

## The ANDYSEZ columns

Way back in 1989, Kent Henderson suggested that I write a series of easy-to-understand columns on various aspects of caves and karst especially aimed at helping guides and others to understand the resource they interpret. Some 52 were written and published in the Newsletter (which later became our Journal).

Although each ANDYSEZ can be found on the ACKMA website in the "Members' Only" area, it has been suggested that some of them could usefully be reproduced in the Journal. Our Editor, Tim Moore, agrees. So here is the first set. They are related and deal with various aspects of limestone. To reach them (and the others) from the Members' area, look right at the top of the page and click on "Proceedings" – you will get a variety of choices – choose 'ANDYSEZ Columns'.

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Andy Spate (Ann Augusteyn)

## Let's Talk About Limestone - Part 1

### ANDYSEZ Number 24 (Journal 28, September 1997, pp 32-33)

I sometimes spend my lunchtimes reading New Scientist in the sunshine in a park near my office (in which I have a micro-rabbit hutch as my workspace). The edition dated 19 July 1997 has an interesting article about the contribution of the lime and cement industry to global carbon dioxide emissions and thus to global warming. More on that later. Thinking about this article suggested to me that we could profitably talk a little about limestones and what role they play in the natural and economic environment. I suppose that we can, for the moment, take the role of limestones and other carbonate rocks as contributors to the aesthetic environment for granted - after all we all gad around enjoying karst scenery above and below the surface.

Limestone is the commonest of the carbonate rocks. It is made up of the metal calcium ( $\text{Ca}^{++}$ ) and of the carbonate ion whose chemical formula is expressed as  $\text{CO}_3^{2-}$ . That is, one part of carbon (a solid) combined with three parts of oxygen (a gas) gets together with an ion of calcium to form the chemical compound  $\text{CaCO}_3$  (= calcium carbonate). However, as I have said many times before - nothing is that simple in nature. Limestone is made up of calcium carbonate but will always be "contaminated" with all sorts of other chemical species from a variety of sources. The most usual "contaminant" of  $\text{CaCO}_3$  will be the metal magnesium.

Magnesium carbonate forms the other end of a spectrum. At the limestone end we have calcium carbonate - at the other magnesium carbonate. But we do have mixtures between with differing proportions of the two metals. At the calcium carbonate end of the spectrum we call the rock, limestone. At the magnesium-calcium carbonate midpoint we call it dolomite; at the pure magnesium carbonate end we call it magnesite. These two latter rocks have different properties from limestone - perhaps we will discuss these later.

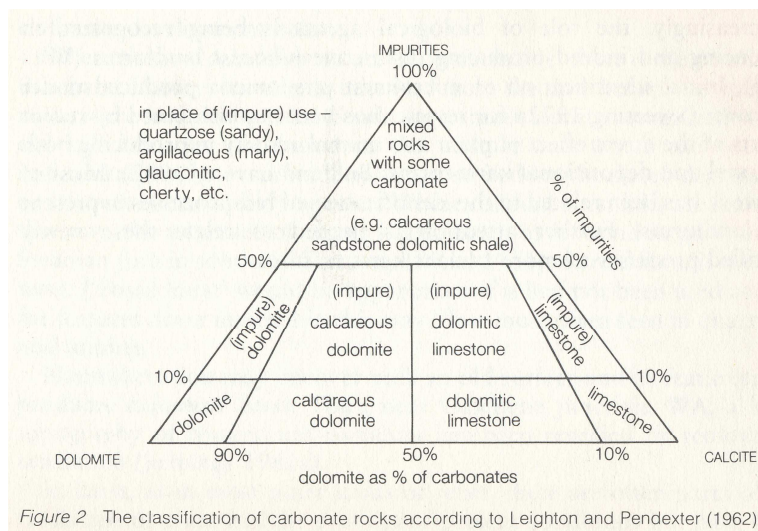
There are lots of other contaminants. Chief amongst these will be silicates (including clay minerals), iron compounds and perhaps organic materials (including hydrocarbons). We can look at these later also if we get round to it.

These three carbonate rocks are vital to our society today.

Limestone is a sedimentary rock. But sedimentation can proceed from a number of directions - and each will produce a rock with different characters. We can have physical, chemical and biological sedimentation of limestone. However, I think that we will look at the different types of limestone and the differing depositional environments which produce limestone and dolomite in a later ANDYSEZ.

Let's talk about concrete! Now!

But, back to global warming and carbon dioxide emissions. According to New Scientist (19 July 1997; page 14) "cement kilns contribute more to the world's output of carbon dioxide than aircraft" (7% versus 5%).

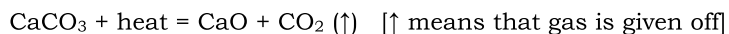


The New Scientist article continued - "CO<sub>2</sub> output is increasing faster [from cement and lime production] than any other industrial source". "This puts it behind power generation and vehicle exhausts but in front of aircraft".

The journal goes on to state:

*Cement production creates CO<sub>2</sub> in two ways: by conversion of calcium carbonate to calcium oxide inside the kilns, and by burning large quantities of fossil fuels to heat the kilns to the 1450°C necessary for roasting limestone.*

We will ignore the fossil fuel question. But look at what happens when we roast limestone for cement or lime production. Let's burn one tonne of limestone - ignoring any impurities:



Note that there are the same number of ions on each side of the equation. What are the molecular weights? Calcium = 40; Oxygen = 16; Carbon = 12. Thus:

$$\text{Molecular weight CaCO}_3 = 40 + 12 + (16 \times 3 = 48) = 100$$

$$\text{Molecular weight CO}_2 = 44 \text{ and molecular weight CaO} = 56. \text{ So } 44 + 56 = 100$$

Note that the molecular weights are the same on either side of the equation - it must be working!

So if we add heat to our one tonne of limestone we produce  $(44/100) \times 1000$  kg of calcium oxide and  $(56/100) \times 1000$  kg of carbon dioxide. These difficult calculations lead to the following results:

$$1000 \text{ kg CaCO}_3 (\text{solid}) + \text{heat} = 440 \text{ kg CaO (solid)} + 560 \text{ kg CO}_2 (\uparrow) \dots \text{**WOW!**}$$

As I said this ignores impurities and is not the chemical description of cement manufacture which is more complex and consists of roasting limestone and shales (as a source of silicates) together. Rather than calcium oxide we get, in this case, very complex calcium silicate compounds. The carbon dioxide output also ignores the contribution from fossil or other fuels burnt to provide the heat.

According to an earlier issue of New Scientist (10 May) several billion tonnes of sand, crushed rock, mixtures of calcium silicate (cement) are mixed with water each year. The mixture reacts to "produce gels which then set into a rock-like mass" called concrete. Concretes continue to harden after setting as the calcium compounds react with carbon dioxide from the atmosphere. The reaction is, in fact, turning the concrete into limestone! This is a much tougher material than the original concrete. Obviously the process is very slow and it is estimated that a large slab might take 30 thousand years to carbonate fully (by which time it has probably eroded away - or been taken to the tip!).

However, someone has been doing some research to accelerate the carbonation process - and to help reduce emissions of the carbon dioxide originally produced in creating the cement. The scientist in question stated "I truly believe that...these materials [hardened concretes] will....replace steel, paper, wood and other conventional materials."

What he is doing is to bathe the concrete in SCCO<sub>2</sub> - Super Critical Carbon Dioxide. SCCO<sub>2</sub> is ordinary carbon dioxide at about 73 atmospheres (~1,000 pounds per square inch) at 31°C. This changes the concrete back to limestone in minutes rather than millennia and produces a material with amazing properties. The compressive strength doubles and tensile strength increases by 75%; the material is tougher and develops a hard impervious outer layer which will withstand acid rain. It is suggested that the method can be used to protect old buildings and statues - but how you actually treat a building *in situ*. This sounds a little difficult?

It just shows you what you can do if you keep limestone in mind! And how things go round in circles. The next ANDYSEZ will talk about limestone and other carbonate rock from more geological perspectives.

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## **LET'S TALK ABOUT LIMESTONE - Part 2**

### **ANDYSEZ Number 25 (Journal 29, December 1997, pp 33-34)**

As Kent's deadline drew nigh yet again I received an email from Ken Grimes offering a GUEST ANDYSEZ! Such an offer is absolutely unprecedented and I wish there were more distinguished Ladies and Gentlemen around of the calibre, competence, scholarship, charm, wit and all-round good chapedness like the Lovely Lady Louisa and her consort, Professor Grimsley.

The last ANDYSEZ discussed some general attributes of limestone and a way of turning concrete into limestone again. Professor Grimsley's valued, and valuable, contribution to the field discusses a particular suite of karst landforms which, whilst not restricted to Australia, have perhaps their best expression here. He also discusses some aspects of the lithology of the rock which hosts syngenetic karst.

Whilst this is not quite what I was going to write for this ANDYSEZ it does fit the general theme that I was going to pursue over the next few issues of the Journal. The next edition will explore limestones more generally; that will be followed by another GUEST ANDYSEZ from Chris Sharples and Ian Household on karst in magnesite (note the deadlines, Ian and Chris).

## SYNGENETIC KARST

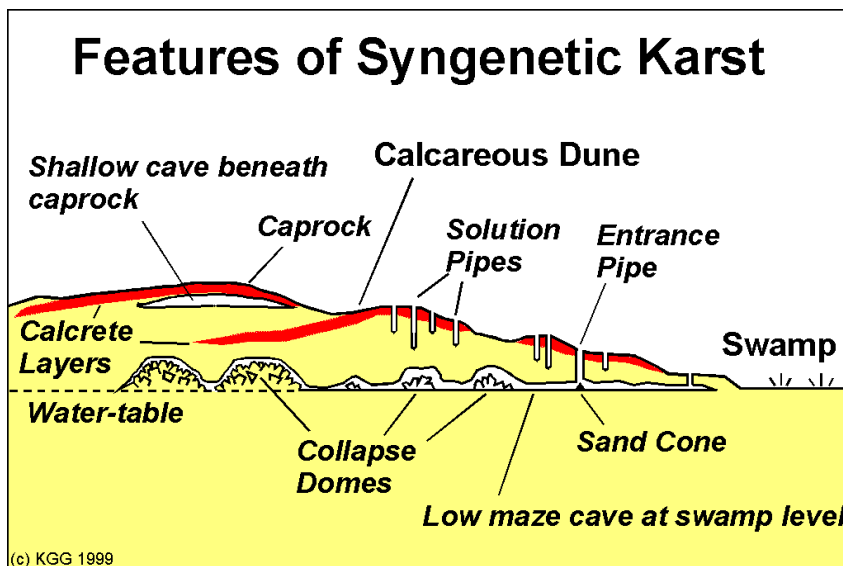
by Professor Grimsley (aka Ken Grimes)

Syngenetic karst is a special feature of the soft calcareous dune limestones found in the coastal regions of southern and western Australia.

The dune limestones are a series of calcareous sand ridges which formed as dunes along the present or prior coastlines during the Quaternary (the last 2 million years, and pretty young by geological standards). The dune ridges are now partly consolidated calcarenites: that is, sandy limestones in which the sand grains are mainly fragments of marine shells that grew in the shallow seas, were washed up onto the beach, and then blown inland. The dune limestone commonly has well-developed bedding. This includes inclined "cross-beds" that trace the series of slip-off slopes of the old dune as it moved forward, and occasionally flatter beds that might represent the associated beach sediments.

In these calcareous Quaternary dunes some karst features are "syngenetic", in that they have developed at the same time as the sand was being cemented into a rock. The term was coined by Joe Jennings in 1968, based partly on observations made by Lex Bastian in WA and Alan Hill in SA. The unconsolidated calcareous sand of the coastal dunefields is converted to limestone gradually by solution and redeposition of calcium carbonate by percolating water. This initially produces a caprock or calcrete layer which is capable of supporting the roof of a shallow cave. The downward percolating water also dissolves vertical solution pipes, and simultaneously cements the surrounding sand.

It then continues to carry dissolved calcium carbonate downward to slowly cement and strengthen the deeper sands. Simultaneously, enhanced mixing corrosion (see ANDYSEZ Number 3) occurs where percolation water meets the water table - typically at the level of an adjacent swampy plain. Initially the soft sand subsides immediately and no cavities remain, but once the rock is sufficiently hardened to support a roof, the solution at the water table results in the development of horizontal caves at that level.



Because the "rock" has limited strength, it collapses easily and breakdown is extensive, particularly in the early stages. As the rock becomes harder, and solution continues at the base of the cave (commonly beneath the rubble piles) larger chambers can form. In some West Australian cave areas, the water flow is concentrated into streams by the surface of an impermeable basement and linear stream caves result.

The main characteristics of syngenetic karst are the development of a cemented (calcreted) caprock near the surface, of vertical solution pipes, and of low, wide, horizontal maze caves either beneath the caprock or at the level of the adjoining swampy plains (see adjacent Figure).

Where the water movement has been concentrated into underground streams, as in West Australia, linear stream caves may develop. Breakdown is extensive; in many cave systems much of the original solutional system at the water-table is now supplanted by collapse domes - typically with the rubble floor rising and falling in parallel with the roof, leaving only a narrow gap for cavers to travel through. Particularly good examples of this can be seen at the Kelly Hill Caves on Kangaroo Island. Re-cemented breccias are seen in the walls of some caves. Subsidence and collapse dolines occur on the surface. In places mass subsidence can generate a chaotic surface of tumbled blocks and fissures.

Solution pipes are one of the most distinctive features of syngenetic karst. They are vertical cylindrical tubes with case-hardened walls, typically 0.5 to 1 m in diameter, which can penetrate down from the surface as far as 20 metres into the soft limestone.

The pipes may contain roots (and root growth may have occurred hand-in-hand with solution of the pipe). They occur as isolated features, or in clusters with spacings as close as a metre or so. Many of the caves are entered via such pipes.

Syngenetic karst development is typical of the Quaternary dune calcarenites; however, the Tertiary limestone at Mount Gambier is also a relatively soft porous limestone, and consequently it shows some of the features of syngenetic karst, in particular the development of solution pipes and calcreted caprocks.

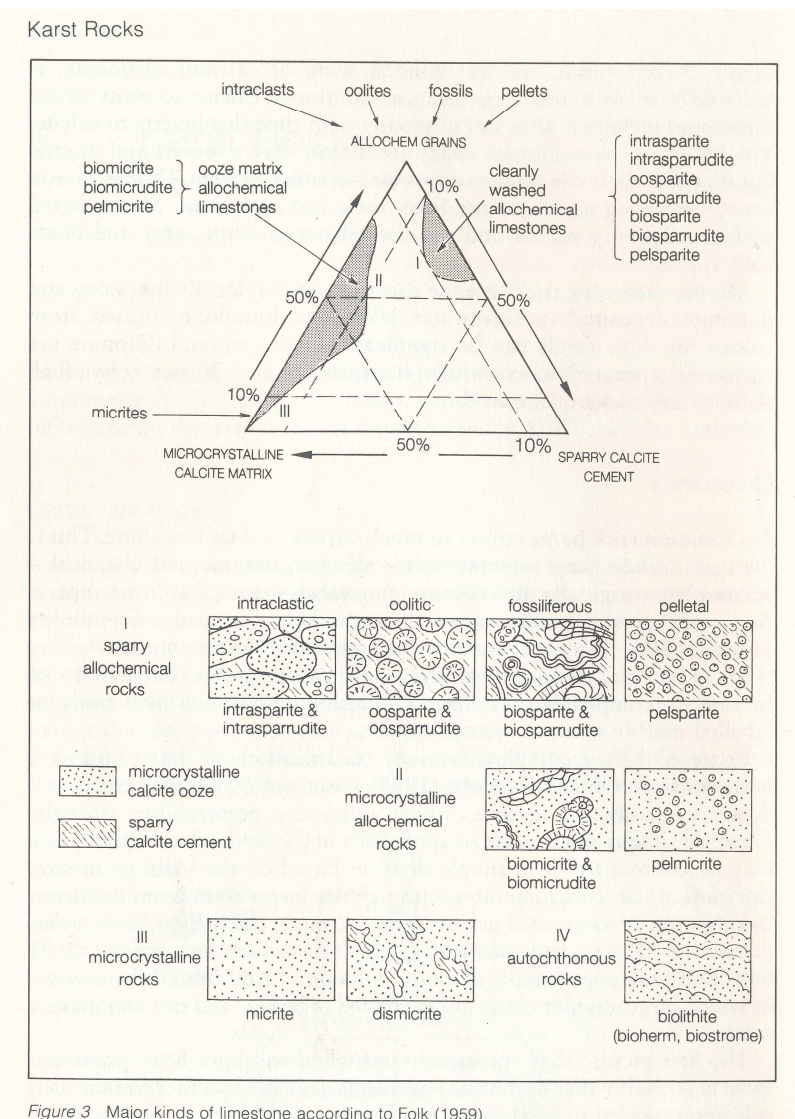
## Let's Talk About Limestone - Part 3 - A Limestone Fairy Tale

### ANDYSEZ Number 26 (Journal 30, March 1998, pp 46-47)

As I indicated in the ANDYSEZ before last, and repeated in the introduction to Professor Grimsley's excellent piece in the last issue of the Journal, I am going to talk a little more about limestone. As we have seen limestone is made up of calcium carbonate (and that there are variations with some of the calcium being increasingly replaced by magnesium) and that there are impurities. But where does it come from...

Once upon a time, a very, very long time ago (before about 3,300,000,000 years ago) there wasn't any limestone (nor even proto-dragons!). And there was something wrong with the atmosphere - there was more carbon dioxide than oxygen. However, proto-dragons began to appear and the great explosion of life began which culminated in the highest life forms yet known (lawyers? cave guides? IOKs? Ministers of the Crown?). These life forms began to use the carbon dioxide and the oxygen and the calcium dissolved in the oceans in increasing quantities to make their skeletons - inside and outside. The composition of the oceans changed such that below an equilibrium depth the levels of dissolved gases and the metal calcium were such that the solid mineral calcite precipitated from solution. The fixing of gases and dissolved metals into limestone, dolomite and so on had begun.

From this time onward the amount of carbonate rock increased dramatically and because there was more around and because it was being re-dissolved and physically reworked and re-deposited a greater variety of carbonate rocks appeared.



Indeed, as Jennings (1985) says of limestones:

No common name covers so much variety as does limestone. This is because a wide range of materials - detrital, organic and chemical - accumulate originally, and because diagenesis - change at low temperature and pressure - is intense through their chemical susceptibility. High temperature and pressure may also metamorphose them to marble, a mosaic of large, clear calcite grains, but limestones become so completely crystalline in diagenesis that they may easily be labelled marble without metamorphism (page 9).

Because of their complexity, many classifications of limestone have emerged. Some basic introductions to these classifications are given in Jennings (1985), Ford and Williams (1989) or Gillieson (1996). Whole shelves of books are devoted to carbonate petrology, depositional environments and so on. Best not confuse our shelves with elves.

Let's try and keep it fairly simple. Ford (1976) suggests that limestones are made up of four basic minerals as follows:

**Calcite  $\text{CaCO}_3$ :** the skeletal material of most marine invertebrates and the main component of limestones.

**Aragonite  $\text{CaCO}_3$ :** the skeletal material of some marine molluscs; sometimes precipitated in warm shallow waters. Compared to calcite it is less stable and more soluble; it often recrystallises to calcite.

**Dolomite  $\text{CaMg}(\text{CO}_3)_2$ :** little known as a primary sedimentary mineral, but commonly results from the invasion of calcite sediments by magnesium-rich brines which cause recrystallisation with dolomite replacing calcite.

**Chalcedony  $\text{SiO}_2$ :** The siliceous skeletal material of a few marine invertebrates, notably Radiolaria. Commonly present in limestones as flint and chert nodules.

Ford goes on to present the following table:

#### COMPONENTS OF LIMESTONE : DESCRIPTION GENESIS

<b>Skeletal</b>	Faunal (e.g. corals, brachiopod shells, etc.) Floral (e.g. algal stem fragments)
<b>Encrustations</b>	Physico-chemical (e.g. ooliths, pisoliths) Algal (e.g. blue-green algal crusts) Weathering products (e.g. travertine, stalactite)
<b>Pellets</b>	Faecal Bahamite pellets (pseudo-ooliths) Algal
<b>Limeclasts</b>	Intra-clasts - fragments of lime sediment from the immediate environment Extra-clasts - fragments of limestone from older formations
<b>Micrite</b>	Automicrite - calcilutite formed in the immediate environment Allomicrite - calcilutite transported from an external source
<b>Sparite</b>	Crystalline cementing material, granular, drusy or fibrous
<b>Biolithite</b>	Organic growth in situ, such as algal stromatolites, coral reefs, etc.

Well, that has made it complicated enough for now. What the hell is calcilutite, I hear you cry! Or indeed drusy? The former is a limestone of "lime muds, with grains smaller than 0.02 mm". Drusy = appearance of being covered in small crystals. That is enough for now, my children. The story continues...

**Note:** The figures on pages 27 and 30 are from Jennings, JN, 1985, *Karst Geomorphology*, Basil Blackwell Ltd, Oxford, pages 8 and 10.

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## Sinkholes – a documentary series

Commencing on Sunday 17 June 2018, SBS Television commenced a week of documentaries on natural disasters. The week kicked off with an interesting three-part series on sinkholes.

During my chat with the President after the second of them, we discovered that we had both watched the program and found it compelling.

His highlight was the vision of a bus in the United Kingdom slowly disappearing down a sinkhole that had suddenly opened in a suburban street as the consequence of the collapse of centuries of unmapped mining activities.

For my own part, the footage of a stand of 30 m or so high trees disappearing in the vortex of a bayou draining into an underground collapsing cavern, caused by water injecting salt extraction mining in Florida, hit the spot.

If you are able to access Internet streaming from SBS On Demand, Andy and I are united in suggesting that these documentaries are well worth watching (if they are still available to be streamed)!

Editor