleothems, deposition takes place in a dark, damp channel where evaporation and photogene biological activity are of minor importance. However, manholes and basins along the aqueduct provide ample ventilation for degassing of CO₂, and aqueduct channels are shallowly buried structures that can warm up and cool down during the seasons, similar to tufa depositing streams. Like tufa, Roman aqueducts tend to form relatively thick layers of carbonate that reveal much, probably sub-annual, detail. Deposits in some aqueducts can also be dated precisely based on building inscriptions and other archaeological data, and the dense nature of calcareous sinter allows for precise U-Th dating (Garnett *et al.*, 2004).

Another reason why Roman aqueducts are of importance to the study of terrestrial carbonates is their man-made nature. The aqueduct channels were built according to the same specifications throughout the Roman Empire, with nearly identical shape and standardized dimensions in Roman feet, and long sections have a constant slope. Deposits in the channels accumulated for tens to hundreds of years, mostly in the same period between the 1st and 4th Century AD, but with different source water composition and in vastly different climate zones, from coastal to Alpine, and from northern Africa and the Middle East to Germany and the Atlantic coast. This means that Roman aqueducts provide a unique "natural" experimental setup where channel shape and slope, water depth and velocity are fixed, whereas other parameters such as climate and water composition varied, with a deposition record of centuries. Roman aqueducts therefore present a unique test bed for truly natural carbonate-

depositional systems of up to sub-annual resolution, including tufa (Andrews, 2006). Aqueduct calcareous sinter can also provide invaluable information on palaeoclimate, palaeohydrology, archaeology, and locally also palaeoseismology.

Deposition of calcareous sinter in a Roman aqueduct is the result of degassing of spring water upon contact with the atmosphere. Rain water that passes through the soil becomes charged with a much higher concentration of CO₂ than is present in the atmosphere and, as a result, dissolves carbonate rocks on its passage through the aquifer. Upon emergence of the water at a spring, the water starts to degas CO₂ until the solution becomes supersaturated with respect to CaCO₃, and calcite is precipitated on the walls and bottom of the aqueduct channel according to the reaction:

Ca²⁺+2HCO₃[−] ← CaCO₃+H₂O+CO₂

The saturation state of the water depends on the amount of dissolved CO₂ and the residence time of water in the carbonate aquifer. If the water is undersaturated with respect to calcite, it has to degas for some time before saturation is reached, and a certain state of supersaturation is usually reached before precipitation starts (Michaelis *et al.*, 1985). Also, after carbonate has been precipitated and the CO₂ content of water approaches that of the atmosphere, no more carbonate will be deposited. An increase in the temperature downstream will also enhance deposition of calcareous sinter, as the solubility of carbonate in water decreases with increasing temperature. As a result, aqueducts usually show first sinter deposition at some distance from the spring. If the aqueduct is long, calcareous sinter deposition may reach a maximum followed by a gradual decrease, and the distal part of the aqueduct may even lack carbonate deposits (Passchier & Sürmelihindi, 2010). As the amount of carbonate precipitation depends mainly on the rate of degassing, turbulence leads to enhanced deposition of calcareous sinter. As a result, steep channel sections and sections just downstream from drop shafts or other sites with high turbulence show the thickest deposits in many aqueducts.

If depositional conditions were constant, a homogeneous or gradually changing chemistry and petrography of calcareous sinter deposits would be expected, but nearly all sinter in Roman aqueducts has regular dark and light coloured lamina couplets. Factors which may have contributed to the formation of this layering include: changes in temperature and composition of the spring water, associated changes in water level and flow speed along the channel; mixing with additional water sources or water loss along the channel; temperature changes along the channel due to annual changes in solar radiation and air temperature; changes in the water composition as a result of the interaction with the aqueduct wall; and biological activity in the channel. If the carbonate saturation level drops temporarily, water may become undersaturated and start to dissolve previously deposited calcareous sinter. As a result, corrosional unconformities may develop. External factors to consider are landslide or earthquake damage and human interference causing diversion or addition of water, or even a temporary stop of the water supply. Finally, in some aqueducts, maintenance gangs may have removed part of the calcareous sinter deposits periodically.

This study aims to determine the factors that control the development of regular, periodic layering in carbonate deposits in Roman aqueducts.

Patara and Aspendos aqueducts

The nature of layering in Roman aqueducts is influenced by a large number of factors but, since the layering is regular, the primary factors probably are seasonal changes in temperature and precipitation. The eastern Mediterranean is characterized by rainy, mild winters and dry, hot summers with almost no precipitation. Because of this strong seasonality, aqueducts in the eastern Mediterranean are an ideal target to investigate the nature of layering in calcareous sinter. For this research, two ancient aqueducts in Turkey were selected, Patara and Aspendos, for which samples were available from earlier archaeological studies. In both aqueducts, water was transported by gravitational flow, and their structure is that of a standard Roman aqueduct with a buried masonry channel or ceramic pipe, including bridges, tunnels, syphons and basins; as such, the two aqueducts are representative of many in the eastern Mediterranean (Öziş, 2006).



Figure-1 Location of the Patara and Aspendos aqueduct channels, and locations of the samples mentioned in the text. Aqueduct channels are in green, sources are shown as green dots. Sample sites are indicated by red dots.

Aspendos is a ruined Greek-Roman city located on a steep-sided hill (30 m high) of Miocene sediments in the floodplains 50 km east of Antalya (antique Attalia; *Figure-1*). The 19 km aqueduct of Aspendos, built in the 2nd century AD, transported water from two springs, Gökçepınar and Pınarbaşı, in the hills north-west of the city (Kessener & Piras, 1998; Kessener, 2000, 2002). The Gökçepınar spring is located at 550 m above sea-level (a.s.1.), with a discharge of 30 to 40 l sec⁻¹ today, while the Pınarbaşı spring, at 440 m a.s.l., discharges 40 l sec⁻¹ (Kessener & Piras, 1998; Kessener, 2000, 2002). Both springs drain aquifers hosted in Mesozoic limestone of the Antalya nappes (Çiner *et al.*, 2008). The slope of the aqueduct varies considerably, with a mean of 27 m km⁻¹. The masonry channel of the Aspendos aqueduct was 60 cm wide and 90 cm high (2 by 3 Roman feet) having walls 40 cm thick (*Figure-2*). The aqueduct incorporated five bridges and five tunnels. The depression north of the acropolis, an alluvial plain, was crossed by means of a 1670 m long inverted syphon (Kessener & Piras, 1998; Kessener, 2000, 2001).



Figure-2 Typical cross-sections of the aqueduct channels of Aspendos and Patara. The Aspendos is built as a buried, vaulted masonry channel. The Patara aqueduct is partly built as a masonry channel covered with large stones, and partly as ceramic pipes. Calcareous sinter deposits are indicated in yellow, opus signinum is indicated in red.

Patara is a ruined Lycian-Roman city and was once one of the most important harbours of southern Turkey (Figure-1). The aqueduct of Patara, built in the 1st century AD, transported water from a source on a thrust contact north of the village of İslamlar at 690 m over a distance of 22.5 km (Figure-1; Büyükyıldırım, 1994; Baykan et al., 1997). Presently, there are several springs around Islamlar with a combined volume of 200 l sec⁻¹; the aqueduct was calculated to have transported 140 to 170 l sec⁻¹ (Baykan et al., 1997). The distribution tank of the aqueduct, at the edge of the city of Patara, lies at 60 m a.s.l. The aqueduct has a strongly variable slope. The upstream third of the aqueduct consists of ceramic pipes 50 to 70 cm in length with an inner diameter of 30 cm and a slope of 60 to 100 m km⁻¹ (*Figure-2*). The second part is a masonry channel, 55 cm wide and 45 cm high, with walls 40 cm thick and a slope of 2 to 10 m km⁻¹. In this section, the channel is covered by massive, irregularly shaped limestone slabs while the inside walls and floor are covered with a waterproof mortar known as opus signinum (Figure-2). The ceramic pipes and the channel were probably not buried, but remained at or close to the surface. Remains of several small bridges can be observed along the course of the aqueduct, while a 20 m deep valley is crossed by means of a 200 m long inverted syphon known as Delikkemer (Büyükyıldırım, 1994; Baykan et al., 1997). The Patara and Aspendos aqueducts ceased functioning in the 3rd and 4th Centuries, respectively, probably in response to earthquakes (Kessener, 2000). Presently, the springs are only used for local irrigation.

Previous work on aqueduct calcareous sinter

There are few studies exclusively dedicated to calcareous sinter in Roman aqueducts, and most publications are additions to archaeological description of sites, mainly from aqueducts in southern France. Layering in sinter is mostly described as an alternation of translucent, sparitic, dense and opaque, micritic porous laminae (Adolphe, 1973; Guendon & Vaudour, 2000; Rodier *et al.*, 2000; Bobée, 2002; Guendon *et al.*, 2002; Garczynski *et al.*, 2005; Dubar, 2006). Most authors assume layering to be annual without further proof, although some apply frequency analysis to the layering (Gilly et al., 1971, 1978; Schulz, 1986; Blanc, 2000; Guendon & Vaudour, 2000; Dubar, 2006). Some authors attributed the translucent coarse-grained laminae to a high water level, and the opaque, fine-grained laminae to dry conditions (Guendon & Vaudour, 2000; Bobée, 2002; Guendon *et al.*, 2002). Adolphe (1973) and Guendon & Vaudour (2000) found evidence for microbiological activity in calcareous sinter and claimed that this may have influenced the formation of the micritic laminae. These micritic laminae are enriched in Fe, Si and Al, possibly due to the presence of clay minerals (Rodier *et al.*, 2000;

Guendon *et al.*, 2002; Carlut *et al.*, 2009; Bobée *et al.*, 2011). Guendon *et al.* (2002) published some spot δ^{18} O analyses for the Fréjus aqueduct (southern France) showing a very similar range for different lamina couplets. Trace element data of calcareous sinter deposits were successfully applied to determine the provenance of water for the aqueducts of Fréjus and Pompeii, both of which were fed by more than one source (Ohlig, 2001; Guendon *et al.*, 2002; Bobée *et al.*, 2011). Finally, a number of previous studies tried to use calcareous sinter deposits in aqueducts to obtain information on paleoseismicity (Meghraoui *et al.*, 2003; Volant *et al.*, 2009; Galli *et al.*, 2010; Sbeinati *et al.*, 2010). Although these studies addressed the problem of layering in aqueduct calcareous sinter to some extent, this article aims at a more thorough investigation of the nature of layering by a combination of analytical techniques and a discussion of factors that may have contributed to its formation.

MATERIALS AND METHODS

Calcareous sinter deposits in the Patara aqueduct channel reach a maximum thickness of 81 mm in the first section of ceramic pipes. Calcareous sinter samples P28 and P2 grew in 30 cm diameter ceramic pipes of the steep section of the Patara aqueduct, *ca* 8 km apart (*Figure-1*), both consisting of dense sinter with dominant sparitic laminae. Sample P28 is from 36.2954°N, 29.4177°E and P2 from 36.2658°N, 29.3668°E (WGS 84 datum). Sample PA1 was obtained from a settling basin in the aqueduct, with dense dominantly sparitic sinter from a gently sloping section of the aqueduct at the upper end of the Patara inverted syphon at 36.2665°N, 29.3671°E; P1 was taken 10 m upstream in the channel. Calcareous sinter deposits in the Aspendos aqueduct reach a maximum thickness of 140 mm in the central sector. Sample A10-1BB is from the bottom of a gently sloping section of the Aspendos aqueduct at 37.0037°N, 31.1467°E. The sample has a well-developed layering with dominant sparitic calcite. A2 is from the aqueduct channel at 36.9828°N, 31.1486°E. Sample AV is from a basin at the upstream end of the Aspendos syphon at 36.9570°N, 31.1677°E. The stratigraphic thickness preserved in these samples is 54.9 mm (P28), 32.8 mm (PA1), 28.1 mm (P1), 21.9 mm (P2), 62.8 mm (A10-1BB), 13.2 mm (A2) and 16.1 mm (AV). The samples were taken from loose fragments, which could be unambiguously related to adjacent *in situ* deposits. All samples were cut perpendicular to bedding. Polished rock slabs and thin sections were examined using optical microscopy and micro-geochemical methods.

Element distribution maps were produced by electron microprobe (EPMA) using a Jeol JXA 8900 RL microprobe (JEOL, Tokyo, Japan) at the University of Mainz on carbon-coated thin sections from Patara and Aspendos. The microprobe was operated at an acceleration voltage of 15 kV and a probe current of 26 nA. The spot size was 5 μ m and the dwell time was 250 ms with a step size of 30 or 3 μ m for mapping the distribution of Ca, Fe, Mg, Sr, Al, Si, K, and Ti. Here, only data from elements that show distinctive results are presented.

A number of samples were also analyzed by laser ablation inductively coupled mass spectrometry (LA-ICP-MS) at the University of Mainz. Analyses were carried out with a New-Wave Research UP-213 Nd:YAG laser ablation system (ESI, Portland, OR, USA) and an Agilent 7500ce ICP-MS (Agilent, Tokyo, Japan). The measurements were carried out using a cross-line scan from top to bottom of the samples at a scan speed of 10 μ m sec⁻¹, a spot size of 100 μ m, a laser energy of 5.13 J cm⁻² and 10 Hz pulse rate. For data reduction, the software "Glitter" was used. Detection limits generally range from 0.1 to 0.001 ppm (μ g g⁻¹) (Jacob, 2006). Helium was used as a carrier gas and Ca was used as an internal standard, with values for CaO determined by EPMA. The standard silicate glasses NIST 610 and 612 were used as external standards, were measured at the

beginning and end of each run and the GeoReM preferred values were used (Jochum *et al.*, 2011). The isotopes measured were ⁷Li, ¹¹B, ²³Na, ²⁴Mg, ²⁷Al, ²⁹Si, ³¹P, ⁴³Ca, ⁴⁷Ti, ⁵⁵Mn, ⁶³Cu, ⁶⁶Zn, ²³⁸U, ²³²Th and ²⁰⁸Pb. Laser tracks were parallel to the micro-milling tracks of the stable-isotope studies. Laser ablation traces on the samples from Patara had to be carefully chosen to avoid high porosity spots. The boundaries between fine-grained and coarse-grained layers are gradual in some samples, which made a direct comparison between optical laminae and trace-element patterns difficult.

Electron-backscatter diffraction (EBSD) analyses were carried out using a TESCAN Vega//xmu scanning electron microscope (TESCAN, Brno, Czech Republic) equipped with a tungsten filament electron source at the GeoZentrum Nordbayern, University of Erlangen-Nürnberg. For EBSD analyses, the thin sections were finally polished using a colloidal silica suspension (SYTON) and subsequently carbon-coated (thickness *ca* 3.5 nm). Full crystallographic orientation data were obtained from automatically indexed EBSD patterns collected in beam scan mode on a 2 or 3 µm grid (working distance 20 mm, 30 kV acceleration voltage). The EBSD patterns were indexed using the program _{CHANNEL} 5.09 (Oxford Instruments, Oxfordshire, UK). The positions of 7-8 Kikuchi bands were automatically detected using the Hough transform routine (Schmidt *et al.*, 1991; Adams *et al.*, 1993) with a resolution of 100 (internal Hough resolution parameter in the software). The solid angles calculated from the patterns. The EBSD orientation data are presented as processed orientation maps. Non-indexed points were replaced by the most common neighboring orientation. The degree of processing required to fill non-indexed data points, without introducing artefacts, was tested carefully by comparing the resulting orientation map with the pattern quality map (Bestmann & Prior, 2003).

Stable oxygen-isotope and carbon-isotope analyses were carried out at the University of Innsbruck. Samples were micro-milled at 0.2 mm intervals in traces 5 mm wide and parallel to the lamination. Hand drilling with a dentist drill was applied for some samples. The sample powders were analyzed using a semi-automated device (Gasbench II) linked to a ThermoFisher Delta^{Plus}XL isotope ratio mass spectrometer (ThermoFisher, Bremen, Germany). Isotope values are reported on the Vienna-Pee Dee Belemnite scale and long-term precision is better than 0.1‰ for both δ^{13} C and δ^{18} O (Spötl & Vennemann, 2003).

The organic content of calcareous sinter samples was investigated by a optical microscopy study, using conventional thin sections. A Nikon Eclipse E400 POL epifluorescence microscope (Nikon, Kingston-upon-Thames, UK) using blue and UV light was used to determine the presence of organic material, mainly humic and fulvic acids, in polished thin sections. Raman spectroscopy was used on samples from both aqueduct sites to determine whether aragonite was present.

The water temperature of the İslamlar source, which originally fed the Patara aqueduct, was measured twice a day over one year from July 2011, using a Hobo digital thermometer (Onset Comp. Corp., Pocasset, MA, USA). Water samples for δ^{18} O analyses were taken at monthly intervals between July 2010 and July 2011 in sealed 3 ml glass bottles and stored at 5 °C until measured in September 2011.

RESULTS

Petrography

Raman spectroscopy showed that the calcareous sinter from both aqueduct sites consists of pure calcite. The optical microstructure of sinter from the Patara and Aspendos aqueducts is very similar (*Figures-3* and *4*). In both aqueducts, layers consist of couplets of alternating laminae of porous, fine-grained, opaque, micritic and transparent, dense, coarse-grained, sparitic calcite. The sparitic laminae consist of elongate, columnar and wedge-shaped crystals oriented at right angles to the lamination. Crystal size in micrite varies between 10 μ m and 40 μ m, while sparite grains are 0.1 to 0.7 mm wide and 0.4 to 9 mm long. The lamina couplets define the layering visible in hand specimen and thin section. In this article, these laminae are referred to as PF laminae (porous, fine-grained) and DC laminae (dense, columnar). All samples are porous to some extent, but the micritic parts of the layers have higher porosity than the coarsely crystalline parts. In hand specimen, the PF laminae are white and opaque, whereas DC laminae are dark brown, the former generally being wider. The thickness of the couplets varies between 0.1 mm and 1 mm. The boundaries between the two types of laminae can be either gradual or sharp (*Figures-3-5*).



Figure-3 Microstructure of the calcareous sinter from Aspendos and Patara, consisting of alternating micrite and sparite laminae. (A) and (B) Different types of sparite DC laminae, some with sharp crystal terminations, others with gradual transitions to the overlying micrite. Thin colour bands are present in the bottom part of each sparite lamina; (C) alternating micrite-sparite layers with oblique "foliation" formed by arrangement of micrite grains. This kind of oblique structure is oriented in the direction of the former water flow (in this case to the right); (D) dominantly sparitic fabric with thin patchy micrite towards the top of the sparite laminae. A series of thin brown bands are visible at the bottom of each sparite lamina; these may be formed by sudden influx of organic material after heavy rainfall, as explained in the text. (A) to (C) Sample A10-1BB, (D) Sample PA1. All scale bars are 1 mm. All images are in an upright position, youngest laminae at the top. Roman numerals refer to individual sparite-micrite lamina couplets.

Boundaries between PF and DC laminae are characterised as follows. Most commonly, the elongate crystals of the DC laminae root in the micrite layer, and while some of these crystals become wider in the growth direction (*Figures-3D* and 5), others become narrower and terminate (*Figure-5*). The effect of this is a clustering of elongate crystals into radial bundles (*Figures-3D*, 4A and 4B). The coarse elongate sparite crystals are usually capped by

micrite along sharp boundaries, showing the outline of the crystal faces against the fine-grained material (*Figures-3A-III, 3A-IV, II* and *4A-I*). In some cases, the opposite is observed; coarse crystals show a sharp boundary towards the underlying micrite, and may grade and taper into the overlying lamina of micrite (*Figures-3A-III, 3B-I* and *3C*). In many cases, isolated elongate sparite crystals are not capped by micrite, but penetrate the micrite layers. In some samples, individual sparite crystals extend across several lamina couplets (*Figures-4A, B* and *F*). A reddish colour banding is widespread, either in the micrite or in the sparite laminae.



Figure-4 Microstructure of calcareous sinter from Patara and Aspendos consisting of alternating micrite and sparite layers. (A) Dominantly micritic fabric without continuous sparite laminae; individual sparite crystals cross all micrite laminae. Roman numarels refer to individual sparite-micrite lamina couplets. (B) Scanning electron microscope orientation contrast image showing dense sparite and porous micrite: (s) sparitic laminae with elongated calcite crystals; (m) micritic laminae with high porosity; (e) elongated sparite crystals that pass through the micritic lamina couplets. (C) Elongate inclusions in sparite grains. (D) Ultraviolet fluorescence image of lamination in calcareous sinter with sharp contacts between sparite crystals (s) in DC laminae, and overlying micrite (m) in PF laminae. (E) Enlargement of (D) in blue light fluorescence. (F) Blue light fluorescence image showing a sharp contact between sparite (s) and micrite (m). Some micrite persists between sparite grains in DC laminae and large sparite crystals (s) grew through a micrite band. In all cases, micrite is more fluorescent than sparite. Notice the fluorescent dark bands (arrows) within sparite crystals. (A) and (B) sample PA; (C) sample P28; (D) to (F) sample A10-1BB.

Some samples rich in micrite from the masonry channel show inclined traces within micritic laminae (*Figure-3C*). These traces are not defined by single crystals, but by variations in the density of the micrite. In addition, from field observations on aqueducts in İzmir (Buca-Vezirağa), Argos, Fréjus and Cologne, it is clear that the inclined traces are three-dimensional linear microstructures that always deflect in the direction of water flow.

This type of oblique trace can therefore be used in ancient aqueducts to determine the paleocurrent direction in isolated remnants of an aqueduct channel.



Figure-5 Electron backscatter diffraction (EBSD) maps of one PF-DC couplet in sample A10-1BB. Colours correspond to the orientation of the calcite crystals, colour coded with respect to Euler angles. (A) All crystals are highlighted. Three subsets (highlighted area in figures that all show the same location) of crystals in the sample were investigated and their crystallographic orientation presented as pole figure. (B) Large crystals in sparitic DC laminae have a preferred orientation with c-axes parallel to the long crystal axis and normal to the layering. (C) Small grains in micrite PF laminae show a nearly random orientation distribution; other crystallographic axes show a weak girdle distribution; (D) Small crystals between the large columnar ones have a similar, near-random orientation as the fine-grained material in the micrite laminae. Pole figures are equal area, upper hemisphere stereoplots. In order to discriminate between +a and -a axes, upper and lower hemisphere plots are presented for the <11-20> direction. Multiples of random distribution (MRD) are colour coded in contoured pole figures (half width 15°, data clustering 5°). Crystallographic orientation data are presented in the pole figures as 1 point per grain. N is the number of grains.

The previous sections describe general properties recognized in all samples from Patara and Aspendos. By comparison with samples from Aspendos, calcareous sinter from Patara is rich in organic matter and has a slightly higher porosity. In the Aspendos samples, the colour difference between PF and DC laminae is more pronounced, but the same crystal structure is found in PF and DC laminae in both aqueducts.

Epifluorescence microscopy observations show that, in all samples, the PF layers with micritic fabric show clear epifluorescence and contain more organic material than the sparitic crystals in the translucent DC laminae (*Figure-4D-F*). Where sparitic crystals grow across micritic layers as in *Figure-4A* and *F*, these are also low in fluorescent organic matter. The only sites where bright fluorescence is also observed in sparite crystals is along the thin brown bands, which are common at the base of many sparitic intervals in the DC laminae (for example, *Figures-3B* and *D*; *Figures-4D-F*).

Electron backscatter diffraction analyses were carried out on samples PA1 and A10-1BB in order to examine the microstructure at higher resolution, and to determine the preferred orientation of the calcite crystals. The alternation of PF and DC laminae is obvious in the EBSD images (*Figures. 4B* and 5). The elongate crystals in the sparitic layers have a very similar orientation, i.e. their c-axes are oriented in the direction of their long axes. The microcrystalline calcite has more variable crystal orientations. Some of the elongate crystals pass through several PF and DC laminae and groups of small crystals occur between elongate grains in the DC laminae. The porosity is usually higher inside the PF laminae. The main difference between Aspendos sample A10-1BB and Patara sample PA1 is in their porosity and microstructure. Sample A10-1BB is denser and has less porosity than PA1, which is mostly micritic, showing many sparitic crystals that transect PF laminae.

Isotopic composition

In sample A10-1BB, δ^{18} O values range from -7.7 to -5.6 ‰ and δ^{13} C values from -10.2 to -6.4 ‰ (*Figure-6A*, Appedix S1). There is a strong anti-correlation across lamina couplets between δ^{18} O and δ^{13} C with a correlation coefficient of r = -0.68. For sample AV, δ^{18} O values range from -7.5 to -5.8 ‰ and δ^{13} C values from -9.9 to -6.9 ‰ (*Figure-6B*). There is an anti-correlation between δ^{13} C and δ^{18} O with a correlation coefficient of r = -0.52. In sample P28, δ^{18} O values range from -6.9 to -6.2 ‰ and δ^{13} C values from -8.9 to -7.8 ‰ and they are positively correlated (r = 0.45; *Figure-7A*). In sample P2 (*Figure-7B*) the δ^{18} O isotope values range from -7.4 to -6.6 ‰ and δ^{13} C values range from -8.4 to -7.2 ‰, showing an anti-correlation between δ^{13} C and δ^{13} C and δ^{18} O with a correlation coefficient of -0.25. For samples AV, A10-1BB and P2, high δ^{18} O values correspond to the DC laminae and high δ^{13} C values correspond to PF laminae. The correlations in P28 are less clear, but here high δ^{18} O values again correspond to the DC laminae. A "Hendy-type test" (Hendy, 1971) was performed to check for isotopic equilibrium conditions, there must neither be a correlation between carbon-isotope and oxygen-isotope values nor a trend in δ^{18} O (Hendy & Wilson, 1968). The data from P28 suggest that this calcite probably was formed close to isotopic equilibrium (*Figure-7C*).



Figure-6 (A) and (B) Stable oxygen-isotope and carbon-isotope results for two samples from Aspendos. Yellow bands represent selected laminae with high $\delta^{18}O$ and low $\delta^{13}C$ values. Notice the strong negative correlation between $\delta^{18}O$ and $\delta^{13}C$. There is good correspondence between periodicity and lamina couplets in the calcareous sinter. Values in Appendix S1. For further explanation see text.



Figure-7 (A) and (B) Stable oxygen-isotope and carbon-isotope results for two samples from Patara. Yellow bands represent selected laminae with high $\delta^{18}O$ and low $\delta^{13}C$ values. There is good correspondence between periodicity and lamina couplets in the calcareous sinter. Values in Appendix S1. (C) Results of a Hendy-type test on sample P28. Samples were taken from a single lamina, near horizontal in the figure. The results show little variation in isotope values, indicating equilibrium conditions. Further explanation in text.

Elemental composition

The EPMA analyses were carried out to investigate gradients in concentration of major elements including Ca, Mg, Fe, K, Si, Sr, Ti and Al across individual samples. Elemental distribution maps were used to distinguish layers with high porosity and progressive transition of each element across lamina couplets. Strontium does not show significant variations. The results for samples from Patara and Aspendos are very similar, although the lamina couplets are clearer in sample A10-1BB (*Figure-8*); the DC laminae consist of nearly pure calcite, while the PF laminae are enriched in Fe, Mg, Si, K and Al. Aluminium was not mapped but was determined by energy dispersive X-ray analysis. The enrichment in Si and, to a lesser extent, in Fe and K, seems to be restricted to micrite; where large sparite crystals grow across micritic laminae, as shown in *Figure-4*, no enrichment is seen (*Figure-8A – Si; Figure-8B – Fe*). In some samples, the detrital elements are concentrated along the top of the PF laminae at the contact with the DC laminae and at the rim of pores (*Figure-8C*).



Figure-8 Electron microprobe (EPMA) elemental distribution map of samples from (A) Aspendos and (B) Patara. (C) High resolution scan showing details of element distribution in a sample from Aspendos. Colour represents count rate, and is a semi-quantitative indication for element concentration in the sample. The maps show enrichment of detrital elements in the PF laminae. In (A), the high values at the top represent a piece of Roman cement in contact with calcareous sinter. In (B), large sparite crystals in the centre show up as high Ca and low Fe and Mg counts, suggesting that the detrital elements are concentrated in the micritic parts of the PF laminae only. Identical parts of the thin section view are given in plane-polarized light. In (C), K and Fe are mostly concentrated around pores (black) and just above these porous zones. This concentration is attributed to the former presence of mucous material of biofilm in the pores.

Trace elements

The LA-ICP-MS analyses were carried out on samples from both aqueducts to get more complete results on a larger number of elements. In all samples, the LA-ICP-MS results were normalized to Ca as shown in *Figure-9*. In the Patara samples, trace elements show a distinct correlation with the lamina couplets. All elements analyzed in the Patara samples are positively correlated with each other. In all samples, Mg and Ba increase in PF layers and decrease in DC layers. Correlation coefficients of Mg and Ba are 0.63 in P2 and 0.73 in P28 (*Figure-9A*). Stronsium shows a weak positive relationship with Mg, with a correlation coefficient of 0.19 in P2 and 0.32 in P28. Uranium is positively correlated with Mg and shows high values in the same lamina couplets with correlation coefficients of 0.18 and 0.42 for P2 and P28 samples, respectively. In sample P2, there is an increasing trend in Mg, Ba and Sr values towards the top of the sample, whereas U remains almost constant (*Figure-9B*). The graph of P28 shows that all trace elements are positively correlated with each other and in-phase (*Figure-9A*). Although all trace elements have their highest values in the PF layers, there are a few maxima that correspond to DC layers; however, this could be due to micrite between sparite crystals along the measurement track.

The samples from the Aspendos aqueduct show a similar trend, but with a more pronounced periodicity and wider maxima, probably because the calcite fabric is more compact than in the Patara samples. The Mg values are generally higher in the PF than in the DC laminae, but the opposite trend can be observed locally; this, again, may be due to sampling micrite instead of sparite along the laser track. In sample AV from Aspendos, the Mg curve shows clear cyclicity with higher values in the PF laminae.

Both samples A10-1BB and AV show an anti-correlation between Mg and Sr with a correlation coefficient of -0.19 and -0.20, respectively (*Figures-9C* and *D*). In sample A10-1BB, the gradual change in crystal size across each lamina at the bottom of the sample is reflected in the Mg values: the curve shows clearly asymmetric peaks. The Sr and Ba curves are positively correlated in both Aspendos samples and the correlation coefficient in AV is 0.54 and 0.24 in A10-1BB. Strontium and Ba are anti-correlated with Mg. The correlation between Mg and Ba is different for each sample, 0.50 in A10-1BB and -0.13 in AV. Uranium does not show any significant correlation with Mg; in samples A10-1BB and AV, U and Mg show correlation coefficients of 0.06 and 0.05, respectively. Uranium is strongly correlated with Sr and Ba and they mostly have their highest values in the DC laminae.

In sample A10-1BB, there is a decreasing trend in Mg, Ba and U towards the upper part of the sample and a slight increase in Sr can be observed that may be related with the fabric change from thick PF layers to thick DC layers (*Figure-9C*). There is also a good correlation between Mg and Ba in sample A10-1BB and the highest values are found in the PF laminae. Strontium and Ba also co-vary, whereas U is anti-correlated with Mg and reaches the highest values in the DC laminae. In sample AV, there is a decreasing trend in trace elements towards the top of the sample, especially in Sr, Ba and U and, to a lesser extent, Mg (*Figure-9D*).



Figure-9 Laser ablation inductively coupled mass spectrometry (LA-ICP-MS) trace element graphs, normalised to Ca. Graphs for $\delta^{13}C$ from **Figures-6** and 7 and shown below the LA-ICP-MS graphs for comparison. Green bands represent layers with a high Mg/Ca ratio; these coincide mostly with PF laminae. In (C), Mg curves are asymmetrical near the bottom of the sample, with sharp upper cut-offs. For further explanation see text.

Modern source water composition

The source at İslamlar, which fed the Patara aqueduct, shows a gradual variation in water temperature between winter and summer from 12.4 to 12.7 °C. The δ^{18} O values of the spring water varied from -7.09 to -7.29 ‰ over one year without clear maxima or minima.

DISCUSSION

Layering is prominent in many terrestrial carbonate deposits such as travertine, tufa and speleothems (Fouke *et al.*, 2000; Matsuoka *et al.*, 2001; Andrews & Brasier, 2005; Pentecost, 2005; Baker *et al.*, 2008; Pedley & Rogerson, 2010). If such layering is annual or seasonal, it can be used for relative dating. In Roman aqueducts, proving the annual origin of the commonly observed layering would facilitate dating of these water supply systems, and precisely constrain the age of floods, earthquakes and other extreme events that affected the aqueducts and the people who depended on their water supply. Carbonate deposits from Roman aqueducts in the eastern Mediterranean are ideal for this kind of study, because rainfall and temperature are strongly bimodal. The layering observed in calcareous sinter from the Patara and Aspendos aqueducts was therefore investigated to determine whether it is annual and, if so, how this can be checked in other carbonate deposits, such as tufa and travertine, is possible. The properties observed in this study and described above are summarised in *Figure-10*.



Figure-10 Scheme of lamina couplets in calcareous sinter from Patara and Aspendos. A summary of the properties of each of the laminae is described in the table below. An interpretation is given in the final box.

Microstructures

Optical microscopy and EBSD studies show that all samples have a similar basic structure with an alternation of DC and PF laminae, although the relative importance of each of these varies; in some cases, one lamina type may be almost completely missing, or may only occur in patches along the layering. Elongate sparite crystals similar to those in the DC laminae are also observed in speleothems and travertine, and can be attributed to growth competition at a free surface (Urai *et al.*, 1991; González *et al.*, 1992; Brasier *et al.*, 2011). The transition between micrite and sparite at the lower boundary of the sparite layers can be explained by a cessation of the nucleation of new crystals, and continued growth of some selected micrite crystals at the free surface, leading to the formation of elongate, parallel crystals. Growth competition amongst these will lead to a widening of the remaining crystals, creating the characteristic radial fanning geometry of the elongate crystals in the sparitic layers (González *et al.*, 1992; Genty & Quinif, 1996); this is supported by the strong preferred orientation of sparite grains as observed in EBSD, whereas micrite grains show a near-random orientation. The coarse, elongate crystals are usually capped by micrite along sharp boundaries (*Figures-3, 4* and *10*). As there is no reason for sparite crystals to stop growing in a saturated solution, this sudden transition must be due to a change in external conditions.

Roman aqueducts maintained a constant water flow as they were the sole water supply of cities. As water flow was continuous during the development of both DC and PF laminae, the variation in crystal fabric may be due to changing temperature, carbonate saturation level or biological activity. As rain in southern Turkey falls almost exclusively during the winter months, discharge of the spring is higher in winter and spring than in summer and autumn; this, in turn, has an effect on the chemical composition of the water. In the dry season, water residence time in the aquifer supplying the springs will be longer, and water will probably be in equilibrium with calcite at the spring. During the wet season, the residence time will be shorter as more water passes through the system. As a result, calcite saturation levels in the water may be higher in the dry season. Water supersaturated with respect to calcite can lead to spontaneous nucleation creating a fine-grained mass of new crystals (Genty & Quinif, 1996). However, it seems unlikely that the increase in supersaturation is high enough to cause an abrupt replacement of sparite by micrite. A biological origin through the formation of biofilms seems most likely (Arp *et al.*, 1999).

In the dry season, when the water temperature increases in the aqueduct channel, discharge is low and biological activity will be enhanced, leading to growth of bacterial biofilms and algae on the channel walls. In the wet season, biological activity will be lower as the temperature in the channel decreases and discharge is higher, leading to higher flow velocity which makes it harder for biofilms to form and remain attached to the channel walls. Observations in water channels in Pamukkale, Turkey, and in still functioning aqueducts at Syracuse, Italy, and Fréjus, France, show that biofilms in aqueducts preferably develop in slow flowing water. Based on these arguments, microstructural observations support the idea that PF laminae form in the dry season in active biofilms (Emeis *et al.*, 1987, Pentecost, 1993, 1998; Zhang *et al.*, 2001; Brasier *et al.*, 2010). This idea is supported by the presence of some sparite crystals that continued growing through the micrite laminae (*Figure-4A*, *B* and *F*); these crystals probably penetrated through the biofilm (cf. Arp *et al.*, 1999).

The EBSD observations show that the small crystals in the PF layers have a near-random orientation, supporting an origin by spontaneous nucleation (*Figure-5*) in a biofilm. The presence of detrital particles may contribute to the creation of nucleation sites (González *et al.*, 1992). Growth of the new crystals will be hampered by the surrounding and growing biofilm and the porous nature of the PF laminae can be explained by the presence of extracellular mucous material of the biofilm between the newly formed crystal network (Arp *et al.*, 1999), or partly by the rapid nucleation of new crystals in a supersaturated solution. The PF laminae in these samples have a structure typical of a collapsed micrite network after mucous membranes decomposed (Arp *et al.*, 1999). Epifluorescence microscopy of thin sections from the Aspendos and Patara samples shows an enrichment of PF layers in organic material (*Figure-4D-F*).

In contrast to tufa deposits, no remains of mosses or algae were found in calcareous sinter. Typical cyanobacterial shrubs and lamination, as observed in tufa and travertine (Freytet & Plet, 1996; Janssen *et al.*, 1999; Kele *et al.*, 2008; Brasier *et al.*, 2011) are absent, although isolated cyanobacterial filaments are present in some of the PF laminae. Sparite crystals in both studied aqueducts commonly contain bundles of narrow tube-like inclusions (*Figure-4C*). Guendon & Vaudour (1986, 2000) interpreted similar structures from the Nimes aqueduct as remains of cyanobacteria. However, the geometry and presence inside sparite crystals seems atypical of cyanobacteria, although a biotic origin for the inclusions cannot be excluded. The absence of photosynthetic micro-organisms in the aqueduct can be explained by the fact that it was built as a closed ceramic pipe, a channel closed off with cover stones (Patara) or a vault (Aspendos): light penetration into the channel must have been very limited, and biofilms were composed of non-photosynthetic micro-organisms.

With increasing discharge and falling temperatures in winter, growth of biofilms slowed, and biofilms broke up by increasing current strength. The nucleation rate of new micrite crystals decreased, possibly aided by an associated drop in calcite supersaturation. Subsequently, the growth of a few preferentially oriented micrite crystals created dense deposits of elongate columnar crystals as described above (Urai *et al.*, 1991; González *et al.*, 1992; Brasier *et al.*, 2011). Lack of biological activity also led to decreasing porosity of the samples, and the DC layers seem to represent an almost abiotic crystallisation from solution. Thus, the absence of biofilms allows chemical precipitation of sparitic material (Pedley, 1992).

Stable isotopes

In the Patara and Aspendos samples, a clear cyclicity of high δ^{18} O values in DC laminae and low values in PF laminae are found (*Figures-6* and 7). Four factors may control this periodicity in the Mediterranean climate of southern Turkey: seasonal changes in the isotopic composition of rainfall in the catchment area of the spring; preferential infiltration of rain water with a distinct isotopic signature in some seasons (Ayalon *et al.*, 1998); enhanced evaporation inside the aqueduct channel during the dry season; and temperature-dependent isotope fractionation during calcite precipitation.

The first two factors are most probably irrelevant for this study area. Rainfall in southern Turkey occurs mostly in winter, and although the infrequent summer rains show higher δ^{18} O values than winter rains, the large karst aquifers feeding the Patara and Aspendos aqueducts do not show this seasonal pattern due to extensive mixing. Present spring water of Patara has a δ^{18} O composition of -7.09 to -7.20 ‰, showing no systematic variation over the year. Mixing probably also eliminates the effect of individual downpours observed by Ayalon *et al.* (1998). Evaporation can be a significant factor in rivers in semi-arid environments (Ihlenfeld *et al.*, 2003) and evaporation might play a role in summer in the aqueducts. However, 10 to 15 % of the water in the aqueduct channel would have to evaporate to account for the observed 2 to 3 ‰ amplitude in δ^{18} O; as the aqueducts are closed pipes or vaulted masonry channels designed to minimise evaporation and it took <12 h for the water to reach the city, it is unlikely that such a high level of evaporation was reached. In addition, the observations discussed above suggest that the DC layers were deposited during the cold, wet season, when evaporation would be at a minimum. Temperature-dependent fractionation is therefore the most likely explanation for the observed cyclicity in δ^{18} O. Both aqueducts are long channels, where the water temperature probably increased downstream; the channel of the Aspendos aqueduct is covered by a shallowly buried vault, the upstream section of the Patara aqueduct consists of partly covered ceramic pipes on a steep mountain slope, while the downstream section is a masonry channel with cover stones, apparently devoid of any soil cover.

The water temperature of the present Patara source was 12.4 to 12.7 °C. Assuming that the Roman source had a similar water isotopic value, and neglecting (the minor effect of) evaporation, the observed δ^{18} O periodicity of calcareous sinter from this aqueduct would correspond to a temperature range of 12 to 16 °C (10 to 14 °C) for sample P28 and 14 to 18 °C (12 to 16 °C) for sample P2, 8 km further downstream using the equation of Friedman & O'Neil (1977; values in parentheses are calculated using the relationship of Kim & O'Neil, 1997). Warming of the water by up to 3 or 4 °C in summer seems realistic for a shallowly buried channel.

A negative correlation is observed between δ^{13} C and δ^{18} O across most of the samples (*Figures- 6* and 7). The δ^{13} C generally reflects soil bioproductivity in the recharge area of the aquifer and the ratio of C3 (trees and shrubs) to C4 (drought-adopted grasses) vegetation (Mattey *et al.*, 2008). In the dry season, a decrease in soil-CO₂ input into the aquifer due to low soil moisture leads to higher δ^{13} C values and vice versa. In many aquifers, however, the amplitude of these seasonal δ^{13} C fluctuations are likely to be attenuated or even eliminated due to mixing effects in the aquifer.

In cave systems, carbonate deposition occurs from a thin water film in contact with a large volume of air. As a result, in many cave systems, ventilation can have an important effect on the carbon-isotopic composition of drip waters and the deposited calcite (Spötl et al., 2005). Degassing and prior calcite precipitation before the water enters the cave can also alter the stable carbon isotopes and can play a role in increasing the isotope ratio. Many cave studies demonstrated that in winter, cave ventilation is high leading to low cave air CO₂ concentrations, and this gives rise to enhanced CO₂ degassing of the drip waters. In summer, degassing is lower because of reduced cave ventilation; as a result, high δ^{13} C is usually common in winter (Spötl *et al.*, 2005). An aqueduct is a different system, with a much higher discharge and a smaller volume of air, and probably not much change in ventilation between the seasons. Because of the large volume of water entering an aqueduct at all times, prior deposition of carbonate before the water exits the spring is unlikely to play an important role in aqueducts. Degassing, however, is important and can increase the δ^{13} C value in water by preferentially removing the lighter ¹²C isotopes from the host water. Additionally, degassing plays a more significant role in summer, with water levels lower and water temperatures higher than in winter resulting in high δ^{13} C isotope values during this time of the year (cf. Boch *et al.*, 2011).

Elemental composition

The EPMA measurements show that PF laminae are enriched in Fe, Mg, K, Al and Si, while the DC laminae are composed of nearly pure calcite (*Figure-8*). A possible explanation is that, in summer, water temperature is higher and water flow less vigorous, leading to the growth of biofilms with extracellular mucous material that can capture detrital particles (e.g. Pedley, 1992; Arp *et al.*, 1999; Brasier *et al.*, 2010; Gradziński *et al.*, 2010). The detrital material could be in the form of sub-microscopic clay particles, since the enrichment in Si, Fe, K and in some cases Mg, does not occur in individual sparite grains that transect the micritic laminae, like those shown in *Figure-4* and *Figures-8A* and *8B. Figure-8C* shows that detrital material is especially enriched close to the pore spaces that may present collapsed micrite around mucous material. Finally, fungi may capture detrital material and bind elements such as Fe, Ni, Zn, Ag, Cu, Cd and Pb onto their surface (Northup *et al.*, 1997). *Figure-8C* shows a case where detrital elements are concentrated near the top of the PF laminae; this might be due to a slight increase in the concentration of clay particles concomitant with the onset of the rainy season, while biofilms are still present. The modern spring at the site of the Roman water capture installations for the aqueduct has a very low suspension load throughout the year, but probably enough to allow biofilms to capture some material. The low level of detrital enrichment in the sparitic laminae can be attributed to the absence of biofilms in times of vigorous water flow (Pedley, 1992; Gradziński, 2010).

Magnesium differs from other elements mentioned above because, in some of our samples, it is not only high in micrite but also in individual sparite crystals growing across several PF and DC laminae, suggesting non-detrital enrichment (Figure-4A). It is tempting to attribute such increased values to a higher water temperature (Gascoyne, 1983, 1992; Ihlenfeld et al., 2003) but this cannot be proved as there is no control on the contemporary water composition or on the composition of the host rock of the spring water. Moreover, at least in sample A10-1BB, an observed asymmetry of the Mg peaks (Figure-9C) is hard to explain as an effect of a seasonal temperature change; the peaks closely follow a gradual transition from sparite to micrite in the PF laminae, followed by a sharp boundary to the next DC layer. This effect is probably due to a gradual enrichment of the water in Mg in response to an increase in residence time of the water in the aquifer at the onset of summer and autumn. Although calcite dissolves slightly faster than dolomite in the initial stages of dissolution, dolomite continues to dissolve after calcite saturation has been reached (Roberts et al, 1998; Fairchild et al., 2000). Prior deposition of calcite in the aqueduct channel can also increase Mg concentrations in the water downstream, but this effect is hard to assess without precise data on calcareous sinter thickness along the channel. The sudden drop in Mg at the start of the DC laminae is probably due to rising water levels and an increase in runoff concomitant with the onset of winter rains. It is interesting that some δ^{13} C peaks also seems to be slightly asymmetric for sample A10-1BB, probably for the same reason (Figure-9C).

Concerning Ba and Sr, Ihlenfeld *et al.* (2003) reported a correlation between δ^{13} C, Ba and Sr due to prior calcite precipitation in the vadose zone. Such a trend cannot be confirmed in study (*Figure-9*). The concentrations of Ba and Sr are affected by a large number of factors for which we have no information (c.f. Ihlenfeld *et al.*, 2003; Carlut *et al.*, 2009). In many speleothem studies, Sr and Ba show an anti-correlation with Mg as they are affected by different processes, but the opposite is commonly seen in the present study: Sr is positively correlated with Mg in some samples. The anti-correlation between Mg and Sr in PF layers may be the result of increased dolomite dissolution with longer residence time of water in the aquifer during dry periods (Ihlenfeld *et al.*, 2003;

Desmarchelier *et al.*, 2006). The crystal growth rate of calcite is one of the main factors that can influence the incorporation of Sr and Ba. A high rate can give rise to higher Sr and Ba values (Verheyden, 2005). In addition, enhanced dolomite dissolution during dry periods can give rise to a negative correlation between Mg and Sr since dolomite has lower Sr and Ba and higher Mg concentrations than calcite.

Concentrations of U show a variable relationship with Mg. Except for the highly positive correlation in sample P28, there is an anti-correlation in several samples. Commonly, U is thought to be associated with organic matter inside the lamina couplets (Ihlenfeld *et al.*, 2003; Johnson *et al*, 2006). High U values are also observed in the present study and this may be the case in P28 (*Figure-9*). On the other hand, U may also be related to the precipitation rate that changes the U flux from soil cover (Ihlenfeld *et al.*, 2003). Alternative factors that may influence the U content are seasonal changes in pH and in the abundance of other dissolved matter (Desmarchelier *et al.*, 2006).

Many sparite laminae contain a series of irregularly spaced brown bands near their base (*Figure-3D*). These appear as bright bands in blue light and UV fluorescence, but do not show any enrichment in trace elements. Therefore, these bands are interpreted as phases of enrichment in dissolved fulvic and humic substances from the soil, washed out during heavy rains in the wet season (Ihlenfeld *et al.*, 2003; Kano et al., 2003; Gradziński *et al.*, 2010).

Obviously, there are some interesting and consistent trends in the distribution of trace elements in aqueduct calcareous sinter. Presently, no studies exist on the distribution of trace elements along aqueducts, and no monitoring studies have traced the behaviour of different elements from the source to the sites of deposition. The aqueducts investigated in this study are fossil, ruined structures and the original water composition and temperatures are no longer available. Further detailed studies and, where possible, monitoring of still functioning aqueducts will be needed to assess the significance of certain trace elements as palaeoenvironmental proxies.

Comparison with other freshwater carbonate deposits

Calcareous sinter from Roman aqueducts is comparable to some extend to flowstone in caves and to ambient temperature freshwater spring and stream tufas. Gradziński *et al.* (1997) reported rhythmically laminated flowstone with detrital enrichment in porous layers. The detrital fraction in those flowstone samples was more abundant and coarser grained than in the present study, probably because water in the wet season was carrying a considerable sediment load.

Brasier et al. (2010, 2011) studied well-layered spring tufa deposits in Greece that are similar to aqueduct deposits, also with a strong cyclicity in δ^{18} O, attributed to seasonal changes in water temperature. However, boundaries between porous and dense layers are sharp and attributed to breaks in carbonate deposition because of a lack of cyanobacterial growth; in summer due to lack of water, and in winter due to low temperatures. These factors play no major role in aqueduct deposits, and make a comparison difficult.

The closest equivalents to the present study, and the only ones with comparable isotope and trace element data are studies of tufa-depositing river systems by Matsuoka et al. (2001), Ihlenfeld *et al.* (2003), Kano *et al.* (2003), O'Brien *et al.* (2006) and Lojen *et al.* (2009). These authors observed a similar periodicity in δ^{18} O and similarly attributed this to temperature-dependent isotope fractionation in the river and evaporation, while a δ^{18} O

periodicity of the spring water is excluded because of either a pronounced wet season (Ihlenfeld et al., 2003) or actual measurements (Matsuoka et al., 2001, O'Brien et al., 2006). The correlation of microstructure, porosity and detrital enrichment in the layering with the seasons differs amongst the tufa studies and with the results presented here. This observation can be attributed to typical characteristics of an open river system over a closed spring water-fed aqueduct such as a higher sediment load in the wet season, a stronger effect of evaporation and strong photogenic biological activity by cyanobacteria. Matsuoka et al. (2001) and Kano et al. (2003) correlated dense micritic fabrics to the summer wet season, and porous micritic fabrics to winter and spring, contrary to the mechanism suggested here for aqueduct calcareous sinter. However, this can be attributed to dominant summer rains rather than winter rains in their river system; studies of European river tufa, with wet winters, observed dense fabrics in winter and porous in summer similar to the aqueduct deposits of this study (Pentecost & Spiro, 1990; Freytet & Plet, 1996; Janssen et al., 1999; Kano et al., 2003). In line with the present study, Ihlenfeld et al. (2003) observed an anti-correlation of δ^{18} O and δ^{13} C, and attributed this to carbonate precipitation in the epikarst of the vadose zone in the dry season. On the other hand, Matsuoka *et al.* (2001) observed covariance of δ^{18} O and δ^{13} C, which is opposite to the findings presented here. These authors attributed the δ^{13} C cyclicity mainly to degassing in the cave system feeding the source and minor degassing from the river itself, and biogenic effects in the river due to photosynthesis. In the case of Matsuoka et al. (2001), degassing is most important in winter and δ^{18} O and δ^{13} C curves are parallel rather than anti-correlated, as observed in the aqueducts of this study occupying a Mediterranean climate characterised by winter rains. Therefore, the observations of Matsuoka et al. (2001) are not in contradiction to the results presented here.

CONCLUSIONS

Calcareous sinter in two Roman aqueducts from the eastern Mediterranean consists of couplets of alternating porous, fine-grained (PF) and dense, coarse-grained (DC) laminae, usually 1 to 2 mm wide. This layering is interpreted as annual, based on the combined interpretation of the microstructure, oxygen and carbon isotopes, and trace elements. The DC layers with elongate sparitic calcite crystals formed in fast moving water during winter and spring when discharge was higher. The PF layers with fine-grained crystals formed in slow moving water in summer or autumn when the discharge was lower during drier conditions. Detrital material may have been more concentrated in the water during the drier summer periods. Biological activity in the channel in summer and autumn may have led to the capturing of detrital material rich in Si, Fe, K, Mg and Al, possibly in the form of very fine clay particles captured by biofilms. During low-flow conditions in summer and autumn, higher water temperatures led to lower δ^{18} O values of PF calcite deposited during summer and to high δ^{13} C values as a result of enhanced degassing. The periodicity seen in crystal structure, porosity, major and trace elements, and stable isotopes is therefore the result of a seasonal pattern, which implies that calcareous sinter in Roman aqueducts is a potentially significant high-resolution data source on climate change during the Roman period. However, more work on a large number of aqueducts in different climatic zones is needed to achieve this goal. As individual aqueducts rarely have more than 100 years of depositional history, neighbouring aqueducts will have to be compared and their stratigraphies correlated, where possible aided by radiometric dating. Following this line, annually laminated sinter from aqueducts could emerge as a new high-resolution environmental and archaeological proxy.

Comparison of calcareous sinter with flowstone and tufa shows many similarities, notably in the relation of δ^{18} O periodicity with temperature, although no other deposit has exactly the same combination of characteristics.
However, calcareous sinter from Roman aqueducts can help to better understand flowstone and tufa deposits as (unintentional) natural experiments in a man-made, controlled environment over a range of different climate and source water conditions.

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SUPPORTING INFORMATION

Appendix S1

Stable isotope data

sample	del13C	del18O	sample	del13C	del18O	sample	del13C	del18O	sample	del13C	del18O
P28-1	-8,25	-6,45	P2-1	-7,24	-7,32	A10A - 1	-9,06	-6,33	A10A - 69	-8,73	-7,33
P28-2	-8,16	-6,30	P2-2	-7,49	-7,06	A10A - 2	-7,14	-7,20	A10A - 70	-9,04	-7,01
P28-3	-7,97	-6,48	P2-3	-7,56	-6,71	A10A - 3	-7,68	-6,92	A10A - 71	-9,61	-6,64
P28-4	-8,21	-6,48	P2-4	-7,95	-6,72	A10A - 4	-8,52	-6,44	A10A - 72	-9,63	-6,52
P28-5	-8,23	-6,61	P2-5	-7,48	-6,82	A10A - 5	-9,08	-5,74	A10A - 73	-8,92	-6,53
P28-6	-8,26	-6,43	P2-6	-7,43	-7,13	A10A - 6	-9,52	-5,64	A10A - 74	-8,04	-6,67
P28-7	-8,30	-6,39	P2-7	-7,50	-7,23	A10A - 7	-7,84	-5,97	A10A - 75	-7,95	-7,26
P28-8	-8,31	-6,53	P2-8	-7,65	-7,19	A10A - 8	-7,80	-6,55	A10A - 76	-8,53	-7,24
P28-9	-8,32	-6,50	P2-9	-7,66	-6,94	A10A - 9	-8,08	-7,09	A10A - 77	-9,23	-6,87
P28-10	-8,39	-6,46	P2-10	-7,58	-6,78	A10A - 10	-8,69	-6,80	A10A - 78	-9,68	-6,47
P28-11	-8,36	-6,51	P2-11	-7,47	-6,96	A10A - 11	-9,11	-6,45	A10A - 79	-10,18	-6,27
P28-12	-8,02	-6,40	P2-12	-7,56	-7,20	A10A - 12	-9,77	-6,17	A10A - 80	-9,91	-6,12

P28-13	-8,42	-6,46	P2-13	-7,53	-7,24	A10A - 13	-9,99	-6,02	A10A - 81	-9,06	-6,55
P28-14	-8,46	-6,57	P2-14	-7,62	-7,18	A10A - 14	-9,16	-5,94	A10A - 82	-8,68	-6,87
P28-15	-8,32	-6,61	P2-15	-7,80	-7,04	A10A - 15	-7,84	-6,79	A10A - 83	-8,18	-7,22
P28-16	-8,47	-6,82	P2-16	-7,90	-6,77	A10A - 16	-7,80	-7,16	A10A - 84	-8,46	-7,13
P28-17	-8,31	-6,69	P2-17	-7,67	-6,97	A10A - 17	-8,42	-6,92	A10A - 85	-8,76	-6,90
P28-18	-8,08	-6,52	P2-18	-7,69	-7,21	A10A - 18	-8,97	-6,41	A10A - 86	-9,69	-6,36
P28-19	-8,29	-6,42	P2-19	-7,74	-7,22	A10A - 19	-9,24	-6,29	A10A - 87	-9,76	-6,15
P28-20	-8,36	-6,47	P2-20	-7,96	-7,16	A10A - 20	-9,25	-5,85	A10A - 88	-9,73	-6,08
P28-21	-8,35	-6,67	P2-21	-8,09	-7,06	A10A - 21	-9,66	-5,97	A10A - 89	-8,05	-6,82
P28-22	-8,29	-6,63	P2-22	-8,00	-6,95	A10A - 22	-8,39	-6,27	A10A - 90	-8,01	-7,40
P28-23	-8,15	-6,55	P2-23	-7,76	-6,88	A10A - 23	-6,40	-6,72	A10A - 91	-8,70	-7,31
P28-24	-8,14	-6,55	P2-24	-7,76	-7,21	A10A - 24	-7,58	-7,28	A10A - 92	-9,11	-6,90
P28-25	-8,30	-6,47	P2-25	-7,83	-7,43	A10A - 25	-8,22	-6,98	A10A - 93	-9,40	-6,50
P28-26	-8,36	-6,53	P2-26	-7,79	-7,31	A10A - 26	-8,88	-6,58	A10A - 94	-9,74	-6,28
P28-27	-8,19	-6,63	P2-27	-7,93	-7,19	A10A - 27	-9,74	-6,51	A10A - 95	-9,85	-6,23
P28-28	-8,13	-6,59	P2-28	-8,04	-6,92	A10A - 28	-9,98	-6,23	A10A - 96	-8,91	-6,47
P28-29	-7,94	-6,49	P2-29	-8,26	-6,86	A10A - 29	-9,58	-6,26	A10A - 97	-	
P28-30	-8,09	-6,50	P2-30	-7,96	-7,09	A10A - 30	-7,31	-6,84	A10A - 98	-8,23	-7,51
P28-31	-8,37	-6,63	P2-31	-7,81	-7,28	A10A - 31	-7,64	-7,31	A10A - 99	-8,69	-7,16
P28-32	-8,42	-6,60	P2-32	-7,85	-7,40	A10A - 32	-	-	A10A - 100	-9,39	-6,94
P28-33	-8,25	-6,53	P2-33	-7,87	-7,27	A10A - 33	-9,26	-6,71	A10A - 101	-9,46	-6,74
P28-34	-8,08	-6,39	P2-34	-7,94	-7,15	A10A - 34	-9,52	-6,49	A10A - 102	-9,33	-6,64
P28-35	-8,19	-6,45	P2-35	-7,85	-6,83	A10A - 35	-9,92	-6,40	A10A - 103	-8,59	-6,68
P28-36	-8,11	-6,50	P2-36	-7,88	-6,94	A10A - 36	-10,15	-6,27	A10A 104	-7,46	-6,80
P28-37	-7,89	-6,38	P2-37	-7,88	-7,19	A10A - 37	-10,00	-6,41	A10A 105	-7,43	-7,31
P28-38	-7,90	-6,28	P2-38	-8,00	-7,18	A10A - 38	-8,79	-6,79	A10A 106	-7,60	-7,36
P28-39	-7,81	-6,24	P2-39	-8,08	-7,15	A10A - 39	-7,52	-7,27	A10A 107	-8,23	-7,07
P28-40	-8,00	-6,39	P2-40	-8,16	-6,97	A10A - 40	-7,91	-7,47	A10A 108	-9,03	-6,70
P28-41	-8,11	-6,61	P2-41	-8,44	-6,87	A10A - 41	-8,64	-6,99	A10A 109	-9,49	-6,55
P28-42	-7,95	-6,57	P2-42	-8,32	-6,97	A10A - 42	-9,48	-6,34	A10A 110	-9,51	-6,40
P28-43	-8,01	-6,52	P2-43	-7,83	-6,95	A10A - 43	-9,95	-6,00	A10A 111	-7,97	-6,57
P28-44	-7,98	-6,70	P2-44	-7,83	-7,21	A10A - 44	-10,05	-5,87	AV - 1	-7,57	-6,15
P28-45	-8,09	-6,68	P2-45	-7,88	-7,21	A10A - 45	-8,95	-6,40	AV - 2	-8,61	-5,75
P28-46	-7,98	-6,44	P2-46	-7,88	-7,10	A10A - 46	-7,96	-7,18	AV - 3	-7,54	-6,35
P28-47	-8,06	-6,36	P2-47	-8,21	-7,04	A10A - 47	-8,52	-6,82	AV - 4	-8,52	-6,44
P28-48	-8,04	-6,44	P2-48	-8,30	-6,99	A10A - 48	-9,28	-6,30	AV - 5	-9,46	-6,18
P28-49	-8,11	-6,56	P2-49	-8,18	-6,91	A10A - 49	-9,65	-6,06	AV - 6	-9,86	-6,24
P28-50	-8,02	-6,57	P2-50	-8,06	-7,06	A10A - 50	-9,52	-5,95	AV - 7	-9,85	-6,45
P28-51	-7,89	-6,51	P2-51	-7,91	-7,00	A10A - 51	-9,39	-6,09	AV - 8	-8,54	-6,95
P28-52	-7,89	-6,51	P2-52	-7,90	-7,12	A10A - 52	-7,70	-6,40	AV - 9	-7,15	-7,13
P28-53	-7,97	-6,26	P2-53	-8,09	-7,10	A10A - 53	-7,47	-7,23	AV - 10	-7,56	-6,49
P28-54	-8,03	-6,35	P2-54	-8,09	-6,98	A10A - 54	-7,55	-7,29	AV - 11	-7,03	-6,78
P28-55	-8,10	-6,26	P2-55	-8,22	-6,86	A10A - 55	-8,30	-7,28	AV - 12	-7,80	-6,74
P28-56	-8,24	-6,57	P2-56	-8,36	-6,87	A10A - 56	-8,87	-6,73	AV - 13	-9,39	-6,51
P28-57	-8,18	-6,50	P2-57	-8,10	-6,93	A10A - 57	-9,33	-6,35	AV - 14	-9,57	-6,64
P28-58	-8,26	-6,57	P2-58	-7,94	-7,02	A10A - 58	-9,89	-6,08	AV - 15	-8,41	-7,04
P28-59	-8,24	-6,47	P2-59	-8,01	-7,08	A10A - 59	-8,58	-6,67	AV - 16	-6,98	-7,50
P28-60	-8,29	-6,94	P2-60	-7,86	-7,13	A10A - 60	-7,40	-7,40	AV - 17	-7,62	-6,97
P28-61	-8,01	-6,46	P2-61	-7,96	-7,13	A10A - 61	-8,05	-7,69	AV - 18	-9,27	-6,47
P28-62	-8,39	-6,75	P2-62	-8,00	-6,98	A10A - 62	-8,63	-7,16	AV - 19	-8,78	-6,62

P28-63	-8,37	-6,46	P2-63	-8,12	-6,85	A10A - 63	-9,40	-6,75	AV - 20	-7,97	-7,34
P28-64	-8,65	-6,64	P2-64	-7,95	-6,78	A10A - 64	-9,70	-6,42	AV - 21	-7,15	-7,47
P28-65	-8,59	-6,68	P2-65	-7,62	-6,79	A10A - 65	-9,16	-6,33	AV - 22	-8,80	-6,68
P28-66	-8,19	-6,32	P2-66	-7,71	-7,06	A10A - 66	-8,84	-6,64	AV - 23	-9,70	-6,28
P28-67	-8,39	-6,49	P2-67	-7,70	-7,20	A10A - 67	-8,31	-6,82	AV - 24	-9,35	-6,49
P28-68	-8,43	-6,53	P2-68	-7,82	-7,09	A10A - 68	-8,28	-7,27	AV - 25	-8,86	-6,74
			P2-69	-7,92	-6,79				AV - 26	-7,73	-7,34
			P2-70	-7,84	-6,74				AV - 27	-6,87	-7,27
			P2-71	-7,83	-6,77				AV - 28	-8,32	-6,56
			P2-72	-7,80	-6,89				AV - 29	-8,82	-6,69
			P2-73	-7,89	-7,03				AV - 30	-8,07	-7,28
			P2-74	-7,89	-7,01				AV - 31	-7,17	-7,25
			P2-75	-8,12	-6,70				AV - 32	-8,65	-6,37
			P2-76	-7,87	-6,61				AV - 33	-9,17	-6,18
									AV - 34	-8,76	-6,64
									AV - 35	-8,42	-7,14
									AV - 36	-9,07	-6,49
									AV - 37	-8,50	-6,63
									AV - 38	-7,31	-7,19
									AV - 39	-8,81	-6,17
									AV - 40	-9,49	-6,04
									AV - 41	-8,86	-6,39
									AV - 42	-8,86	-6,66
									AV - 43	-9,22	-6,55
									AV - 44	-9,02	-6,92
									AV - 45	-8,56	-6,82
									AV - 46	-9,19	-6,49
									AV - 47	-9,07	-6,60
									AV - 48	-8,99	-6,52
									AV - 49	-9,44	-6,31
									AV - 50	-8,42	-6,75
									AV - 51	-8,77	-6,60
									AV - 52	-9,59	-6,20
									AV - 53	-9,22	-6,41
									AV - 54	-8,17	-6,63
									AV - 55	-7,61	-6,54
									AV - 56	-8,93	-5,82
									AV - 57	-7,77	-6,52
									AV - 58	-7,73	-6,02
									AV - 59	-8,19	-5,83
									AV - 60	-7,19	-6,59

Chapter 3

Environmental and depositional controls on laminated freshwater carbonates: an example from the Roman aqueduct of Patara, Turkey

Abstract

Carbonate deposits in Roman aqueducts are a new high-resolution data source for environmental changes during the time of the Roman Empire, notably in the fields of palaeoclimate and spring hydrology. In order to separate environmental effects from those related to depositional setting, laminated carbonate deposits were systematically compared along the entire length of one exceptionally well-preserved ancient aqueduct channel, that of Patara, Turkey. The carbonate deposits are composed of alternating dense, coarse-grained and porous, fine-grained laminae. The former formed in the dry, warm season and the latter in the wet, cool season. The relative importance of both laminae types depends on the location within the aqueduct: dense, coarse-grained laminae dominate in steep sections of the aqueduct, while porous, fine-grained laminae are mostly found on gentle slopes. This is attributed to the flow velocity of the water, since fast flow on steep slopes hampers the development of biofilms. Oxygen isotope data measured in carbonate profiles show oscillations with increasing amplitude downstream reflecting increasing water temperatures in the channel, while evaporation plays a minor, damping role on these oscillations. Carbon isotope values show an abrupt increase where an open masonry channel replaces a closed conduit made of ceramic pipes. This increase is probably due to stronger degassing of CO₂ in the open channel. If these local parameters are taken into consideration, carbonate deposits in Roman aqueducts hold high promises as seasonally resolved archives of hydrology, climate and - in tectonically active regions - recorders of large, destructive earthquakes. Bringing such data from several aqueducts together will be a powerful tool for reconstructions of palaeoclimate, spring hydrology and historical earthquakes in the Mediterranean region.

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INTRODUCTION

Laminated freshwater carbonate deposits such as tufa, travertine and speleothems have been the focus of many studies in recent years (Pentecost, 2005; Pedley & Rogerson, 2010; Alsonso-Zarza and Tanner, 2010; Fairchild & Baker, 2012). These carbonate deposits form continuously, thereby recording changes in climate, aquifer characteristics, vegetation cover and other environmental factors. An analysis of the structure, trace element and stable isotope composition of such deposits, in combination with dating, can therefore yield relevant data on

long-term environmental and ecological changes over periods of 10^2 to 10^6 years (e.g. Sasowsky & Mylroie, 2004; Pentecost, 2005; Pedley & Rogerson, 2010). As such, freshwater carbonate deposits are of great importance to understand natural changes on a variety of timescales, which may be distinguished from anthropogenic effects.

Most freshwater carbonates show layering defined by variations in color, microstructure and/or composition. This layering is usually interpreted as an effect of changes in water composition, temperature and/or biological activity (Pentecost, 2005; Pedley & Rogerson, 2010). In many deposits, part of this layering is highly regular and commonly interpreted as annual (Matsuoka et al., 2001; Kano et al., 2003, 2004; Ihlenfeld et al., 2003; O'Brien et al., 2006; Brasier et al., 2011). Many other types and frequencies of laminae and layers occur on shorter or longer time scales. The main difficulty in unravelling the nature and origin of layering in freshwater carbonates is the complex environment in which they form, and the many competing factors that can influence the microstructure and chemistry of these deposits.

Recently, carbonate deposits in Roman aqueducts have been suggested as a potential high-resolution palaeoenvironmental archive for the Mediterranean region and Western Europe (Carlut et al., 2009; Sbeinati et al., 2010; Carlut et al., 2011; Sürmelihindi et al., 2012). Aqueducts are one of the most impressive legacies of the Roman Empire. Typically built as long roofed masonry channels, these gravity-driven water transport systems brought water from springs, rivers and lakes to cities, farms and mines. The channels were up to 1.2 m wide and 250 km in length (*Figures-1* and *2*) and transported up to 200,000 m³ of water per day (Bedon, 1997; Hodge, 1992; Wikander, 1983). During the Pax Romana (25 BC - 200 AD), a time of great economic prosperity, almost every Roman city acquired its own aqueduct. Nearly 1400 major and numerous smaller aqueducts are presently known (ROMAQ database, 2012). As the Romans preferred hard water, many aqueduct channels contain carbonate deposits with a layering similar to riverine tufa (Matsuoka et al., 2001; Kano et al., 2003, 2004; Ihlenfeld et al., 2003; O'Brien et al., 2006; Brasier et al., 2011). These deposits are known as "calcareous sinter", or in short as "sinter" (Grewe, 1986, 1992; Sürmelihindi et al., 2012).

The microstructure of calcareous sinter depends on a number of factors such as water temperature and composition, impurities, biological activity, height of the water level and flow speed (Sürmelihindi et al., 2012). All these factors can change with time, e.g. the temperature of water in the channel and micro-organisms living on channel walls being different in summer and winter, or in the dry versus wet season. As a result, most sinter deposits show a clear, regular layering with an alternation of sparitic and micritic laminae (Sürmelihindi et al., 2012) (*Figures- 3* and *4*). However, the relative development of sparite and micrite is strongly variable, even within one sample and some aqueducts even contain only porous micrite (Ephesus Değirmendere aqueduct – Passchier & Sürmelihindi, 2010) or only dense sparite (Bellegarde aqueduct - Carlut et al., 2011).

Contrary to the hydrology of most natural freshwater carbonate deposits (Kano et al., 2004), water flow characteristics in Roman aqueducts are straightforward and easy to model: the channels are rectangular, and commonly have the same dimensions along the entire length of the aqueduct. The channels were usually covered to avoid contamination, while the water discharge was usually kept constant. Water in the channels flowed for many decades without interruption, in some cases up to 800 years (Sbeinati et al., 2010). These factors set aqueducts apart as "long-term man-made experiments" of carbonate deposition, giving rise to a high-resolution archive of layered carbonate formed under controlled conditions over several centuries. As such, calcareous sinter can act as a high-resolution benchmark for the study of freshwater carbonates.



Figure-1 Map of the Patara aqueduct and sampling sites. Bedrock geology after Yerli et al. (2011).

The study of calcareous sinter as a high-resolution archive in palaeoclimate and archaeoseismology has started only recently (Passchier & Sürmelihindi, 2010; Sürmelihindi et al., 2012). Early work on calcareous sinter mainly focused on solving archaeological problems (Gébara et al., 2002; Guendon & Leveau, 2005) and questions about the provenance of water for Roman aqueducts, such as those of Nîmes (Fabré et al., 2000; Carbon et al., 2005; Volant et al., 2009), Fréjus (Guendon et al., 1998; Dubar, 2006; Bobée et al., 2010), Pompeii (Ohlig, 2000) and Ostia (Carlut et al., 2009). Palaeoclimate data were first recorded from calcareous sinter by Garczynski et al. (2005) and Dubar (2006). Archaeoseismology data have so far been derived from Roman aqueducts in Italy (Galli et al., 2009; 2010), Syria (Meghraoui et al., 2003, Sbeinati et al., 2010), and France (Levret et al., 2008; Volant et al., 2009).

Although it is evident that calcareous sinter represents a valuable archive in geology, palaeoclimate and archaeology, it is less clear how this archive can be exploited, how data can be retrieved from the deposits, and how reliable such proxy data are. Most studies mentioned above focused on a single sample, taken somewhere along an aqueduct channel: however, this is only a valid procedure if the characteristics of sinter stratigraphy do not vary along the channel. In this paper a well-exposed Roman aqueduct in Patara, southern Turkey, is investigated in order to study changes in structure, layering, and composition of the sinter along the length of the channel. One critical question is in which part of the aqueduct annual layers are best developed.



Figure-2 Field aspects of the Patara aqueduct. (a) Delikkemer inverted siphon supported by a wall. (b) Detail of the siphon conduit made of single perforated blocks of marble. (c) Fragment of a typical ceramic pipe from the steep slope between İslamlar and Akbel, with attached sinter. The pipes have an inner diameter of 30 cm. (d) Schematic presentation of the two main types of channel, ceramic pipes and masonry channel. (e) Remains of the masonry aqueduct channel between Akbel and Delikkemer in a gently sloping part of the aqueduct. Side walls and cover stones have fallen away. (f) Section of the aqueduct channel near Tavas bridge where the cover stones are partly preserved (background).

Patara aqueduct

Patara, the capital of the Roman province of Lycia, was one of the main ancient maritime and commercial centers of the eastern Mediterranean, on the southwest coast of Turkey (*Figure-1*). Because of its wealth and function as an important port in the eastern Mediterranean, Patara needed an aqueduct, both for the city and for the supply of visiting ships. The aqueduct transported water from sources near the village of İslamlar at 680 m a.s.l. over a distance of 23 km to Patara at 50 m a.s.l. (*Figures-1* and 3). The aqueduct comprises five bridges as well as a stretch of pressurized conduit, an inverted siphon locally known as Delikkemer (*Figures-2a* and *Figures-2b*). There seem to be at least two stages in the development of the aqueduct (Baykan & Işık, 2010; appendix 3).

The first stretch of 5.4 km, along the steep western slope of Kışla Mountain down to the community of Akbel, originally consisted of a masonry channel, presumably of Hellenistic age, of which only scant relicts remain (*Figure-3a*). This stretch was later replaced, probably by the Romans, by a single line of 55-58 cm-long ceramic pipe elements with an inner diameter of approximately 30 cm and a 4-5 cm thick wall (*Figures-2c* and *3a*). The pipeline was laid directly on the ground alongside the abandoned channel and locally positioned on low walls or in rock cuts (*Figures-1, 2c* and *2d*). Downstream of this stretch, from Akbel to the city, a masonry channel was laid out consisting of foundation slabs, walls 45-50 cm thick and some 40-45 cm high made of roughly hewn blocks bound in concrete, and large covering stones with a flat bottom and a convex top (*Figures-2d* and *Figures-2f*). Presumably, this was the original Hellenistic channel that was later refitted by the Romans. On the inside, the channel floor and walls are covered by a waterproof mortar known as *opus signinum*, the usual procedure for Roman aqueducts. The channel has a mean width of 53-55 cm, but a relatively shallow depth of only 40-45 cm (*Figures-2d* and *2f*, Baykan, 1997). The aqueduct is in a ruined state, with nearly all ceramic pipes destroyed and only preserved as a string of fragments, while the masonry channel lacks its covering stones for most of the length of the aqueduct (*Figure-2e*). Nevertheless, most parts of the structure are well enough preserved to understand its functioning.

The Patara aqueduct has a structure different from most other Roman aqueducts, which normally consist of a masonry channel with a depth between 2-5 times the width, a vaulted roof, and inspections shafts to facilitate access to the channel for maintenance and cleaning. Such aqueduct channels were usually buried over long stretches to prevent damage, contamination of the water, excessive heating and evaporation in summer, and frost damage in winter. This was not the case in Patara, where the masonry channel sits for most of its length on top of the Mesozoic marble basement (*Figures-2a, d* and *2e*), with the exception of short trenches cut in the rock where the rock face was steep or rock spurs had to be passed. Likewise, many remnants of the ceramic pipes were found lain out on top of the bedrock rather than buried. Probably, the hard Mesozoic marble and thin soil cover over which most of the aqueduct was built precluded excavation of a trench for the aqueduct channel over its entire length. The covering stones and ceramic pipes were apparently just topped with a thin layer of soil or even left uncovered (*Figure-2d*). This rather unusual construction, with a wide, shallow channel only covered by large covering stones and a stretch of ceramic piping laid out directly on the bedrock meant that the water in the aqueduct was much more exposed to temperature changes than in typical buried aqueducts. The use of closed pipes and heavy cover stones also means that carbonate deposits could not be easily removed and seem to be completely preserved.

The Patara aqueduct channel shows a variable slope. In the first 4.4 km of its course the water descended from 680 to 280 m a.s.l., while in the remaining stretch of 18.6 km to the water distribution basin at 60 m a.s.l. - the "castellum aquae" - it descended only 220 m (*Figures-1* and *3b*). The mean gradient varies from 135-45 m/km in the first section to 8-9 m/km for the remaining section to the city.

(a) schematic channel shape



Figure-3 (a) Schematic presentation of the main elements of the Patara aqueduct. (b) Profile of the aqueduct of Patara. Note vertical exaggeration. The steep slope between the source and Akbel was originally carried out as a masonry channel, some remains of which were found. It was later replaced by 30 cm diameter ceramic pipes. Observation points of sinter, with location numbers, are indicated. (c) Slope of the aqueduct. (d) Sinter thickness along the aqueduct. Maximum thickness is reached in the ceramic pipes and masonry channel on the steep slope before Akbel, while a second increase in thickness occurs in second steep section between points 101 and the Delikkemer siphon. (e) Mean thickness of lamina couplets. This could not be established for all samples (f) Sinter microstructural types observed along the aqueduct. Sinter with dominant dense, course sparite is dominant in the steep sections and in the ceramic pipes. Sinter with dominantly porous, fine-grained micritic material is found in the masonry channel in sections with a shallow slope.

The most spectacular structure of the Patara aqueduct is the Delikkemer inverted siphon, which consists of a line of perforated marble blocks with dimensions of about 80 x 85 x 50-55 cm, each weighing up to 900 kg, built on top of a 200 m-long and 10 m-high 'cyclopean' wall. (*Figures-2a* and *2b*). The perforated blocks form a closed conduit 28 cm in diameter that transported the water under pressure across an 18 m-deep mountain saddle. In the terrain alongside the cyclopean wall remains of ceramic pipe elements were found with an outer diameter of some 30 cm and a wall thickness of 5-7 cm. According to an inscription found on the wall, the siphon was destroyed by an earthquake in the first century AD and subsequently repaired (Şahin, 2007; Işık et al., 2008). Most of the ceramic pipe fragments found here probably belong to this earlier stage, destroyed by the earthquake.

MATERIALS AND METHODS

A detailed field survey of the aqueduct's course and the archaeological remains of the channel were made, as well as field observations, detailed photography and measurement of sinter in the channel (Figure-2). At each locality, the density and approximate grain size (sparitic or micritic) of the sinter deposits on fresh surfaces was noted. Sinter was studied at 25 locations along the 22 km-long aqueduct (Figures-1, 3 and 5). Sinter samples of the most characteristic types and from different depositional environments were collected, i.e. in ceramic pipes and in the masonry channel, and in sections with differing slope. A total of eight samples were taken during earlier archeological surveys and during our own field campaign (Figure-4). Two samples, P28 and P2 were already described in detail in an earlier paper (Sürmelihindi et al., 2012), and only a summary is presented here. Additional samples investigated for this study are P19, P20, P101, P1 and Pa1. Sample sites are indicated in Figure 1 and 3. All samples were taken as small loose pieces of calcareous sinter that could be linked to in-situ material, in order not to damage the ancient structure. Samples P28, 19 and 20 are from ceramic pipes in the first 5.4 km of the conduit. P2 is a small sample from a fragment of thick walled ceramic pipe found at the foot of the Delikkemer siphon wall. This was probably part of the pressurized siphon pipe that was destroyed by the earthquake (Sahin, 2007; Isik et al., 2008). Pal is from a small basin situated at the upstream side of the Delikkemer siphon, which has been completely destroyed: it is only the unusual width of the sinter fragment in outcrop which shows that it is not derived from a normal channel. Samples P101 and P1 are from the masonry channel. *Figure-4* shows sections through each of the samples.

The samples were cut in the laboratory using a thin diamond saw and two mirror-image rock slabs were taken from each sample, separated only by the saw cut. One of these slabs was used to make polished thin sections and the other was polished. The microstructure was investigated by transmitted-light microscopy. The relative percentage of micritic and sparitic sinter was estimated using enlarged photographs of the thin sections.



Figure-4 Representative slabs and thin sections of sinter from the Patara aqueduct. Either thin sections (P28, P1, Pa1, P2) or hand specimens (P19, P20, P101) are shown, depending on what medium shows the internal structure best. Samples are arranged from upstream to downstream. Rectangles indicate the position of the stable isotope traces of **Figure-6**.

Stable oxygen and carbon isotope analyses were carried out at the University of Innsbruck. Polished slabs of all samples were micromilled at 0.2 mm intervals in traces 5 mm wide and parallel to the lamination. Sites for micromilling were chosen in the least porous and well-laminated parts of the samples. At least 50 isotope sub-samples were obtained from most slabs. The sample powders were analyzed using a semi-automated device (Gasbench II) linked to a ThermoFisher Delta^{plus}XL isotope ratio mass spectrometer. Isotope values are reported on the VPDB scale and long-term precision is better than 0.1‰ for both δ^{13} C and δ^{18} O (Spötl & Vennemann, 2003).

In order to assess the stable isotope data, the original İslamlar spring that fed the Roman aqueduct was monitored. Its water temperature was measured twice a day over a period of one year starting from July 2011, using a Hobo digital thermometer. Water samples for δ^{18} O analyses were taken at monthly intervals between July 2010 and July 2011 in sealed 3 ml glass vials. In July 2012 a test was made in the ruins of the Patara aqueduct to determine the evaporation rate of water in summer (see Appendix 2).

RESULTS

Carbonate sinter structure

Carbonate sinter was studied in detail along the length of the Patara aqueduct at 25 sites. At eight of these sites, samples could be taken that were sufficiently solid and unweathered for microscopic and stable isotope investigation. Calcareous sinter is present along most of the aqueduct channel, but there is no sinter deposition in the first km after the source (*Figure-3*). No samples were taken from the older, Hellenistic channel (*Figure-3*) since the samples were too strongly weathered. In the last 3 km of the aqueduct, the thickness of the sinter is reduced to less than 2 mm. Sinter thickness reaches a maximum in the ceramic pipes of the first, steep section of the aqueduct at around 3.5 km from the source, and in the older masonry channel that preceded it at around 5.4 km from the source, at the bottom of the steep slope towards Akbel (*Figure-1* and 3). A second thickness maximum occurs shortly before the Delikkemer inverted siphon, between 10 and 11.5 km. Exceptions are the sites of samples P101 and P2, which are discussed below.

Carbonate sinter from Patara is similar to that of other aqueducts (Garczynski et al., 2005; Bobée et al., 2010; Carlut, 2011; Sürmelihindi et al., 2012) in that it is composed of alternating laminae of two types: dense, nonporous laminae composed dominantly of sparite grains and porous fine-grained laminae composed dominantly of micrite (*Figures-4, 5*). Sparitic laminae tend to be brown and transparent in hand specimen, and PF-micritic ones are white and opaque (*Figure-4*). In thin section, however, sparite laminae tend to be colourless and micrite laminae, because of their small grain size, appear darker (*Figure-5*). Because of this possible source of confusion, reference to laminae is either given as dominantly sparitic or micritic. Sparite grains are elongate and mostly occur in radiating bundles with the apex at the bottom of the laminae, growing out of the micritic laminae with a gradual transition. These large sparite crystals are commonly capped by micrite, after which the growth of sparite started again in the next layer. The sparitic laminae are mostly dense with low porosity, while the micritic ones are generally more porous (Sürmelihindi et al., 2012). Laminae are variable in thickness and expression; where dense, sparitic laminae dominate, porous micritic laminae are commonly patchy and discontinuous and vice versa (Sürmelihindi et al., 2012). The microstructure of the sinter samples is strongly variable along the length of the aqueduct. In general, sinter is dominantly coarse crystalline, sparitic and dense, with little porosity in the ceramic pipes of the first 5.4 km of the aqueduct (*Figures-3, 5*). Lamina couplets can easily be counted in this type of dense material. Abundant fragments of the pipes and sinter indicate that sinter in the pipes was not deposited in a concentric way, but in a half-moon shaped depositional setting, indicating that the pipes were not running full during the initial stages of operation (*Figure-2c*). Individual layers and groups of layers can be laterally correlated in the stratigraphy of calcareous sinter from ceramic pipes in the first 5.4 km of the aqueduct in all observed locations and samples.

Dense, sparitic sinter with a clear layering is also found attached to fragments of ceramic pipes located below the Delikkemer siphon bridge (sample P2, *Figures-4, 5*). These pipes were apparently running full under pressure and were part of earlier versions of the inverted siphon.

In the masonry channel sections, calcareous sinter is generally micritic and porous, although there is an exception to this between 10 and 11.5 km (*Figure-3*): there, massive, dense sinter is present, both along the walls of the channel and at the top of the Delikkemer northern ramp (*Figures-4, 5,* samples P1, Pa1). Sinter is still dominantly micritic, but less porous than in any other part of the masonry channel.



Figure-5 Schematic presentation of channel types and sinter development along the Patara aqueduct. Dense sinter is dominant at sites of fast water flow, while porous sinter is common in gently inclined aqueduct sections where flow was slow. Typical microstructures of sinter from the Patara aqueduct are shown in insets below. Samples P28, P19 and P2 consist dominantly of thick dense sparite with minor thin micrite laminae; sample Pa1 consists dominantly of dense sparite and micrite, while sample P101 consists exclusively of porous micrite. Crossed nicols.

Comparison of sample microstructures

The internal structure of calcareous sinter was compared and a subdivision made according to the relative abundance of dense and sparitic, or micritic and porous laminae. Samples are described in descending order along the aqueduct channel (Figures-4, 5). P28, P19 and P20 are samples taken from ceramic pipes and have a similar microstructure. All three samples share certain prominent layers and layer groups, and can be correlated with other pipe samples up and downstream over 5.4 km. P28 is a sample of dense sinter and shows the typical alternation of micrite and sparite layers, although some domains have wider and more dominant sparite or micrite laminae. 76 lamina couplets were counted in total. P19 is dominantly sparitic with large, elongated calcite crystals. The micritic layers are thinner than the sparitic ones (Figures-4, 5). At least 45 lamina couplets are visible, many with sub-annual laminations. Calcareous sinter is more porous close to the top of the sample, and the sample may not be complete. P20 is similar to P19 and P28 in microstructure with dense calcareous sinter, but the layering is less developed. This sample contains at least 57 lamina couplets (Figures-4, 5). P101 is a sample of dark, micritic layers with high porosity and few central laminae with sparitic material (Figures-3, 5). The high porosity in this sample is largely caused by stacked larval tubes of *Chironomidae* (Brasier et al., 2011). It is difficult to distinguish or count lamina couplets in most of P101 due to its high porosity. The boundaries between different laminae are not sharp but undulous. P1 is a sample of dense sinter with wide and dominant micrite laminae. Prominent sparite-rich laminae are present near the base of the sample (Figures-4, 5). In the top half of the sample an event horizon of sparite is present, which shows a sharp, unconformable boundary to the overlying micrite laminae. At least 36 laminae pairs were counted, but laminae become dominantly micritic and more porous in the top 10% of the sample, making it difficult to count layers there. Pal is a sample of dense sinter with 20-30 % sparite. Many large, elongated sparite grains transect several lamina pairs throughout the sample. The sample is more sparitic than sample P1 with 36 well-defined annual layers. Sub-annual layers are common in sparite-dominated laminae. Samples Pa1 and P1 show a very similar stratigraphy, and most lamina couplets can be correlated between the two samples. Although P101 is also from the same channel, its porosity limits correlating the lamina pattern with that of P1 and Pa1. P2 is a sample of dense, non-porous sinter and consists for 70 % of sparitic laminae (Figures-4, 5). The sample has strong sub-annual layering and the boundaries between micritic and sparitic laminae are sharp and regular where 17 lamina couplets were counted. The mean thickness of lamina couplets for all studied samples is shown in *Figure-3d*. Lamina thickness generally

corresponds to total sinter thickness, and reaches maximum values in the ceramic pipes and in the steep section shortly before Delikkemer (0-5.4 km and 10-11 km). Samples P101 and P2 are an exception as discussed below. In many samples, notably in P101, Pa1 and P2, sparite grains contain thin, hair-type filament structures in a radial fashion towards their top and in contact with overlying micrite (Sürmelihindi et al., 2012). These filament structures are possibly biogenic in origin (Carlut, 2011).

Stable isotope results

Figure-6 shows the results of δ^{18} O and δ^{13} C measurements of the eight samples. Samples P28 and P2 were described in Sürmelihindi et al. (2012) and only the main trends are shown here. No material downstream from Delikkemer was analyzed since the sinter is highly porous and the layers are too thin to resolve any cyclicity

using the micromilling method. Table 1 gives maximum and minimum values for the samples, and correlation coefficients for δ^{18} O and δ^{13} C. The correlation coefficient generally decreases downstream along the aqueduct. In the upstream samples from ceramic pipes and especially in P19, a weak cyclicity in δ^{18} O is visible, which does not coincide with the visible lamination in the sample: several cycles are usually contained within one lamina couplet. Further downstream, and especially in samples P1, Pa1 and P2, δ^{18} O shows a strong cyclicity with an amplitude locally exceeding 1 ‰. This type of cyclicity corresponds to the observed lamina couplets: high δ^{18} O values correspond to dense sparitic laminae and low values to porous micritic laminae. The relation with δ^{13} C, however, is less persistent; in samples with a strong periodicity the δ^{18} O and δ^{13} C curves are usually anti-correlated. In other samples, however, no consistent patterns are observed.



Figure-6 Stable isotope curves of six samples from the Patara aqueduct. Samples P28 and P2 are from Sürmelihindi et al. (2012) and are shown here for comparison. Below each set of curves part of a polished rock slab is shown where micromilling samples were taken. Each indentation at the top of the milling tracks represents 1 mm. All graphs are to scale.

Figure-7 shows box plots summarizing the stable isotope data displayed in *Figure-6* and Table 1. The red boxes that represent δ^{18} O in *Figure-7* show the 50% and mean values of the isotope curves. There is a gradual decrease in main δ^{18} O values, while δ^{13} C values are divided into two clusters: the lower cluster coincides with sinter deposited in ceramic pipes (P28, P19, P20, P2), while the upper ones are found in sinter deposited in open masonry channels and basins (P101, P1, Pa1). Notice that P2 is from a ceramic pipe, and that the δ^{13} C value fits this category, even though the sample was found at Delikkemer, 5.5 km downstream from the other ceramic pipe sections.

Modern water composition

The source at İslamlar, which fed the Patara aqueduct, shows a gradual variation in water temperature between winter and summer from 12.4 to 12.7 °C. δ^{18} O values of the spring water varied from -7.3 to -7.1‰ over one year without clear maxima or minima. Calcite δ^{18} O values that would result from water of this composition at the temperature of the source range from -6.4 to -6.6‰ VPDB (Friedman & O'Neil, 1977). These values were added to *Figure-7* for comparison with the values of Roman calcareous sinter.

DISCUSSION

Microstructure

Most studies of riverine tufa and of sinter in Roman aqueducts are based on only one sample from a channel. Our sampling strategy of the Patara aqueduct shows that the microstructure of calcareous sinter in different parts of the aqueduct is distinct, varying from dense layered and sparite-dominated to porous non-laminated micrite, with as much variation in microstructure as between solid speleothems and porous spring tufa. Samples P28 and P101 have a very different microstructure (*Figures-3, 4*), but were deposited in the same channel and from the same water. Certain parameters such as water velocity and channel type must therefore be responsible for the observed differences in microstructure and isotope composition of these sinter samples.

Sürmelihindi et al. (2012) have shown that layered calcareous sinter in Roman aqueducts in the eastern Mediterranean is composed of an alternation of dense, coarse crystalline laminae, built of parallel elongate sparite crystals, and a porous equigranular mass of micrite crystals. The latter were shown to form in the dry, hot season when biofilms form on channel walls, which inhibits chemical precipitation of sparite, and encourages micrite nucleation in the mucous biofilms; later, when the biofilms biodegrade, the remaining micrite develops a characteristic high porosity. The dense sparitic laminae were shown to form in the wet, cool season with high discharge and low temperatures that inhibit the growth of biofilms and cause abiotic growth of sparite (Sürmelihindi et al., 2012).

The general season-defined alternation of dense sparitic and porous micritic sinter described above is confirmed in nearly all observation points and samples of the Patara aqueduct. In addition, a change in sinter microstructure was observed laterally along the aqueduct channel (*Figure-3f*). In some aqueduct sections, one particular laminae type clearly dominates: dense sinter is dominant between 0 and 5.4 km in the ceramic pipes, and between 10 and

12 km in the masonry channel (*Figure-3f*). More porous sinter is found between 5.4 and 10 km, and downstream of 12 km. The sections with dense sinter coincide with a relatively steep slope of the aqueduct channel (*Figure-3*), while the first 5.4 km of the aqueduct are also in ceramic pipes. P2 contains identical, sparitic and dense sinter as P28, P19 and P20, even though it was found 5.5 km downstream (*Figure-4*). This sample was part of an inverted siphon pipe with fast, pressurized water flow.

Since dense sinter is not exclusively restricted to ceramic pipe sections, a possible reason for a change in density along the aqueduct channel could be in the velocity of the water flow. In fast flowing water, biofilms of microorganisms, in which micrite forms, cannot grow, and sparite forms instead. In shallow sections, with slow water flow, biofilms form and micrite dominates. The presence of biofilms can explain the high porosity of the sinter in shallow sections of the aqueduct.

An interesting contrast can be seen in the first 5.4 km of the channel, which is built on a steep slope (*Figure-3d*). The ceramic pipes contain dense, sparite-dominated calcareous sinter, while remains of an earlier Hellenistic masonry channel at the same sites show porous micrite-dominated sinter (*Figure-3*). Both generations of the aqueduct were fed by the same water source. The masonry channel in this section, however, was not steep like the ceramic pipes, but was laid out as a relatively gently dipping channel section, probably connected with drop shafts (*Figure-5*). This can explain the difference in sinter microstructure: water flow in the channel sections was slow, as in the other gently dipping sections of the aqueduct channel.

The ceramic pipes are closed and dark, and therefore inhibit the growth of photosynthetic microorganisms such as cyanobacteria and green algae that could contribute to sinter growth (Pentecost, 2005). Penetration of light into the masonry channel section of the aqueduct could theoretically have played a role, as gaps in the cover of the channel may have existed. This can no longer be checked, however, because of the ruined state of the aqueduct. However, no fossils of photosynthetic microorganisms were found in any of the samples from Patara and it is therefore likely that also the masonry channel, covered with large stone slabs, was sufficiently closed to inhibit growth of photosynthetic microorganisms. Other, non-photosynthetic microorganisms must be responsible for the formation of biofilms in the channel.

Thickness of the deposits

Near the source and near the end of the aqueduct, sinter is very thin or even absent. This is the usual pattern of aqueduct channels with carbonate-undersaturated spring water, where sinter deposition only starts after supersaturation is reached as a result of CO_2 degassing. The maximum thickness of the deposits is found further down the channel, after which the deposition thickness decreases due to approaching thermodynamic equilibrium. In addition to this general trend, channel slope is of prime importance for sinter thickness (*Figures-3c, d*): maximum values are reached in the steepest sections of the aqueduct (*Figures-3c, d*). In these sections, water was more turbulent and degassing of CO_2 increased leading to an enhanced deposition of carbonate in all seasons. The same relationship between sinter thickness and channel steepness was observed in other Roman aqueducts (e.g. Garczynski, 2005). *Figure-3* shows that in the first steep 5.4 km of the Patara aqueduct CO_2 degassing must have been considerable, and much of the carbonate in solution was deposited in this section. The

channel type can also play a role: in the ceramic pipe section a maximum thickness is reached after 3 km, after which the thickness decreases, possibly because degassing was hampered by the closed nature of the pipes (*Figures-3d, e*). In the masonry channel, a maximum is reached near Akbel, at the bottom of the steep slope, after which deposition thickness gradually decreases, with the exception of an increase in the steep section between 10 and 12 km. Sinter thickness does not increase in the last steep section (22-23 km), though. In this terminal part carbonate deposition was minor, probably because the CO_2 concentration in the water approached that of the atmosphere, so that no further degassing could take place even on a steep slope.

In most samples the thickness of the sinter correlates with the mean thickness of individual laminae (*Figures-3d*, *e*). Sample P2 is different because its laminae are unusually thick. Enhanced turbulence in the inverted siphon may be responsible for this anomaly. Equally interesting is the thick sinter of P101, whose lamina couplets in the dense central part are actually thinner than those of dense samples such as P1 and P19. There is no reason to argue that P101 contains more lamina couplets than other samples in the channel. The main reason for the excessive thickness of this sample is its unusually porous nature with a very small amount of sparite and with numerous stacked chironomid larval tubes (Brasier et al., 2011). As a result, the density of this sample is 1.85 g/cm³ compared to 2.20 g/cm³ for sinter of P1. A similar relationship was seen in the Değirmendere aqueduct of Ephesus and the still functioning Roman aqueduct of Syracuse, where *Chironomidae* larval tubes also cause excessively thick sinter deposits.

In general, the thickness of calcareous sinter along an aqueduct is the result of at least four competing factors: (1) distance from the source as a function of carbonate saturation; (2) channel slope and (3) channel type as a function of degassing rate, and; (4) microbiology in the channel which can lead to enhanced porosity and overall thickness of deposits. The thickness of individual laminae is mostly influenced by (1), (2) and (3) while the relative proportion of dense sparitic and porous micritic laminae in sinter depends mostly on (2).

Stable isotope results

Results of δ^{18} O measurements in the downstream samples show a cyclicity in both δ^{18} O and δ^{13} C that coincides with the lamination. As explained in Sürmelihindi et al. (2012), δ^{18} O maxima coincide mostly with the dense sparitic laminae, while minima coincide with porous micritic laminae. *Figure-6* and 7 show that the amplitude of the δ^{18} O curves gradually increases downstream.

A cyclicity in δ^{18} O as observed in *Figure-6* is also seen in tufa deposits (Pentecost, 2005) and can be due to three different processes; seasonal oscillations in δ^{18} O of the source water; seasonal differences in the evaporation rate of water in the channel; and a seasonal difference in water temperature. Our water monitoring data clearly show that no significant intra-annual variation in δ^{18} O exist in the aqueduct water. The reason for the cyclicity must therefore be variable evaporation and/or temperature in the channel during the year. Since the Patara aqueduct was built as a ceramic pipe or masonry channel directly on the bedrock, the water in the aqueduct must have been subject to significant heating in summer. However, an increase in water temperature and the very dry local climate could also have increased the evaporation rate in summer. Evaporation would increase the δ^{18} O value of the water and hence the δ^{18} O of depositing sinter. A temperature increase of the water, however, would lead to a

decrease of δ^{18} O of the sinter due to isotope fractionation. Since both temperature and evaporation reach maximum values during summer in a Mediterranean climate, it is essential to know which process dominates, in order to correctly attribute the different lamina types to individual seasons. This is possible because temperature and evaporation have opposite effects on δ^{18} O values of the sinter.



Figure-7 Box plot of stable isotope data of **Figure-5** arranged in the sequence in which they appear along the aqueduct (from left to right). $\delta^{18}O$ values decrease gradually along the aqueduct, while the amplitude of the curves increases. $\delta^{13}C$ attains maximum values in the channel section. For further explanation see text.

Based on the distribution of sinter in the ceramic pipes, the travel time of the water from the spring to Patara is estimated at 6-8 hours (Appendix 1). The highest amplitude in δ^{18} O cycles occurs in sample Pa1 (2 %), 11 km downstream from the source, halfway along the aqueduct. It probably took the water less than 4 hours to reach this point (Figures-6, 7). From the calculated total water volume of the aqueduct and the daily evaporation maximum, evaporation is estimated to between 0.4 and 1.2% of the water in 6-8 hours, or 0.2-0.6 % in 4 hours (Appendix 2). However, 18 % of the water would have to evaporate in 4 hours in order to cause a 2 ‰ amplitude of δ^{18} O as observed in Pa1 (Kendall & Coldwell, 1998; Gat & Confiantini, 1981). Clearly, evaporation in the aqueduct was insufficient to cause the observed cyclicity, mainly because of the relatively short the time it took for the water to reach the sampling sites along this relatively steep aqueduct. Changes in the temperature of the water are therefore the most likely explanation for the observed cyclicity (cf. Kano, 2004). Our measurements of the temperature on the lower side of the cover stones of the aqueduct in their present state show that it varies from 29-35°C during the daytime in summer (Appendix 2). It is clear that during its 8 hours-journey from the source to Patara the water temperature rose significantly downstream. A 2‰ variability in δ^{18} O corresponds to an 8°C increase in temperature of the water in summer, compared to that in winter. This temperature increase is a minimum estimate, since any evaporation in the channel would tend to decrease the amplitude of the δ^{18} O cyclicity. Such a significant increase in water temperature is likely for this aqueduct because of its unusual construction method (Appendix 2). The water temperature at the spring presently varies between 12.4 and 12.7°C and this temperature is significantly lower than the air temperature in Patara in summer and partly also in winter (Appendix 2).

Based on the arguments given above, it is clear that the δ^{18} O cyclicity observed in the sinter of the Patara aqueduct is due to differences in water temperature between winter and summer. Evaporation played a minor role and had a dampening effect on the cyclicity so that temperature fluctuations may have been larger than those indicated by the measured δ^{18} O cyclicity. The gradual increase in the δ^{18} O amplitude downstream can be attributed to a gradual increase in water temperature from the source to the city. It is interesting that this cyclicity is even observed in those parts of sample P101 where no layering is visible at all. This implies that high-resolution δ^{18} O profiling can be used to determine the distribution of seasons in a sample, even if no layering is visible.

The relationship between δ^{18} O and water temperature confirms that dense sparitic laminae formed during the cool, wet season, and porous micritic laminae in the dry, warm season (Sürmelihindi et al., 2012). Bobée et al. (2010) and Carlut (2011) suggested the opposite relationship and correlated dense layers with the dry season for sinter from the Fréjus and Bellegarde Roman aqueducts in France. Rainfall in this part of southern France is bimodal, however, and this seems to lead to more complex calcareous sinter. Moreover, a comparison with their work is difficult because they did not use stable isotope data, and based their work exclusively on major element data.

In contrast to the large amplitude cyclicity that correlates with visible lamination in samples P1, Pa1 and P2, the upstream samples P28, P19 and P20 – which were deposited in ceramic pipes – show a weak cyclicity that includes several cycles in one macroscopically visible lamina couplet. This cyclicity therefore seems to be subannual and is possibly related to subannual warming or cooling of aqueduct water in the ceramic pipes in excessively hot or cold periods. The fact that such effects are not observed further downstream may be due to the greater mass of stonework of the masonry channel and its cover; any short-term warming or cooling of water upstream will be damped by the heat capacity of the lower aqueduct.

Figure-6 shows that the δ^{13} C curves are more complex than the δ^{18} O curves. What is clear, however, is that cyclicity of δ^{13} C also gradually increases downstream, while the correlation with the δ^{18} O curve weakens. Sürmelihindi et al. (2012) suggested that a negative correlation between δ^{13} C and δ^{18} O could be due to enhanced degassing of CO₂ in summer in the aqueduct channel. Such a correlation seems indeed to be dominant in the channel section. However, segments of positive and negative correlation alternate along the profiles, and this implies that the mechanisms responsible for the δ^{13} C cyclicity also varied in time at any site.

The box plots in *Figure-7* show the same information as *Figure-6*, but now compressed in order to compare variations in δ^{18} O and δ^{13} C along the channel. The range of the box plots is considerable, not only due to the cyclicity of both δ^{18} O and δ^{13} C, but also to an overall decrease or increase with time in some samples. Nevertheless, there is still a clear gradually decrease of δ^{18} O values downstream. This is probably due to the gradual increase in water temperature downstream in both summer and winter.

 δ^{13} C values show an interesting switchover in *Figure-7*: samples P28, P19, P20 and P2 have relatively low values, while P101, P1 and Pa1 are up to 1‰ higher. The lower values are mainly found in the first 5.4 km of the aqueduct while higher values dominate further downstream. Although the first 5.4 km of the aqueduct coincide with the steepest slope, this does not seem to be the reason for the observed trend. Instead, a correlation exists between low δ^{13} C values and the pipes in which the material was deposited: P28, P19, P20 and P2 are all

deposited in pipe sections. Since high δ^{13} C values are correlated here with enhanced degassing, the most likely explanation for the observed trend is restricted degassing in the closed pipe sections, and enhanced degassing in the open masonry channel.

Application to palaeoenvironmental studies

About 1400 major aqueducts and thousands of small ones of the former Roman Empire are preserved, constituting a completely untapped and potentially highly important seasonally resolved archive of climate and hydrology between 200 BC and 400 AD for the Mediterranean region. Further afield, there are similar historic water channels with carbonate deposits worldwide.

This study shows that calcareous sinter in Roman aqueducts are annually laminated. Information on historical seasonal temperature variations can be obtained from such deposits provided the following conditions are met: (1) data are needed on the shape and burial depth of the channel; (2) the stratigraphy should be analyzed along the length of the channel as presented in this paper, in order to find the optimal sampling spots; (3) the magnitude of stable isotope variation of the source water and evaporation should be determined in order to calibrate the stable isotope temperature fractionation effect. Source characteristics can be obtained by monitoring the spring water where possible or, if the source is no longer active, by analysis of proximal sinter close to the source. Estimates of evaporation can be made by local evaporation experiments and model calculations of temperature in the aqueduct channel.

Information on spring hydrology characteristics, and indirectly on past annual precipitation, is also stored in aqueduct sinter deposits. Although many large springs, like the source of the Patara aqueduct, discharge throughout the year they typically show a delayed response to periods of heavy rain or draught. A resultant change in water level in the aqueduct channel will be reflected by onlap or offlap of sinter on the aqueduct walls and a change in the thickness of the carbonate laminae. As a result, precipitation levels can be obtained from the sinter provided no regulation of the water level took place by human intervention. In case of regulation, layer thickness and vertical extent can still be used to identify periods of low water level, but other methods such as clay content of the sinter must be used to reconstruct maximum discharge events.

Sinter deposits can also carry information on seismic events. Sample P2 contains 17 annual layers, which corresponds well with the period of time between the first construction of the aqueduct and its repair, as indicated on a local inscription (Sahin, 2007; Işık et al., 2008).

Dating of sinter sections can be performed using archaeological methods such as coin finds or epigraphy (Şahin, 2007; Işık et al., 2008), or U-Th dating (Frank et al., 2002; Sharp et al., 2010). The latter can provide a resolution of better than 10 years, provided the carbonate deposits contain only a limited amount of inherited Th (Sharp et al., 2010). In practice, this means that the clay content of sinter deposits should be very low to allow U-Th dating. Finally, since nearly major 1400 aqueducts are known from the Roman Empire, many areas (Italy, southern France, Greece, western Turkey, northern Algeria and Tunisia) have a dense distribution of aqueducts, less than 50 km apart (ROMAQ database, 2012). In these areas, a comparison of the data can serve to validate the regional significance of reconstructed temperature and precipitation series, and to obtain stacked century-scale time series.

CONCLUSIONS

1. In calcareous sinter from the Patara aqueduct dense sparitic and porous micritic laminae represent the wet, cool and, dry, hot seasons, respectively, and one lamina couplet represents one annual depositional cycle.

2. Calcareous sinter can be used to measure the number of years an aqueduct was operating if the oxygen isotope data show clear annual cycles. Counting couplets in macroscopically layered samples is straightforward and can be checked by δ^{18} O data. This means that it is possible to determine the duration of deposition also for non-layered specimens, based solely on the isotope profile.

3. Sinter microstructures can vary strongly along a specific aqueduct; hence lateral sampling is needed in order to establish suitable sites for detailed work.

4. In Patara, lateral variations in sinter type are mainly due to a change in water flow velocity, but water temperature and the channel type may also play a role. Sinter is dense and sparitic in fast flowing, turbulent water where biofilms do not grow. Sinter is porous and micritic in shallow aqueduct sections where biofilms develop.

5. The amplitude of δ^{18} O cycles increases downstream, most likely in response to a gradual warming of the water by several degrees in summer. The δ^{18} O baseline also gradually decreases downstream, again reflecting warming of the water. Evaporation played a minor role only.

6. δ^{13} C values are either correlated or anti-correlated with δ^{18} O, partly due to variations in the rate of degassing in the channel and kinetic fractionation. δ^{13} C values are significantly higher in masonry channel sections than in ceramic pipes due to enhanced degassing in the former.

7. The type of conduit in which the sinter was deposited - ceramic pipes or masonry channel - has only a limited effect on the microstructure and the δ^{18} O values.

8. Aqueduct sinter is a potentially relevant palaeoenvironmental archive for climate, spring hydrology and archaeoseismology during Roman times.

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Appendices

(These appendices have been submitted as complementary material to the paper)

Appendix 1 – Calculation of the travel time of water in the aqueduct

The 22.5 km-long Patara aqueduct can be split, for its channel characteristics, into two parts. From the source at İslamlar village to the Akbel pass it consisted of ceramic pipes 55-58 cm in length with an inner diameter of about 30 cm (*Figures-1, 2c*). The pipeline, covering a 412 m fall over a distance of 5.35 km, is supposed to have replaced its Hellenistic predecessor, a combination of open channels and drop shafts. From observations on the sinter in pipe remains it could be concluded that the pipes did not run full, but it was not clear to what height the water ran inside the pipes.

From Akbel at 277 m a.s.l. to the Patara distribution tank at 86 m a.s.l. the water was transported by means of an open masonry channel, whose trajectory can largely be followed. In some aqueducts, the water height in the channel can be derived from height of sinter deposits of the channel walls. In the Patara aqueduct, no such data could be obtained due to the present poor state of preservation of the upper parts of the channel (*Figures-2e, f*). Based on investigations by Baykan et al. (1997) the profile of the aqueduct and the bed slope along the trajectory could be established (*Figures-5a, b*). The trajectory may be divided into sections having a more or less constant slope, averaged as given in Table A1.

Section	Length (m)	Mean slope (m/100m)
Ι	5350	7.7
IIa	475	4.5
IIb	832	1.53
IIc	356	2.52
IId	2851	0.13
III	1230	6.58
IVa	3272	0.08
IVb	5323	0.12
V	2797	1.93

Table A1. Sections of Patara aqueduct with slope (after Baykan et al., 1997).

At 5.74 km downstream from Akbel, at the end of section III, the water passed a depression about 30 m deep by means of the 'Delikkemer' pressure line ('siphon') made of perforated stone blocks having a bore of 28 cm and placed on top of a 10 m high 'cyclopian' wall. (*Figures-2a, b*). Neither the start nor the end of the pressure line (the header tank and the receiving tank of the siphon) have been identified.

Travel time

The travel time from the source at İslamlar to the distribution tank at Patara is set by the velocity V of the water and the distance. Two empirical formulas are generally applied to determine the velocity V of the water and the discharge Q, the Manning/Strickler- and Chézy formulas (Schneider, 1996, 13.20).

Manning/Strickler formula:

$$V = K * R^{2/3} * S^{1/2}$$

with

K = Manning/Strickler's roughness factor in $m^{1/3}s^{-1}$

R = hydraulic radius = A/P in m

S = energy gradient = bed slope for uniform channels in mm⁻¹

A = cross-sectional area of water stream in m^2

P = wetted perimeter in m

A and P remain approximately constant for a uniform channel with fixed bed slope. The Manning/Strickler's roughness factor may be determined from tables in handbooks (e.g. Schneider, 1996, 13.21).

Chézy formula:

 $V = C * R^{1/2} * S^{1/2}$ with $C = Chézy \text{ coefficient} = (8*g)^{1/2} * 2*\log(14.84*R/k) \text{ in } m^{1/2} \text{s}^{-1}$ k = Nikuradse equivalent sand roughness / absolute roughness in m $g = \text{gravitational constant} = 9.81 \text{ ms}^{-2}$

k may be determined from tables in Schneider (1996)

The discharge Q in m^3 /sec follows from Q = V*A.

As all (sub) sections have different bed slopes, the velocity in each section varied, depending on the height of the water in the channel or in the pipes. Since the water height cannot be established from the preserved remains, the velocity V and discharge Q for the pipeline between İslamlar village and the Akbel pass (section I) was calculated assuming a water height of 10, 15 (pipe running half full), 20 and 25 cm inside the 30 cm pipes applying both the Manning/ Strickler and Chézy formulas, and averaging the results. Applying the Manning formula 'backward' for the calculated discharges Q, the water depth D and the velocity V for each section of the about 50 cm wide masonry channel was determined: observed channel widths vary from 50 to 55 cm (Baykan et al., 1997). Dividing the length of each section by its related water velocity yields the travel time per section, and

thus the total travel time can be established. Finally, the discharge of the pressure line was estimated and compared with the results from this procedure.

For the roughness factors in both equations the modern values for concrete were used, which are considered to be close to that of sinter (Hodge, 1992). The calculated velocity V and discharge Q for section I, using K = 60 for the Manning/Strickler roughness factor and k = 5 mm for the Chézy formula (concrete), are shown in Table A2.

Water height (m)	V - Manning ms ⁻¹	V - Chézy (ms ⁻¹)	V average (ms ⁻¹)	$Q(ls^{-1})$
0.1	2.43	2.51	2.47	51
0.15	2.96	3.08	3.02	107
0.2	3.28	3.43	3.35	168
0.25	3.37	3.53	3.45	217

Table A2. Calculated velocity and discharge for different water heights in pipe section between İslamlar and Akbel.

For the calculated values for the discharge, the water depth, water velocity, and travel time for each open channel section were calculated (Tables A3a, b). As expected, the water flows at maximum velocity in section III of the masonry channel, where the slope is steepest.

Section					
	$Q(ls^{-1})$	51	107	168	217
	D (m)				
IIa		0.06	0.09	0.12	0.16
IIb		0.08	0.13	0.18	0.22
IIc		0.07	0.11	0.15	0.18
IId		0.19	0.32	0.44	0.56
III		0.05	0.08	0.11	0.13
IVa		0.22	0.39	0.55	0.68
IVb		0.19	0.33	0.47	0.58
V		0.08	0.12	0.17	0.20

Table A3a. Calculated water depth D in masonry channel per section for values of discharge.

Section					
	Q (ls ⁻¹)	51	107	168	217
	V (ms ⁻¹)				
IIa		1.6	2.12	2.4	2.8
IIb		1.2	1.5	1.7	1.8
IIc		1.4	1.8	2.0	2.2
IId		0.5	0.6	0.65	0.7
III		1.9	2.4	2.8	3.1
IVa		0.4	0.5	0.54	0.55
IVb		0.55	0.6	0.65	0.7
V		1.3	1.2	1.8	2.0

Table A3b. Water velocity V in masonry channel for different values of discharge.

From the calculated velocity data and the length of the sections the total travel time (summation of all travel times for individual sections) may be calculated for each value of the discharge (Table A4). As a discharge in excess of 217 l/sec appears unrealistic, the travel time may be set between 6.12 and 8.2 hours (Table A4).

Discharge Q (ls ⁻¹)	Total travel time (s)	Total travel (hours)
51	29520	8.20
107	25310	7.03
168	22945	6.37
217	22049	6.12

Table A4. Total travel time for different values of discharge Q.

Delikkemer pressure line.

Since the Delikkemer inverted siphon of the Patara aqueduct consists of closed pipes, which were running full, the dimensions of the structure can be used to make an estimate of the amount of water it may have transported per second. Since the aqueduct has only once channel, and no water seems to have been removed from the channel before the siphon bridge, this would also limit the amount of water that may have passed through the upstream part of the aqueduct. This can therefore be used, to further restrict the travel time of water from the İslamlar spring to Patara.

Based on archeological remains, the start and end of the 28 cm diameter Delikkemer pressure line cannot be accurately established, and therefore only rough calculations can be made about the discharge of the siphon. Baykan states a conservative length L of 380 m and a difference in elevation Δh of 3.75 m between start and end of the siphon (Baykan et al., 1997). Kessener (unpublished) estimated a length L of 500 m, and, from observations on the elevation of the masonry channels upstream and downstream from the pressure line a difference in elevation Δh of about 9 m.

Applying the Darcy-Weisbach formula for pressurized conduits, the water velocity V may be calculated from these data, assuming turbulent flow (Schneider, 1996, 13.11):

$$V = \sqrt{\frac{2*g*I*d}{\lambda}}$$

with

$$I = \Delta h/L$$

d = diameter of conduit in m

$$\frac{1}{\sqrt{\lambda}} = 1.14 - 2 * \log\left(\frac{k}{d}\right)$$

k = absolute roughness in m

 $g = gravitational constant = 9.81 ms^{-2}$

Results are shown in Table A5, taking k = 5mm, d = 280 mm.

	Length (m)	$\Delta h(m)$	V (ms ⁻¹)	Q $(1s^{-1})$
Baykan	380	3.75	1.1	67
Kessener	500	9	1.5	91

Table A5. Estimated water velocity and discharge of the Delikkemer pressure line.

The discharge Q of the Delikkemer siphon according this estimative calculation was about 70-90 ls⁻¹. Table A2 shows that the water height in the pipes from İslamlar to Akbel must therefore have been slightly below 15 cm, which means that the pipeline was running about half full. For the masonry channel the water depth therefore did not surpass 40 cm (Section III, Table A3a), in agreement with archeological data on channel dimensions. Referring to Table A4 this limits the total travel time to between 7 and 8 hours.

Appendix 2 - calculation of evaporation and water temperature increase

Evaporation

On 26 July, 2012 a simple experiment was carried out in the preserved aqueduct channel of Patara where it is intersected by the main road (km 7.5). 1 cm diameter cylindrical glass vials were placed in the dry ancient aqueduct channel, in the shade of the aqueduct cover stones to determine how much water would evaporate in a period of 8 hours. The vials were filled to the top without a meniscus. The outside temperature on this day varied between 25° C (5 am) and 38°C (2 pm), with a 3 Bft wind, while the temperature of the cover stones and walls of the aqueduct were 29°C at 10 am, and 35 °C at 6 pm. Between 10 am and 6 pm, the water level fell by 2 mm. In the Roman aqueduct channel, evaporation may have been less since the channel was closed, and humidity must have been higher that in the present, ruined state of the aqueduct channel. Nevertheless, based on this value of 2 mm, a total of 0,002 x 0,55 x 17000 m = 18.7 m³ of water would have evaporated along the masonry aqueduct in
8 hours in the daytime in summer for the 17 km of masonry channel and a channel width of 55 cm. The total water volume of this 17 km section can be calculated from the calculated depths in Appendix 1 (Table A3a) to 1455-4358 m³. This implies that, if the channel was open to the atmosphere with manholes or gaps in the cover, at most 0.4 - 1.2 % of the water evaporated in 8 hours between the source and the city.

Temperature increase of the water

The heat flow Q from the channel walls to the aqueduct water can be given as

 $Q = \Lambda \cdot T_{d} \cdot A / d$ (Fourier's law)

where Λ is the heat conductivity coefficient (Watt/m.K), usually taken as 3.5 for limestone; T_d is the difference in temperature of the source water and the outside the aqueduct channel; d is the thickness of the channel walls. A is the wet surface of the channel. Warming of the water by ΔT is given by the equation:

 $\Delta T = Q.t/m.\alpha$

Where t is time the water took to pass a certain aqueduct segment; m is the mass of the water and α is the specific heat capacity of the water, usually given as 4.19 Joule/gram.K

Combining these equations for a small volume of water of dimensions V=dl.b.h with a density of 10^6 g m⁻³ that moves downstream gives a temperature increase of Δ T:

 $\Delta T = (\Lambda . T_{d.} (2h+b).L)/(d.h.b.\alpha.v 10^{6})$

Where L is the length of a channel segment. If the aqueduct is divided into sections of equal channel dimensions and slope, it is possible to calculate the final temperature that the water will have reached in Patara at the end of the channel (T_P , 22 km), at Akbel (T_A , 6 km) and at the site of Delikkemer, where the last sample Pa1 was taken (T_D , 11 km). For an initial water temperature at the source (T_S) of 12°C, and a channel wall thickness of 0.3 m, the increase in water temperature is strongly dependent on what happens in the first 6 km of the channel in the ceramic pipes. Assuming that these pipes, with a wall thickness of 5 cm, were not covered, they caused a considerable increase in temperature (Table A6):

T _W	Ts	T _A	T _D	T _P
20	12	15.2	15.9	17.2
25	12	17.2	18.3	20.4
30	12	19.3	20.7	23.6

Table A6. Water temperatures (°C) reached in the Patara aqueduct based on three different temperatures of aqueduct channel wall (T_W) on the outside of the channel, for a non-covered aqueduct

Table A6 shows that in summer, when the mean temperature of the cover stones may have been between 25°C and 30°C, an increase of 5-9 °C is certainly possible at the site of Delikkemer (samples Pa1, P2) where the largest cyclicity of δ^{18} O was measured. This value corresponds with the estimated temperature increase from the actual δ^{18} O measurements. In Patara, the temperature increase would even be higher, 8-12°C, since it is near the end of a shallow section of nearly 11 km length.

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Chapter 4

General Conclusions

Calcareous sinter deposits from Roman aqueducts usually consist of layers mostly 1-2 mm wide that contain a couplet of two different laminae; fine-grained, porous (PF) and coarse-grained, dense laminae (DC). Based on a study of the microstructure, stable isotope and trace element geochemistry, these laminae couplets have been identified to be the result of seasonal changes in the climatic cycle. Coarse-grained laminae represent fast flowing water conditions in the wet season and fine-grained laminae slow flowing water in the dry season. This result is different from earlier work on Roman aqueducts, which was only based on either trace element concentration or stable isotope results, as explained in Chapter 2.

The results of stable carbon and oxygen isotope, trace and major element analyses and investigation of different crystal structures highlight a clear periodicity in many calcareous sinter samples. Sinter deposits from Roman aqueducts with such a periodicity are potential proxies for palaeoenvironmental studies in science and archaeology.

Calcareous sinter can be used to measure the number of years that an aqueduct was operating if the oxygen isotope data show clear annual cycles. Counting couplets in macroscopically layered samples is straightforward and can be checked by δ^{18} O data. This means that it is possible to determine the duration of deposition also for non-layered specimens, based solely on the isotope profile.

The results of geochemical and especially stable isotope analyses show that calcareous sinter has the same depositional process and similar characteristics to other terrestrial carbonate deposits.

Development of sinter porosity and layering can vary significantly from one aqueduct site to another. Differences are mainly due to different amounts of organic activity, which again may be due to variations in water flow velocity, temperature and water composition.

Biological activity in aqueducts is limited since the channels are dark areas like cave settings. Nevertheless, several biological indicators were observed which means that biological activity may also have played a role in formation of the laminae couplets.

Detailed investigation of the Patara aqueduct shows that the microstructure of calcareous sinter can vary strongly, being more porous or dense, from one point to another along a single aqueduct line. Differences are linked to changes in slope and channel type and relative distance from the source: they are therefore interpreted as an effect of changes in water flow velocity, biological activity and temperature. Sinter is dense and sparitic in fast flowing, turbulent water where biofilms do not grow, whereas it is porous and micritic in shallow aqueduct sections where biofilms develop. The best sampling strategy is therefore needed in order to collect the most suitable samples to solve specific problems: a randomly taken sample from somewhere along an aqueduct may not be suitable in most cases.

In the Patara aqueduct, cyclicity of δ^{18} O results from alternation in water temperature which influences oxygen isotope fractionation during carbonate deposition. It is not the effect of evaporation, nor the effect of a

periodicity in the stable isotope composition of the spring that fed the aqueduct. The resulting curves of δ^{18} O show mostly anti-correlation with δ^{13} C curves. Along the aqueduct line, the amplitude of δ^{18} O cyclicity increases downstream, while δ^{18} O values were also generally lower downstream as a result of gradually increasing water temperature. Cyclicity in δ^{13} C may reflect variations in the rate of degassing in the channel and in kinetic fractionation.

Suggestions for future work

The work presented in this thesis was the result of a detailed study of calcareous sinter deposits from only two aqueducts. As there are probably close to 1000 aqueducts with sinter, in a range of different climatic and geographic settings, a number of other representative types will have to be studied in order to check the general applicability of the findings of this thesis, and to obtain new data. Aqueducts in NW Europe, such as Cologne, in northern Africa, such as Carthago, and the large aqueducts of Rome have the highest priority. Comparison of various sinter types to see which factors play a role in the development of different fabrics is a key study topic to understand the system in a better way.

The promising first results of calcareous sinter study show the expected similarity between calcareous sinter and other terrestrial carbonate deposits. For this reason, it will be important to compare speleothem, flowstone, travertine and tufa with sinter deposits from aqueducts. As aqueducts are more regular and a simpler deposition system than most terrestrial carbonates, they can help to interpret some structures in natural carbonate deposits. Moreover, dendrochronology and the study of sediments from lakes and harbors that are adjacent to aqueduct sites can be another possible comparison, which we can correlate with sinter.

The most important suggestion for future work is: dating of calcareous sinter has to be improved, or even set up by using new dating methods. So far, the U/Th method is most likely the best method for dating sinter, but the problem that has to be solved is the common high initial Th content of sinter samples. Palaeomagnetic dating is a promising possibility, but should be tried out in a number of aqueducts to clear up the problem of accurate sample orientation.

A more extensive database is necessary for calcareous sinter from Roman aqueducts. For this reason, there should be more multidisciplinary works with archaeologist, engineers, biologist, geologist and geographers. In addition, a large central collection of sinter samples should be set up like in cave studies.

Monitoring of still functioning aqueduct sites is a key part of any future work, which can show us modern conditions that form calcareous sinter. Both modern sinter deposits and water samples should be taken at regular intervals over a number of years. Sampling recent sinter from different points of an aqueduct will give us more insight in the effects of water velocity, channel type or biological activity. Unfortunately, there appear to be very few Roman aqueducts that still function.

Investigation of biological activity in recent sinter deposits is also a high priority and it will be interesting to learn more about bacterial activity in running aqueduct water for the first time. Such a study can show, which

types of bacteria and other microorganisms were active and common in aqueduct channels and what was their role in the formation of sinter.

Calcareous sinter has the potential to produce high-resolution palaeoenvironmental data from Roman times. It is certainly possible to obtain palaeotemperature records with a resolution of months, and possibly better, and additional data on precipitation and on extreme climate events such as droughts or floods. For this, it will be necessary to investigate a number of neighboring aqueducts to see effects of the same events, and to calibrate the results by means of dendrochronology and aqueduct monitoring. An option worth trying is also to find sub-recent aqueducts, from the 19th and 20th century, for which weather records already exist: recent sinter from those aqueducts could help to interpret the Roman fossil sinter for which there are no weather records.

Ultimately, for archaeology, sinter deposits can give significant information on water supply systems of ancient cities and even indirectly an estimation of the population size of those cities. Calcareous sinter can also help to answer questions about construction and maintenance of the water supply, like in the case of our work in Ephesus, and on the quality of drinking water in ancient cities like in the Aqua Marcia. Therefore, the synergism between archaeologists, hydrology engineers and we, geologists, is a *sine qua non*.

Chapter 5

This appendix section presents unfinished work and research in progress, which could not be included in the two papers, Chapters 2 and 3, that form the core of this thesis due to limited space.

Monitoring studies

Monitoring work has been initiated in 2010 and is a still ongoing project of the study. The results will presumably be published by the end of 2013, after sufficient data will have accumulated.

From the analyses presented in this thesis, it will be clear that nearly every structure or geochemical trend observed in calcareous sinter can be explained by several mechanisms treated in this thesis, and others that are waiting to be investigated. Meanwhile, from the findings, there are two ways to determine which mechanism was actually dominant; by comparison studies of a large number of sinter types, deposited under different conditions and actual observation of the process depositing the modern sinter, plus the conditions under which it occurs. As the sinter is fossil, this is only possible in Roman aqueducts that still function today, or modern aqueducts built in the same manner. About a dozen such aqueducts have been localized, but not all of them are accessible for political and technical reasons. In the ones that are available, one would ideally monitor water properties such as depth, flow velocity, temperature, chemistry and biological content continuously. In practice, this is not possible. Water chemistry can only be properly measured in the laboratory, and this can be realised by taking water samples. On the other hand, parameters such as pH and CO₂ content of the water are likely to change rapidly after sampling, and have to be measured on the spot (*Figure-1*). If a structure to be monitored is close by, it could in theory be sampled at short intervals. Unfortunately, all monitoring sites that were localised are far from Germany and because of travel costs, they can only be visited twice a year, although an attempt was made to obtain water samples at more regular intervals.



Figure-1 Active pH measurement. After the first two calibrations with pH 7 and 10, the pH of the spring water is measured.

For a monitoring study, the aim is to take water samples, where possible, and to track water temperature and chemistry at regular time intervals in at least some of the monitoring sites. In addition, growth plates should be inserted in the aqueducts to collect deposits of sinter on clean surfaces of a range of materials. This will help to interpret the results from Roman channels. This growth plate is a metal plate meant capture modern calcareous sinter deposits on them (*Figure-2*).

The first monitoring studies have started in 2010 in the Roman aqueduct of Windisch (Switzerland). In Windisch, only temperature was measured during two visits, in February and in July. The difference in temperature between summer and winter was nearly 8 degrees, although no variation was visible over periods of up to three days. No further study was made of this aqueduct since it does not deposit sinter and the amount of water in the channel is very small because part of it is now diverted. In addition, the upstream part of the channel underlies a built-up area, and water chemistry and temperature is probably influenced by activities there.

The monitoring studies were set up at four other sites: Fréjus, southern France; Galermi, Sicily; Aqua Virgo; Rome; and Patara, Turkey. All sites have still functioning springs, some now used for agricultural purposes. However, all springs and associated aqueducts have different structure and properties.

An important dimension of monitoring is an attempt to sample the modern sinter that presently grows in Roman aqueducts. For this, "growth plates" were prepared which consist of galvanised steel plates on which a number of different materials were attached such as copper discs, calcite single crystals, and slabs of calcareous sinter fragments and granite, in an attempt to grow sinter over a known period of time. *Figure-2* shows first results from the Galermi aqueduct in Sicily. The Figures show three stages in sinter building over a period of two years. At left, one of the original plates as it was inserted in the aqueduct channel: in the centre, a plate after one year: and at right, after two years of growth with approximately 1 cm of sinter accumulation. The plates are presently still accumulating sinter, and will be analysed in 2013.



Figure-2 These growth plates are used in the Galermi aqueduct. From left to right: a new plate before insertion; a similar plate after one year of deposits; the same plate after two years of exposure.

Stable isotope analyses

At all four sites, visits were made 1-2 times per year to locally measure pH, conductivity and carbonate hardness, using a MERCK carbonate hardness test (Merck 111103) (*Figure-1*). At such occasions, water samples were taken for trace element analysis and δ^{18} O analysis of the water. These samples have partly been analysed and await further data accumulation. In Patara, water samples are being taken at a monthly basis by a local person to get a better idea of the distribution of trace elements and δ^{18} O throughout the year. *Figure-3* shows first results of

 δ^{18} O analyses carried out on water samples from Patara over a period of 24 months. Water samples were taken at the İslamlar source of the Patara aqueduct at monthly intervals in glass bottles without included air, and stored at 5 °C in a fridge. They were analysed in the laboratory in Innsbruck, as described in Chapter 2. It is clear from *Figure-3* that there is no systematic seasonal variation in δ^{18} O, and this result was used in the interpretation section of Chapter 3.



Figure-3 δ^{18} O measurements of water from the source of the Patara aqueduct over the period July 2010-2012.

Temperature measurements

The first results of ongoing temperature monitoring in four Roman aqueducts which still carry water are shown in *Figure-4*; The Aqua Virgo in Rome; the Patara aqueduct in Turkey (Chapter-3); the Fréjus aqueduct in France, and the Galermi Aqueduct of Syracuse, Sicily. These graphs are quite different which means that it is necessary to take this difference into account when modeling aqueducts.

Data on these aqueducts are available on the ROMAQ website (<u>www.romaq.org</u>). The water temperature was measured automatically two times per day using a HOBO data logger. At all four sites, temperature measurements are still ongoing.

The Virgo aqueduct was built for the city of Rome in the first century AD and is 20.9 km long and almost completely buried, with few bridges. It has an underground source, but with manholes that allow exchange of air with the atmosphere. The water of the Aqua Virgo was already famous in antiquity for being completely clear, even after storms, which means that it is perfectly sealed against contamination. It is the only aqueduct of ancient Rome that is still functioning, and feeds the famous Trevi fountain. A HOBO thermometer was placed in the channel in cooperation with the Roma Sotteranea organization for our study in November 2010. It was set to measure the temperature twice a day at the bottom of the channel at a water depth of about 60 cm in a tunnel below the Villa Medici in Rome, 19.5 km from the source. The aqueduct transports up to 1500 l/second. The aqueduct carries unsaturated water that does not deposit carbonate, but is interesting because it is an example of a closed channel fed by a source, similar to many antique Roman aqueducts that do deposit sinter.

The Patara aqueduct is 23 km long and described in more detail in Chapter-3. The aqueduct is no longer functioning, but several karst sources still exist near the original intake of the aqueduct, feeding small channels meant for irrigation while one channel drives a water mill. A HOBO thermometer was placed 100 m from the source in an open channel. The aqueduct transported up to 90 l/second (see Chapter 3) but the source that is

being monitored presently supplies no more than 30 l/second. Here, a local restaurant owner is taking samples once a month for the isotope and chemical analysis.

The Gallo-Roman city of Fréjus (Forum Julii) was getting drinking water from two source areas, Siagnole and Foux. The aqueduct was originally 43 km long, and the first 5 km have been reconstructed in the 19th century to supply the town of Fayance with water. This section of the aqueduct takes its water from the large open karst source of Siagnole and the channel is near the surface, covered with slabs, or shallowly buried. The remainder of the aqueduct to Fréjus does not function any more. We placed a HOBO thermometer in a water basin 5 km from the Siagnole source at the end of this still functioning part of the aqueduct, where it has been measuring since February 2011. The aqueduct transports up to 580 l/second. The Siagnole Water Board is taking samples of the water for us at monthly intervals for isotope and chemical analysis. Growth plates were positioned at two sites. The first site is in the upstream part of the channel where no sinter is deposited because the water is not yet saturated in carbonate. The second plate is in the area saturated with carbonate.

The Galermi aqueduct is originally a Greek aqueduct, which dates back to third century BC and which was providing the historical city of Syracuse with water. The aqueduct is 29 km long, mostly buried, while the first few km have been excavated in a limestone cliff. It is still functioning, now supplying water for agriculture, and is cleaned out at regular intervals. This aqueduct is special because it takes its water from the Calcinara River, about 1 km from the source at a point where the carbonate starts precipitating, forming tufa terraces downstream. The Calcinara River is fed by a large karst spring. A HOBO thermometer was placed in the excavated part of the channel, 700 m after the intake from the river and 1.7 km from the source, open to the atmosphere through numerous windows in the cliff. The aqueduct transports up to 150 l/second. Water monitoring takes place here twice a year (*Figure-2*). Moreover, a local volunteer takes water samples inside the aqueduct channel once every three months. Water samples are collected from three different sites. HOBO temperature loggers are located at two locations in the Galermi aqueduct. The loggers are placed near the bottom of the channel in protected sites where the flow rate is relatively low.

The Aqua Virgo shows a very constant temperature throughout the year with a bulk variation of less than 0.5 degrees. There are also a few abrupt deviations, which are interesting since they only show a deviation from the mean towards lower temperature (*Figure-4A: inset*). These deviations seem to occur at the coldest periods in winter. A possible explanation is that the source provides water of constant temperature year round, and that the water in the tunnels above the aqueduct has about the same temperature of 15-16 degrees. If the outside temperature is higher, which in Rome will be in most of the year, there is little exchange with the atmosphere; however, if the outside temperature falls significantly below 15 degrees, cold air may flow into the channel to replace the now warmer air in the channel, and cool down the aqueduct water.

In Patara, the spring water temperature also varies slightly over the year, with a minimum in winter and maximum in summer but less than 1 degree deviation over the year (*Figure-4B*). There are small peaks in summer of increasing temperature, which may be due to a slight warming of the water in the open channel leading to the site where we measured the temperature. These measurements were referred to in Chapter 3.



Figure-4 Water temperature measurements from the monitored aqueducts. Numbers below the graphs are in the form "month.year". The extreme peaks at the start and end of some measurement series are recording air temperature before and after the thermometers were placed in the water.

more exposed nature of the 5 km long channel to external temperature changes. There is a curious, rapid decrease in water temperature at the onset of winter, which will have to be compared with local weather records.

The temperature in the Galermi aqueduct is very different from the other three (*Figure-4D*). Here, the temperature varies over more than 7 degrees during the year, with numerous sizable deviations from the main pattern. Clearly, this channel is very exposed, especially the first open stretch of river before the aqueduct starts. The tunnel section of the aqueduct is also exposed to warming and cooling through the numerous windows. It is this type of Roman aqueduct that would be most suitable to reconstruct climate in ancient time.

In conclusion, karst sources seem to show very little variation in temperature over a year, and the water temperature can be well regulated in an aqueduct channel if it is buried all the way. Depth of burial of the channel will have influence on the temperature profile in the channel. Water taken from open rivers will show the largest temperature variations.

Aspects of Roman aqueduct sinter

Bacterial aspects in thin sections

Calcareous sinter from the Roman aqueducts contains a number of small-scale structures, visible in thin section using optical microscopy, which may be due to bacterial or algal growth that we must consider. Therefore, in January 2012, thin sections of calcareous sinter were investigated at the Freshwater Biological Association in Windermere, England, together with Dr. Allan Pentecost to examine biological activity in calcareous sinter samples. Dr. Pentecost is a specialist on freshwater carbonates, especially travertine and tufa deposits. Some tufa sites in the region were also visited and sampled together with Dr. Pentecost to see in-situ examples. Besides regular thin sections, some samples were treated with EDTA (Ethylenediaminetetraacetic acid) to remove carbonate encasing possible organic remains in fossil and modern carbonate samples.



Figure-5 General observations of biological structures in aqueduct sinter are; (a) filament structures; (b) possible cyanobacteria colonies; (c) and (d) possible clotted fabric; (e) larval tubes of Chironomidae. (a-b) P10-1; (c-d) P10-4; (e) Değirmendere aqueduct, Ephesus. Width of images (a) 0.3 mm; (b) 2 mm; (c) and (d) 0.6 mm; (e) 18 mm.

Figure-5 shows some of the structures observed in thin sections from the Patara aqueduct and in a hand specimen from Ephesus. In general most of the thin sections contain fine-grained dark material that is probably indicative of a high organic content of calcareous sinter deposits, which made it difficult to observe or follow specific types

of bacterial growth. Nevertheless some of the observations are indicative of bacterial activity in aqueduct channels. The most common structures are (*Figure-5*);

- * Clumping and clotted fabrics;
- * Filament structures;
- * Some rare cyanobacteria colonies;
- * Branching tube and larval tube structures

No bacterial structures were observed in samples dissolved in EDTA.

Epifluorescence microscopy

We examined some of the thin sections from different aqueduct sites by epifluorence microscopy at the University of Innsbruck (*Figure-6*). The epifluorescence shows a regular alternation of bright and dark bands that coincides with the lamination in the samples. PF (porous, fine-grained) layers are most luminous, probably due to their relatively higher organic content (*Figure-6*).



Figure-6 Epifluorescence images of selected samples from the Patara aqueduct. (a) P19B; (b) sample P2. The structure in the centre is almost certainly of organic origin; (c) P19. All examples show blue light epifluorescence.

Types of lamination

A large number of thin sections of calcareous sinter were investigated for this study, both from Turkey and elsewhere in Mediterranean. In most cases, thin sections show similar microstructures to the samples described in Chapters 2 and 3. Calcareous sinter deposits show a prominent lamination, which is usually regular and continuous. In some of the thin sections, there are also distinct layers that can disturb the regularity (*Figure-8*). These are either discontinuities, or extremely silt rich, fine-grained or otherwise outstanding layers known as event horizons (Chapter 1). Laminations are usually annual (Chapters 2 and 3) but in some thin sections, it is

also possible to see sub-annual layers, which are possibly formed over a daily or longer time base. Some examples of such structures are shown in *Figure-7*.



Figure-7 Selected microstructures from thin section of aqueduct sinter **a**; typical sub-annual layers; **b**, **c**, **e**, **f**; typical annual laminations **d**; continuous calcite crystals transecting the lamination.



Figure-8 Large sample from Aspendos showing the entire stratigraphy of an aqueduct channel. The arrows mark discontinuities (event horizons). The middle part of the sample is a second layer of opus signinum that was apparently added by Roman workers due to a problem that occurred in the channel (e.g. an earthquake or a flood event). Width of sample 61 cm.

3D Computer Tomography

 μ -X-Ray computer tomography (CT) is a non-destructive method to study the 3D internal structure of small samples. The subject sample is slowly rotated over 360° and individual 2D steps are registered by the detector and recorded in a database which is used for modelling a 3D image of the sample. This method will show contrasts of density, and therefore this is suitable for identifying the porosity of sinter samples. *Figure-9* shows results of a pilot study on samples of the Patara and Aspendos aqueducts. As can be seen in the photos, some individual dark and compact lamina couplets were marked as reference points. The layers with high porosity

from fine-grained, light colored laminae couplets are clearly visible in *Figure-9*, and can clearly be distinguished from denser laminae. In the Patara sample, some of the long sparite grains that transect the lamination (Chapter 3) are visible. Since the shape of the porosity was not of great interest for this study, and could also be observed in thin section, 3D tomography was not extensively used. In samples with more complex porosity, the method could be useful.

Patara





Figure-9 3D tomography results on samples from Patara and Aspendos. Tomograph images are shown at left, and normal light photographs of the slabs at right.

SEM (Scanning Electron Microscopy)

The SEM at the Earth Sciences Department in Mainz was used for a pilot study on sinter microstructure. In *Figure-10*, fine and coarse grained crystals can be seen easily. The EBSD method was preferred during further studies due to its suitability to show laminae couplets at a larger scale, and crystal orientation.



Figure-10 SEM images showing examples of variable grain size in a sinter sample from Aspendos.

EPMA (Electron probe micro-analyzer) analysis

Selected element maps measured on polished thin section of aqueduct sinter that were not included in Chapter 2 are presented here. In general, they show the same features as discussed in Chapter 2.



Figure-11 Sample A10-1BB (Aspendos). In this figure, cyclicity along the sample is prominent. On the right side, Ca is dominant along the sample. Meanwhile, contrary to Ca, Mg shows a relative increase and decrease over a certain period, even in the homogeneous lower part of the sample.



Figure-12 Sample A10-1BB (Aspendos), upper part of *Figure-11* enlarged. On the left side, the original thin section can be seen with lamina couplets. Mg content is slightly higher than Fe content but both have positive correlation along the sample.



Figure-13 Sample A10-BA (Aspendos). On the right the original, nicely layered thin section image. At the top of the Fe, Mg and Si images, there is a red area which shows where opus signinum starts. Ca is again dominant in all areas, whereas Fe, Mg and Si show positive correlation with each other and reach their highest concentration where Ca is relatively low.

Calcareous sinter samples from Cologne (Köln) and the Aqua Marcia, Rome differ from the general form of sinter deposits. In deposits from both aqueducts, we can see another type of lamination which in the case of Cologne maybe subannual, while some components may even represent a daily lamination. On the other hand, the Aqua Marcia samples contain a lamination that represents a longer period than annual lamination (*Figures-14 and 15*).



Figure-14 EPMA analysis result of the Cologne sample. Mg content is slightly higher than other detrital elements. Especially in the Al and Si images, it is curious to see sub-layers which are very thin, and may point out daily laminations. Porous areas can be seen as dark domains.



Figure-15 EPMA result of the Aqua Marcia sample. The elemental map of the sample is interesting in showing distinct laminae couplets which can represent event horizons. There are also layers related with longer climatic cycles. Insets show patterns oblique to the lamination, possibly enrichment in or between crystals. As can be seen from the original thin section image, the sample is very clean, without a high organic content. This is an anticipated result as the Aqua Marcia was well-known with its high quality, clean water, even in Antiquity.

LA-ICP-MS (Laser Ablation- Inductively Coupled Plasma-Mass Spectrometry)

In Chapter 2, trace element chemistry of the Patara and Aspendos aqueducts is discussed. It was impossible, however, to show all measured data in the paper, and some of the additional graphs and more interesting examples are therefore shown below. The bands colored in green, correspond to fine-grained, porous layers in the samples.



Figure-16 P10-19 (Patara sample from a ceramic pipe) upper section. A positive correlation especially between Mg, Sr and to some extend also Ba isotopes can be seen in the figure. Higher values of these trace elements correspond to light colored, porous areas, although the U/Ca ratio curve is not as clear as others. The correlation coefficient between Mg/Ca-Sr/Ca is 0.53, Mg/Ca-Ba/Ca is 0.30 and for U/Ca, it is 0.26.



Figure-17 P10-19 (Patara) bottom section: the bottom section shows the same chacteristics as the upper section of the sample. The P10-19 sample has slightly higher Mg/Ca ratios inside the light-coloured layers. The correlation coefficients for this sample are; Mg/Ca-Sr/Ca, 0.10; Mg/Ca-Ba/Ca, 0.60; Sr/Ca-Ba/Ca, 0.20; Mg/Ca-U/Ca, 0.20.



Figure-18 This graph of sample PA1 (Patara) show the same kind of trend in Mg/Ca and Sr/Ca as other samples, with slightly higher values inside fine-grained layers. The correlation coefficients for this sample are; Mg/Ca-Sr/Ca, 0.34; Mg/Ca-Ba/Ca, 0.25; Sr/Ca-Ba/Ca, 0.12; Mg/Ca-U/Ca, 0.19; Sr/Ca-U/Ca, 0.07.



Figure-19 This A2 (Aspendos) sample, like all Aspendos samples, is well-layered with some porous areas. The Mg/Ca ratio curve shows high peaks in fine-grained, light colored layers. The correlation coefficients between Mg/Ca-Sr/Ca and Mg/Ca-Ba/Ca are 0.44 and 0.25, respectively.

Stable oxygen and carbon isotopes

In Chapter 2 and 3, stable isotope measurements of the sinter samples from the Patara and Aspendos aqueducts are discussed. Besides these measurements, however, additional examples from the same aqueducts and also from other ones were investigated. This material is not published yet, and the more interesting examples are shown below in following figures. Both micro-milling and hand-drilling results are shown. The main problem with hand-drilling was to drill accurately in neighbouring layers: as lamination is very thin, you can drill two layers at once and that can give inaccurate results. Micromilling is always to be preferred in these thinly laminated samples, and most of the hand drilling examples were therefore not published.



Figure-20 Sample A2(Aspendos) is quite remarkable for its very clear cyclicity in both isotope curves. The higher $\delta^{18}O$ values obviously correspond to darker, coarse-grained laminae couplets. There is a strong anti-correlation between $\delta^{18}O$ and $\delta^{13}C$ curves with a correlation coefficient value of -0.63.



Figure-21 This A10-1BB (Aspendos) sample is one of the best examples of layered sinter found anywhere. This sample was also analysed by micromilling, which gave better resolution, and this figure only shows the hand drilling image. Even with this rough method, the cyclicity is recognizable. The correlation coefficient between two isotope curves is -0.26, with a very high anti-correlation. The numbers of the horizontal scale indicate the number of hand-drilling. The length of the sample is 6,1 cm.



Figure-22 Sample P20c represents mostly porous sinter with up to 60 % micrite laminae from an aqueduct channel in Patara. The annual layering is not as clear as in other examples and it is hard to distinguish each lamina type. The transition between laminae is relatively gradual. There is not a single layer that can be use for correlation with the other calcareous sinter examples. This makes it likely that P20c represent a different period than the other samples, and could be a part of an older, Hellenistic channel. δ^{18} O values range from -6.79 to -3.55‰ and δ^{13} C values from -7.43 to -3.86 ‰. There is a high positive correlation across laminae couplets between δ^{18} O and δ^{13} C with a correlation coefficient of 0.85. The sharp peak at left may be due to contamination from the soil overlying the sample.



Figure-23 This hand-drilling graph is from sample P19 (Patara). This sample was also investigated by micromilling, which gave better resolution. The correlation coefficient between $\delta^{18}O$ and $\delta^{13}C$ is 0.50. The weak cyclicity which was mentioned in Chapter 3 can also be seen here. The numbers of the horizontal scale indicate the number of hand-drilling. The length of the sample is 4.6 cm.



Figure-24 This P10-14 (Patara) sample is a channel sample with high porosity. The $\delta^{18}O$ and $\delta^{13}C$ isotope curves are quite flat and correlation coefficient between two isotope curve is 0.73 which means there is very little kinetic fractionation.



Distance from the top (mm)

Figure-25 Sample X3 (Xanthos), Turkey. This aqueduct was providing water to ancient city of Xanthos, which was a neighbor city to ancient Patara. The correlation coefficient is between $\delta^{18}O$ and $\delta^{13}C$ is 0.24. Water samples were taken from Greek springhouse at Xanthos as a preparation for further study.



Figure-26 Sample EDC4 (Ephesus, Turkey) is from a ceramic pipe from a Byzantine aqueduct water supply. Inside dark, coarse-grained layers, δ^{18} O has relatively higher values. The correlation coefficient between two isotopes is 0.47. The high peak in the middle is probably an artifact.



Figure-27 This HYR6 (Hierapolis) sample from Turkey, was only investigated by hand drilling. The correlation coefficient between $\delta^{18}O$ and $\delta^{13}C$ is 0.56, therefore these two stable isotope curves have a positive correlation along the sampling track. Calcareous sinter from Hierapolis is very dense with low porosity, which is ideal for sampling but the resulting $\delta^{18}O$ curve is quite flat. There can be several reasons for such relatively constant isotopic values; lack of source water composition changes during the operating period, minor evaporation and minor temperature changes. Too little is known about this aqueduct at present to decide which factor is relevant here. The numbers of the horizontal scale indicate the number of hand-drilling. The length of the sample is 8.9 cm.



Figure-28 Micromilling results from the Aqua Marcia. This is only the top part of the larger sample which is presented in **Figure 29**. The higher $\delta^{18}O$ values correspond to dark, coarse-grained layers. $\delta^{18}O$ and $\delta^{13}C$ have anti-correlation along the sampling track with correlation coefficient of 0.01.



Figure-29 Aqua Marcia sample investigated by hand drilling. The correlation coefficient between $\delta^{18}O$ and $\delta^{13}C$ is 0.33. Hand-drilling only shows the main trends along the sample. The numbers of the horizontal scale indicate the number of hand-drilling. The length of the sample is 8.9 cm.



Figure-30 This micromilling graph is from a recent sample in one of the monitored aqueducts from Galermi, Syracuse (Italy). It is obvious to see that, where the darker laminae start growing, $\delta^{18}O$ values increase. This is similar to Roman aqueduct sinter. The correlation coefficient between $\delta^{18}O$ and $\delta^{13}C$ is 0.34.



Figure-31 The micromilling data of Sikyon, Greece. This work was the first pilot project to investigate the isotopic composition of sinter deposits. The result was quite promising; higher $\delta^{18}O$ can clearly be seen in dark and coarse-grained layers. There is an anti-correlation between $\delta^{18}O$ and $\delta^{13}C$ and the correlation coefficient is 0.08.



Figure-32. The hand drilling of the same Sikyon sample from **Figure-31**. Due to the hand drilling method, it is not easy to distinguish which lamina has higher $\delta^{18}O$ values. The correlation coefficient between $\delta^{18}O$ and $\delta^{13}C$ is 0.34. The numbers of the horizontal scale indicate the number of hand-drilling. The length of the sample is 6.3 cm.

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