SOLUTION AND PRECIPITATION OF LIMESTONE IN THE CHILLAGOE KARST AND OPPORTUNITIES FOR DATING LANDSCAPE DEVELOPMENT.

David Dunkerley.

ABSTRACT

Solution of limestone in the Chillagoe area proceeds rapidly at the rock surface but concentrations of calcium carbonate reach levels of only 50 ppm or so. In the soil and near-surface environments, much additional material is dissolved, such that concentrations in bore water and in springs reach 300-400 ppm dissolved carbonates. Spring waters in the area undergo rapid degassing of carbon dioxide upon reaching the surface and consequently set down secondary carbonates (travertine and tufa) along stream channels. Rates of carbonate accumulation observed at present suggest that existing accumulations of stream travertines may be no older than Holocene. However, there are widespread relict travertines in the Chillagoe area, often located as terraces and benches set above present stream levels, which relate to much earlier periods of limestone solution and spring precipitation.

A number of these relict deposits have been sampled by diamond drilling and their ages will be determined through the use of Uranium-Thorium radioisotope dating. The chronology of travertine accumulation should equate approximately to that of upland (tower, pediment, etc.) solution and hence provide us with a partial view of the timing of landscape evolution in the karst.

INTRODUCTION

The karst landscapes of tropical Australia pose a series of interesting questions about landform evolution which are deserving of scientific study. The landscape features developed in these areas must also be documented and understood because of the increasing resource pressure arising from the development of Northern Australia, and the growth of visitor numbers. These pressures result in conflicts between development and the protection of natural features.

Among the geomorphic issues which warrant attention are the nature of the landscapes themselves (notably the tower-and-pediment assemblage), the weathering processes and geochemistry, and the age and evolution of the towers, pediments, caves, springs, and other karst features. There are also issues related to archaeology, hydrology, and the management of biota.

Several field visits have been made to the Chillagoe area in order to continue the investigation of issues such as these. This work follows on from earlier studies in the area such as those of Wilson (1974), Lundberg (1976), Jennings (1982), and many others. The present paper addresses in particular the nature of solution and precipitation of carbonates in the Chillagoe area and the use which may be made of the products of these chemical processes in dating aspects of landscape evolution there.

SOLUTION OF LIMESTONE IN THE CHILLAGOE KARST

Analyses of water chemistry within a study area around Chillagoe have been made during three field seasons, in the summers of 1980/81, 1983/84, and 1987/88. The particular goals of the water sampling program were to examine the nature of solute loads and solute uptake in a seasonally arid karst area, both at the surface, and within the groundwater system, and to examine the relationships between weathering processes and the lithological characteristics of the several limestone and marble varieties represented in the area (see Dunkerley 1983). A second objective was to document the processes involved in the deposition of secondary carbonates at springs and along drainage lines. These studies were seen as a necessary precursor to attempts to understand past weathering processes, and to study the timing of landscape development in this solutional environment.

The collection of water samples has involved several procedures. Firstly, water collected in natural rock solution pans, or dripping from overhanging rock outcrops, was collected manually; secondly, artificial catchments were constructed on rock outcrops to direct run-off water into sampling bottles. These collecting sites were set up to enable sampling of water which had freshly fallen onto rock outcrops, and travelled no more than a metre or two in contact with the rock surface; residence times on the rock surface were measured in seconds. To facilitate collections of this kind, artificial barriers of silastic compound were set up across the slope of the outcrop, directing all intercepted down slope flow into a length of polyethylene tubing set in to the lowest point on the barrier, and hence into a collecting bottle placed lower down. The mouths of bottles were protected against rain entry by a covering plastic envelope (apparatus described by Dunkerley 1984). Thirdly, samples have been collected from springs and streams, as well as artificial water bores, in the karst.

After collection, all water samples were promptly returned to a field laboratory where pH and conductivity were determined. Over the following day, selected additional chemical analyses were performed by standard titration techniques. Subsequent analyses of saturation levels were made using the WATSPEC computer program (Wigley, 1977).

TABLE 1.
AVERAGE WATER CHEMISTRY PARAMETERS FOR THREE LITHOLOGIES
(surface run-off water lumped with solution pan samples)

Site	pH	Cond.	Total	Ca	Mg	pCO_2	SIc	SId
Coarse marbles	7.82	81.9	34.1	32.7	1.6	3.36	-0.82	-2.42
Fine marbles	8.06	87.6	41.3	39.9	2.4	3.52	-0.38	-1.28
Fossiliferous limestones	8.04	100.9	41.9	40.6	1.8	3.42	-0.27	-1.52

[SIc and SId are the mineral saturation index for calcite and dolomite, respectively; pCO_2 is -log(PCO2) where PCO_2 is expressed in atmospheres.]

The results of this work will not be presented here in full. However, a summary of the most general results from three rock types is included in Table 1.

Table 1 summarizes the results obtained when all the collected data from particular rock types are lumped. These data include those derived from installed run-off collectors, as well as from water collected from solution pans after rain.

It can be seen from this table that the fine-textured fossiliferous limestones (e.g. in Royal Arch bluff) are the fastest to move into solution. This is indicated by the highest mean total and calcium hardness values (reflected in the highest mean electrical conductivity), and the nearest approach to saturation in the collected waters. Least rapid to pass into solution are the coarse-textured marbles such as those of Dome Rock: the mean total and calcium hardness of samples from this site is about 18% less than at Royal Arch, and the samples displayed greater mean undersaturation. The marbles of intermediate texture (e.g., Racecourse Tower; Donna Bluff) are also intermediate in terms of rate of entry into solution. The three lithologies are very similar in terms of the computed equilibrium concentration of carbon dioxide required in the associated gas phase, at a mean value of 3.43, very close to the expected atmospheric value of 3.47. The distribution of measured pCO_2 values is shown in Figure 1.

These results clearly imply that solutional weathering and the development of minor solutional features at the outcrop level proceeds most rapidly on the fine-textured rocks and least rapidly on the coarse marbles. However, they say nothing in detail about the way in which solution rates and solution processes vary across the complicated surface of a typical fluted bluff outcrop, or about the rate at which solute uptake varies through time during the period in which water is in contact with the rock surface, nor about relative solution rates among tower and pediment areas. However, they clearly indicate the kinds of dissolved limestone quantities collected by fresh water as it interacts with the limestones- in all cases less than 50 mg/litre average total hardness (expressed as $CaCO_3$ equivalent). Much additional material must be taken into solution in the weathered zone at the soil-bedrock interface, where the water is enriched with carbon dioxide from the soil atmosphere. This is shown by the chemistry of springs, discussed in the next section.

CHEMISTRY OF SPRINGS, STREAMS, AND GROUNDWATER

There are many small springs in the Chillagoe karst which apparently flow perennially, generally associated with the deposition of secondary carbonates encrusting the channel. Six springs have been studied, and several of these sites have been sampled both at the resurgence itself and at intervals down the spring- fed channel in order to look at rates of deposition of secondary carbonates. Information on the processes involved in the present-day deposition of secondary carbonates is necessary for a proper understanding of the origin of fossil or relict tufa or travertine deposits in the Chillagoe area. The work on

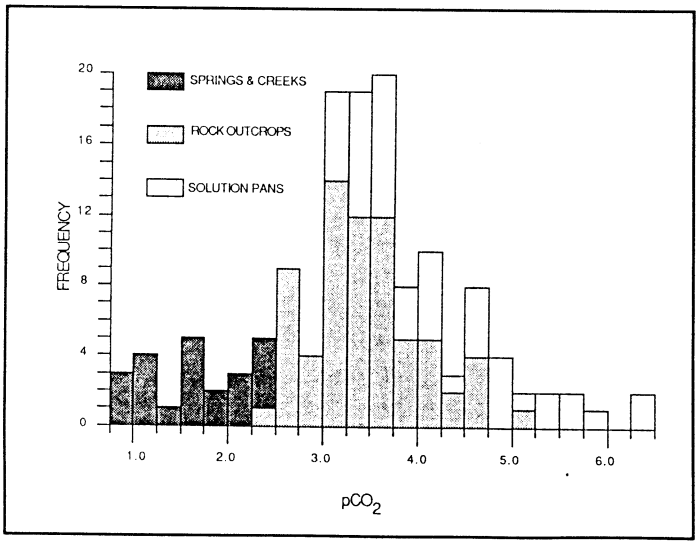

Figure 1: Distribution of calculated pCO_2 values, using all data.

Proceedings of 17th Conference of the ASF 1988

depositional processes has been undertaken for its own value, but also as a precursor to dating and interpretation of the secondary deposits.

The deposition of secondary carbonates involves at least three distinct sets of processes. First, there are chemical effects which arise as spring waters rise to the ground surface after having percolated downward through the soil and zone of weathered bedrock into pore spaces within the underlying limestone. Such waters are normally enriched in dissolved carbon dioxide as a result of passage through the soil, and cooler than surface waters. Hence, on reaching the surface they are warmed (as well as agitated) and tend to lose CO_2 to the atmosphere in the process of degassing. This forces the solution into supersaturation, and once a sufficient level of supersaturation is reached, the deposition of carbonates begins. Previous work (Jacobsen and Usdowski 1975; Dunkerley 1981, 1987) has indicated that precipitation generally occurs where SIc is greater than 1 (i.e., with concentrations of more than 10 times saturation levels). Only slight accumulation occurs at lower levels of supersaturation.

Secondly, there is the role of evaporation. In the dry season especially, evaporative loss of water from spring-fed streams is large, and this is enhanced if they are impounded to form a cascade of large pools by natural tufa barriers. This evaporative loss again forces the solution into progressive supersaturation, and causes secondary carbonate deposition. This process has been documented in the Chillagoe area by Dunkerley (1984).

The third group of processes, not yet investigated at Chillagoe, involves a more direct role of aquatic biota. In particular, the growth of mosses and algae in the water may contribute substantially to the chemical changes required to initiate deposition. This has been investigated at other sites (e.g., see Pentecost and Lord 1988). Comparing water chemistry between day and night has been employed by some workers as a means of revealing the role of photosynthesis by plants in affecting the water chemistry (e.g., see Jacobsen and Usdowski, 1975; Usdowski et al. 1979).

Much deposition at Chillagoe is believed to result from processes in the first group, following emergence of water at the ground surface. The change in environment involved here may be considered in terms of the characteristics of water samples collected from deep bores and from springs before alteration in the chemical properties. Samples of deep ground water were obtained from water bores at the Chillagoe marble quarries and at the Red Dome gold mine. The sample at the Red Dome site was pumped from a depth of 165 m below the terrain, and presumably reflects concentrations in the deep circulation water below the karst area. Samples were obtained from 5 springs in the Chillagoe-Mungana-Rookwood area, all of which displayed deposits of secondary carbonates (travertine and tufa) along the stream channel below the spring.

Results from the sampling of deep groundwater and spring water are tabulated (see Table 2). The results indicate a mean total hardness of 284 ppm as $CaCO_3$, with a maximum of 388 ppm at the Red Dome bore.

The composition of the waters was about 80% calcium carbonate and 20% magnesium carbonate, in terms of hardness. Mean pH was 6.9, with mean SIc of 0.104, indicating close approach to saturation. SId in contrast displayed a mean value of -0.54, indicating slight undersaturation with respect to dolomite. Mean theoretical equilibrium carbon dioxide level in the spring and bore waters was 1.22, corresponding to about 6% CO_2; the value correlated well with pH of the sample ($r = 0.94$).

Mean total hardness is about 7 times that of surface run-off waters, which displayed a value of less than 40 ppm as $CaCO_3$ (Table 1). Surface run-off waters were also considerably more undersaturated than the deep waters, especially with respect to magnesium carbonate. It is not possible to comment on the temperature difference of the waters in situ as the samples were always collected at the surface after warming had undoubtedly already occurred during upward passage through the rock.

However, it is clear that waters with a mean PCO_2 of 1.22 would undergo rapid degassing upon reaching the surface where the free air value is about 3.4. There is clearly a large groundwater store (since the springs in the district are perennial) and so we may make the assumption that the groundwater residence time has probably always been sufficiently long for water to reach calcite saturation. In times of moister climate in the Chillagoe district, with consequent more vigorous and sustained plant growth and soil microbial activity, it would be reasonable to assume that even greater concentrations would have been reached in the groundwater, and therefore for more extensive tufa deposition to have taken place at the surface. The possibility of greater surface run-off from adjacent impermeable rocks needs to be recalled, however: in causing dilution of the karst waters, such allogenic water would have acted to reduce the tendency for tufa deposition. Active dissolution of some of the tufa by run-off water might also have been active at spring sites, which in the Chillagoe district tend to be located at geological contacts, which are exploited by rising groundwater as conduit sites.

Rates of carbonate precipitation have already been described for Ryans Creek at Mungana (Dunkerley 1987). This spring has total hardness in the range 280-300 ppm, a pH of close to 7, and SIc of about 0.05. In the form of a major sequence of tufa barriers, it precipitates carbonates over a distance of 1-2 km below the spring; the deposited material is almost entirely calcium carbonate, so that the magnesium hardness actually rises downstream.

TABLE 2.

WATER CHEMISTRY - SPRINGS AND BORES
(mean values)

Samples included	pH	Cond.	Total	Ca	Mg	pCO_2	SIc	SId
All data	6.86	711	284	257	31	1.22	0.10	-0.54
Bores	6.97	709	289	253	36	1.39	0.16	-0.23
Springs	6.82	738	294	269	29	1.13	0.10	-0.64

The loss of calcium carbonate amounts to about 130 ppm, or about 50%, over the first kilometre. At an estimated average flow rate of 5 l/minute, this amounts to about 1 kg per day, or about 1 m^3 of tufa in about 6-7 years. Thus a deposit 2 km long, over a depositional surface 50 m wide, and built up to a depth of 1 m, could form in about 16000 years. This can be taken as no more than at best an order-of- magnitude rate estimate, and in times of altered climate, the accumulation rate would almost certainly have been different for reasons already mentioned. However, it indicates that tufa barriers of the dimensions of those found on Ryans Creek need be no older than perhaps Holocene, and that these may indeed only have begun forming as the climate of this area became drier (because of reduced allogenic surface water input).

Similar studies have been made at a spring in the Rookwood area, which rises with a total hardness of about 300 ppm, a pCO_2 of 0.98, and calcite saturation. This spring has set down a series of tufa barriers and water sampling indicated a decline in hardness to about 95 ppm after 350 m of surface flow, which appears to be the downstream limit of significant tufa deposition at this site at present.

RELICT TUFA AND TRAVERTINE DEPOSITS OF CHILLAGOE AREA

Field inspection at many sites within the karst revealed substantial accumulations of travertines lying well above present-day stream beds. The volume of secondary carbonates involved in these deposits is considerably greater than that associated with active deposition on streams at present. These deposits had earlier been mentioned, but not described in detail, by De Keyser and Wolff (1964) who employed the older term calsinter (see definitions at end of paper). Some of these materials were apparently quarried earlier this century. The deposits are generally undergoing breakdown and erosion at present. The travertines were located in relation to the geologic structure, by inspecting sites at geologic boundaries, close also to large expanses of limestone. Generally the tufa and travertine deposits begin at about the line of geologic contact and extend downstream, often siting on the Devonian granites, or in some cases, on marbles resulting from the granitic intrusions (see Jennings 1982 for a sketch). One such deposit is located on Chillagoe creek; there are excellent exposures at the rail bridge crossing. The level surface on which the rail line sits is the surface of the relict travertines. Inspection of the banks of Chillagoe creek indicates the presence of an internal stratigraphy of travertines of varying character; these were mapped and sampled. The materials are generally cream to buff in colour, have a bulk density of about 2.36 g/cm^3, and are composed of secondary calcite intermixed with detrital grains of whole rock (limestone fragments) and quartz grains presumably derived from weathering of the granites adjacent to the limestones. Older travertines low in the site stratigraphic column appear to have lower porosity than the recent deposits forming active tufa barriers.

Sampling was done by collecting drill cores having a diameter of 100 mm. Drilling was performed with a portable motorized diamond drill with pumped water for cooling and removal of rock particles. Cores were extracted from many travertines in the area. It is proposed that these materials be dated by isotope techniques.

The considerable accumulations of tufa clearly must relate to periods of substantial dissolution of the limestone source areas (the towers, caves, and shallow vadose zones). Therefore, the chronology of tufa accumulation should equate essentially with the chronology of tower formation. Probably only the most prominent travertines have at present been located, and these are probably relatively recent in terms of the history of tower development. Older fragments may well be found in sites at higher levels in the terrain, where they have been protected from subsequent erosion, although there may have been almost complete removal of these materials by subsequent solution. The other source of dateable secondary carbonates is, of course, the caves themselves; however, the volume of material available is generally much smaller and the detrimental effect of sampling much greater in the cave environment, so that work on these materials should only proceed with due care and when other avenues have been exhausted.

The dating techniques which might be employed for age determination on the tufas and travertines include

- radiocarbon isotope dating
- Uranium-Thorium isotope dating
- Electron spin resonance (ESR) radiation-dose dating
- thermoluminescence (TL) radiation-dose dating (on detrital mineral grains from igneous rocks).

The Uranium-Thorium dating technique has been widely applied to age determination for secondary carbonate materials (travertines, soil carbonates, etc.: see for example Ku et al. 1979; Schwarcz, 1980, Goff and Shevenell 1987). It is hoped to date samples from the Chillagoe deposits with this technique, the aim being to establish a chronology of tufa accumulation, and hence, indirectly, a chronology of solutional activity in the landscape as a whole.

The secondary carbonates also provide a potential record of past environments in the Chillagoe area, which it is hoped to exploit in a later stage of the research. In particular, the stable isotopes of carbon and oxygen undergo fractionation during deposition, recording a temperature effect in so doing; this can be interpreted if the geochemistry of deposition is understood (e.g., see Turi 1986). Pollen and spores are incorporated into the carbonates as they are laid down, and these preserve a record of the vegetation communities of the time. These fossil materials can be extracted and identified readily (e.g. Weinstein-Evron 1987).

Details of the locations of the travertines samples and of any dates available by that time will be presented at the Conference.

DEFINITIONS

Definitions of the terms tufa, travertine, and calc-sinter are provided below. These are taken from the American Geological Institute Glossary of Geology (Bates and Jackson 1980). It should be noted that in present usage only surface deposits would be referred to as travertines; secondary carbonates set down in caves would be referred to as speleothems.

SINTER A chemical sedimentary rock deposited as a hard incrustation on rocks or on the ground by precipitation from hot or cold mineral waters or springs, lakes, or streams; specif. siliceous sinter and calcareous sinter (travertine). (Glossary p.584).

TUFA A chemical sedimentary rock composed of calcium carbonate, formed by evaporation as a thin, surficial, soft, spongy, cellular or porous, semifriable incrustation around the mouth of a hot or cold calcareous spring or seep, or along a stream carrying calcium carbonate in solution, and exceptionally as a thick, bulbous, concretionary or compact deposit in a lake or along its shore. It may also be precipitated by algae or bacteria. The hard, dense variety is travertine. (Glossary p.669).

TRAVERTINE A dense, finely crystalline massive or concretionary limestone, of white, tan, or cream colour, often having a fibrous or concentric structure and splintery fracture, formed by rapid chemical precipitation of calcium carbonate from solution in surface and ground waters, as by agitation of stream water or by evaporation around the mouth or in the conduit of a spring, esp. a hot spring. It also occurs in limestone caves, where it forms stalactites, stalagmites, and other deposits. Synonyms: calcareous sinter; calc-sinter. (Glossary p.663).

ACKNOWLEDGEMENT

The author would like to record his thanks to Tom Robinson for kind assistance and hospitality during visits to North Queensland.

REFERENCES

BATES, R.L. and JACKSON, J.A. (Eds.) 1980. **Glossary of Geology.** Virginia: American Geological Institute, 749pp.

DUNKERLEY, D.L. 1981. Chemistry of a tropical tufa-depositing spring near Mt. Etna, Queensland: a preliminary analysis. **Helictite**, 19: 15-21.

DUNKERLEY, D.L. 1983. Lithology and micro-topography in the Chillagoe karst, Queensland, Australia. **Z. Geomorph.**, N.F., 27: 191-204.

DUNKERLEY, D.L. 1984. The influence of lithology on solutional processes, Chillagoe karst, North Queensland. Paper presented at Second Conf., Australian and New Zealand Geomorphology Group, Broken Hill: 5pp.

DUNKERLEY, D.L. 1987. Deposition of tufa on Ryans and Stockyard Creeks, Chillagoe karst, North Queensland: the role of evaporation. **Helictite**, 25: 30-35.

GOFF, F., and SHEVENELL, L. 1987. Travertine deposits of Soda Dam, New Mexico, and their implications for the age and evolution of the Valles caldera hydrothermal system. **Bull. Geol. Soc. Am.**, 99: 292-302.

MISCELLANEOUS

JACOBSON, R.L. and USDOWSKI, E. 1975. Geochemical controls on a calcite precipitating spring. **Contrib. Mineral. Petrol.**, 51: 65-74.

JENNINGS, J.N. 1982. Karst of Northeastern Queensland reconsidered. **Tower Karst (Chillagoe Caving Club Occasional Paper) No. 4**, pp.13-52.

KU, T.-L., BULL, W.B., FREEMAN, S.T. and KNAUSS, K.G. 1979. Th230 - U234 dating of pedogenic carbonates in gravelly desert soils of Vidal Valley, Southeastern California. **Bull. Geol. Soc. Am.**, 90: 1063-1073.

LUNDBERG, J. 1976. **The geomorphology of Chillagoe limestones: variations with lithology**. Canberra: A.N.U. M.Sc. thesis, 175pp. (unpub.).

PENTECOST, A. and LORD, T. 1988. Postglacial tufas and travertines from the Craven district of Yorkshire. **Cave Science**, 15: 15-19.

SCHWARCZ, H.P. 1980. Absolute age determination of archaeological sites by uranium series dating of travertines. **Archaeometry**, 22: 3-24.

TURI, B. 1986. Stable isotope geochemistry of travertines. pp.207-238 in P. Fritz and J. Ch. Fontes (Eds.) 1986. **Handbook of environmental isotope geochemistry. Vol. 2: The Terrestrial Environment B**. Amsterdam: Elsevier, 557pp.

USDOWSKI, E., HOEFFS, J., and MENSCHEL, G. 1979. Relationship between 13C and 18O fractionation and changes in major element composition in a recent calcite-depositing spring - a model of chemical variations with inorganic CaCO3 precipitation. **Earth Planet. Sci. Lett.**, 42: 267-276.

WEINSTEIN-EVRON, M. 1987. Palynology of Pleistocene travertines from the Arava Valley, Israel. **Quat. Research.** 27: 82-88.

WIGLEY, T.M.L. 1977. WATSPEC: a computer program for determining the equilibrium speciation of aqueous solutions. British Geomorphological Res. Grp., **Technical Bulletin 20**, 48pp.

WILSON, P.A. 1974. Observations of the geomorphology of the Chillagoe limestones. **Proc. 10th A.S.F. Conf.**, 69-73.

Dr D.L. Dunkerley
Dept. of Geography and Environmental Science
Monash University
Clayton, Victoria 3168.

WHERE'S THE HISTO?
HISTOPLASMOSIS IN CHILLAGOE CAVES AREA, NORTH QUEENSLAND, AUSTRALIA

Eileen M. Carol

ABSTRACT

Ideal climatic and ecological conditions in many caves in the Chillagoe area suggest the existence of Histoplasma capsulatum. A study in progress proposes to identify those caves that may be reservoirs for the organism, subsequently presenting a potential health risk for cave visitors. Soil samples collected from caves containing bat and bird (swiftlet) populations are being processed by the Division of Mycotic Diseases, at the Center for Disease Control, Atlanta, Georgia. Preliminary results from 15 caves have been negative, though a more precise technique will be utilised in further collections. Histoplasmin (intradermal) skin testing of cavers intends to identify the possibility of cave exploration as one source of Histoplasma capsulatum exposure.

Eileen M. Carol,
Family Nurse Practitioner Program,
Nursing Department,
Sonoma State University,
Rohnert Park, CA. 94928. U.S.A.