

We now have pleasure of another guest ANDYSEZ. This is extremely pleasing for me as it means that I don't have to think for another few months until Kent and The Sicilian come hunting again.

As members will have noted from the last Journal we have become interested in magnesite. What is this, I hear you cry? Well, it's another rock wot has karst developed upon and in it. Carbonate rocks, of which limestone is the most common worldwide, come in a variety of

breeds. At the limestone end of the spectrum we have calcium carbonate (CaCO_3), in the middle there is dolomite ($\text{CaMg}(\text{CO}_3)_2$) and at the other end there is magnesite (MgCO_3). You will never find any of these mineral species – there is always an infinite array of shades of grey and impurities. Struth, Andy is trying to say that things are variable and not simple again!

Anyway, a roll of drums, a fanfare of trumpets... Introducing Mr. Ian Houshold on:

MAGNESITE KARST IN TASMANIA

Recently I have been helping to document karst features and processes in the crystalline magnesite deposits of northwestern Tasmania - a mine or two are currently proposed. As a result, Andy asked me to write a guest SEZ on the topic - something which I felt a little uneasy about at the time and have become more so as the work progressed. Most karst research has focused on limestone, a far smaller amount on dolomite and, unless the technological wizardry of our library system has missed something, no field research appears to have been undertaken into magnesite karst processes at all.

Feels like the time I had to drive the work Hilux through the mouth of the Thornton River on the West Coast - dark tannin water from the east, breaking waves from the west, soft sand underneath and no insurance. So, in the best public service tradition I shut my eyes, revved the donk and dropped the clutch.

Here are some ideas ripe for undermining, battering and insidious corrosion. It's not hard to get caught up in the excitement of something new even if it may mean getting sea water in your snorkel! So all you budding Julias, Andys, Daves, Kevins and Pauls (and the real ones too!), please get back to me with your ideas.

In previous SEZs, Andy has guided us through the intricacies of the limestone solution process. Beyond an understanding of the basic carbonic acid solution system, he has described a myriad of things which determine regional differences in those processes: climatic effects, lithology and rock structure, turbulent and laminar flow regimes, foreign and common ions, ionic strength effects, mixing corrosion, boundary layers and diffusion rates and so on. [Did I really do all that? Ed.] The things that make the Nullarbor caves different to Tasmanian ones, the Kimberley to Mt. Arthur.

Something which Andy hasn't looked at in detail yet, but which influences karst processes in most carbonate karst are the effects of magnesium present in the carbonate rock. My

experience is mainly in Australia, so I'll have to restrict my comments to here.

Magnesium and karst processes

Magnesium and calcium combine with carbonate ions to form three main species of magnesian carbonate rock: low to high magnesium limestone, dolomite ($\text{CaMg}(\text{CO}_3)_2$), and at its greatest concentration - magnesite (MgCO_3). These three carbonates are only occasionally pure. Some calcium will be found in magnesite and some magnesium in calcite. There is very rarely a pure 50-50 split of calcium and magnesium in dolomite. Many different minerals form impurities of varying concentration. The different proportions of magnesium to calcium in carbonate rocks have a significant effect on both rates and styles of karst development. Most limestone sequences have magnesium or dolomitic beds interspersed amongst calcite layers, influencing the shapes of caves and the solution rates which produce them.

Where the proportion of magnesium to calcium is less than 1%, it has been shown that solubility of the carbonate actually increases over pure calcite (Picknett 1972, Picknett & Stenner 1978). No one appears to know exactly why this happens as the common ion effect indicates that the opposite should occur. The upshot being that water may become more aggressive by passing from one limestone to another that contains more magnesium, or by mixing of waters containing different magnesium concentrations. When the proportion of magnesium exceeds 15%, solution is progressively retarded (Marker 1973). Where these form interbeds in limestones, solution tends to be restricted and directed towards purer calcium carbonate and low magnesium calcite.

Magnesite distribution

A quick look at a karst distribution map (e.g. Gillieson and Smith 1989) shows limestone to be

the most common karstic rock in Australia. Massive dolomite is scattered about the northern Australian landmass, however the region's most complex dolomite karst systems are found in Tasmania. In comparison with these rocks magnesite is very restricted.

Magnesite is found in either a massive, usually crystalline form, or as veins and alteration products of ultramafic rocks such as serpentinites. In some localities magnesite occurs as concretions in the soil profile, precipitated from magnesium rich groundwater. Whilst the vein and soil deposits are reasonably widespread, they are very small, and therefore of no real consequence for karst processes. Only the larger sedimentary and metamorphic deposits have the size and structure necessary to support karst. There are three main areas around the country where massive magnesite is found; in NW Tassie, in the northern Flinders Ranges, and at Rum Jungle in the NT. Large amounts of nodular, soil magnesite are found in Queensland. This Kunwarara Deposit, north of Rockhampton, covers several square kilometres, and contains more than 98% $MgCO_3$. A new mine has recently been commissioned here.

The Tasmanian magnesites are found in four main areas, cropping out over a distance of approximately 60 km amongst Precambrian rocks between Arthur and Pieman rivers. The three largest bodies are found in the Central Creek/Arthur River/Keith River district, (3 km x 400 m), the Lyons River (3 km x 400 m) and in the valleys of Main and Bowry Creeks to the SW of Savage River (6 km x 500 m). All of these deposits are around 3-400 m deep and associated with mineralized schists and amphibolites (Sharples 1997).

In the Flinders Ranges, sedimentary magnesite crops out as 1-5 m thick beds within the Skillogalee dolomite. Of more karstic interest, crystalline magnesite deposits are found to the NW of Balcanoona in lenses up to 100 m wide, 400 m long and 60 m deep (Mc Callum 1990).

At Rum Jungle, magnesite crops out in the apparently misnamed Proterozoic Coomalie and Celia "Dolomites". These are in fact predominantly coarsely crystalline magnesites with secondary dolomite. The magnesite crops out only sparingly in the area with very little surface outcrop. The area contains massive base-metal sulphide and uranium deposits, with the uranium genetically related to the magnesite (Aharon 1988).

The Tasmanian, Balcanoona and Rum Jungle deposits all appear to be metasomatised dolomite. That is, all of the original calcium was leached and replaced by magnesium from warm, magnesium rich waters associated with regional tectonic activity. The beds in the Skillogalee dolomite appear to be primary sedimentary magnesite deposited in shallow, warm seas with other evaporites. Clive Calver, who shares this

project with me, is presently analysing carbon and oxygen isotopes of the Tasmanian magnesites; he has already analysed the Skillogalee. This will tell us if they are in fact altered dolomites or primary sediments, as the isotope ratios are very different.

I have been lucky enough to have had a good look at the Tasmanian and South Australian crystalline magnesites, but not those in the Northern Territory. Radon contamination aside, they could be very interesting karstically, given the rainfall and associated rocks, although the reported limited outcrop and relief do not bode well for major surface-accessible caves. That's the easy bit, now to work out what is going on.

Magnesite solution in theory

Probably the best key to an understanding of karst processes in magnesite is the literature on karst in dolomite. This at least contains some field relevant studies, as well as laboratory tests specifically directed to analyzing karst processes, with relevant assumptions incorporated. The general textbook which deals most completely with karst processes in dolomite is Ford & Williams (1989) who, quoting the experiments of Busenberg and Plummer (1982), suggest that the solution of dolomite, at least in the initial stages, occurs as two consecutive processes involving solution of the calcite, then of the magnesite component.

When fresh dolomite is exposed to water with varying concentrations of CO_2 , the more reactive calcium carbonate is dissolved, leaving the rock surface greatly enriched in magnesite. Magnesite, although more soluble than calcite in pure water (more of it will go into solution), is far slower to dissociate into its component ions and disperse into the liquid. This controls the rate of the solution reaction. It is only when more calcite is exposed through the dissociation of magnesite that the more reactive calcite component is dissolved.

A corollary to this is, that once magnesium ions are in solution they are far more strongly attracted to water molecules than are calcium, making it much more difficult to precipitate them from solution. It is almost unheard of to find dolomite or magnesite stalactites or stalagmites, even in dolomite caves. [That's why there are no dolomite stalactites in Tantanoola - at last I know why! Ed.] Almost always the calcite will precipitate first, and only when all of the calcite has precipitated will the magnesite crystallize. Often this will only occur under conditions of evaporation or of biological intervention in the case of moonmilk. (Harmon et al. 1983).

But why is calcite more easily dissolved than magnesite? Neither Ford & Williams (1989) nor Busenberg & Plummer (1982) shed any light on this.

As a last resort there are always first principles. By this I mean such things as descriptions of the physical and chemical behaviour of magnesite found in physical chemistry texts. These can be of some use, but I have found that serious misunderstandings can occur if these, generally laboratory based, ideas are transferred into field situations without experiment. The enormous complexity of the biophysical world will often mean that a process you never even thought of will have a greater effect than something you read about in a laboratory text. However, they do provide good sources of questions and hypotheses to be tested, so that's all I'll do here.

There are some basic differences in the physical chemistry of calcite and magnesite. Magnesium ions have a smaller ionic radius than calcium ions, because they have less electrons. The distance between the nucleus of the magnesium ion and the carbonate ion is less than that between the calcium ion and the carbonate, therefore the ionic bond within individual molecules is stronger.

In an ideal crystal (a bit closer to what exists in nature!) the lattice energy (the energy required to break a crystal into its component ions) is similarly stronger for magnesite, as is the hydration energy of magnesium (the energy required to break an ion's electrostatic bond with water molecules when in solution). The relationship between a crystal's lattice energy and the hydration energy of its component ions will determine its solubility in water (Lee 1991). In the case of magnesium and calcium carbonate, Mg^{2+} has a hydration energy approximately 20% higher than Ca^{2+} , whereas its lattice energy as a carbonate is about 12% higher. This has the dual effect of making it more soluble but, because of the stronger ionic bond, less reactive. In other words you can get more magnesite into solution, but it takes longer to get it there.

So much for the theory. Pure water is very rarely found in nature, neither are pure calcite, dolomite nor magnesite. In Tasmanian

pH	Cond uS/cm	Ca mg/l	K mg/l	Mg mg/l	Na mg/l	Cu ug/l	HCO ₃ mg/l	Cl mg/l	F mg/l	SO ₄ mg/l
8.0	1010	125	3.10	55.1	17.0	4	200	26	0.51	320

Obviously this water has seen some dolomite as well as magnesite, however the sulphate level is instructive.

Carbonic acid

Busenberg and Plummer's (1982) experiments show that solution rates in dolomite (controlled by the solution rate of the magnesite component) increase predictably with the concentration of CO₂ in water. Similarly, Baker (1986) dissolved both calcite and dolomite in water both at atmospheric levels of CO₂ and at elevated levels

magnesite karsts at least three natural acids may affect the chemistry of the system:

- sulphuric acid generated by highly mineralised metal sulphide deposits in shales surrounding and interbedded with the magnesite, and pyrite veins within it,
- organic acids produced by the decay of fibrous peats formed below a dense, cool temperate rainforest, and
- high levels of CO₂ generated by the respiration of these rainforest plants and abundant soil biota

Magnesite solution in the field

Laboratory and field tests show that there is a gradation of reactivity with weak acids between calcite, dolomite and magnesite. 10% hydrochloric acid will make limestone fizz wildly, dolomite will fizz slowly if you scratch it first, and magnesite will not fizz at all. If the acid is heated some fizzing will reluctantly take place.

Sulphuric acid

In Western Tassie the most common naturally occurring weak inorganic acid is sulphuric acid, produced in reasonable quantities through the oxidation of sulphide deposits (the same process which, when artificially accelerated, leads to some of our more chronic acid mine drainage problems such as at King River, and re-solution of speleothems in Exit Cave as a result of quarrying exposing oxidisable minerals).

The karst hydrology of Tasmanian magnesites is complicated by the presence of natural warm springs associated with deep circulation through the pyritic shales and magnesite rocks. Four warm springs are now known, one artificially created when an exploration drillhole intersected warm water at a depth of 300 m and was, apparently, impossible to block. Drill logs show that water-filled cavities are found at that depth, as a result of solution by warm dilute sulphuric acid. The following table illustrates one water sample from this source:

and found that more of both carbonates was dissolved reaction at higher CO₂ concentrations.

So, the carbonic acid processes we all understand still apply in magnesite solution, they are just slower.

Organic acids

The third component, the contribution of organic acids to magnesite solution, has fortunately

been studied by Bill Baker, recently retired from the Mines Dept. in Hobart. For those who have not seen western Tasmanian water, it is of a consistency such that Tasmanian swaggies needed to carry only salt beef and flour, the tea is provided on the house. Water originating in buttongrass moors may have pH as low as 3.5. These 'blanket bogs' consist of peats often many metres thick, watered by up to 3 metres of rain annually. In slightly better drained or less frequently burned areas, dense rainforest has developed with its own special brand of peat soils; red-brown fibrous peats which pump out a slightly less acidic brew (pH 3.7 - 4). Many Tasmanian karsts are influenced by such waters.

The magnesite deposits receive water from fibrous forest peats from both subsoil sources and surface streams. The streams are often less acidic than soil waters because they are diluted to some extent by direct runoff. Baker (1986) found that natural waters in Western Tasmania ranged from 5-500 mg/l concentration of humic

substances, depending on whether the water came from creeks or soils, buttongrass or forest catchments. About 90% was in the form of humic acids.

He extracted these substances from natural waters, made up known concentrations, tested the solubility and solution rates of natural calcite, dolomite and magnesite samples, then compared them with solution by atmospheric and enhanced concentrations of CO₂ in water. He did this to test an earlier idea that solution by humic acids may in fact be due to solution by CO₂ generated by the decay of the humic substances, rather than by the humic acids themselves.

Bill found that humic acids markedly increased the rate of solution of all three carbonates, and that this dissolution was due primarily to the action of the organics rather than any CO₂ which was produced:

Metal dissolved (mg) after 24 hrs extraction by:				
Mineral	Metal determined	H₂O/Atmos CO₂	H₂O/Enriched CO₂	Humic extract 500mg/l
Calcite	Ca	0.65	2.75	17.40
Dolomite	Ca	0.25	0.45	7.50
	Mg	0.14	0.33	5.67
Magnesite	Mg	0.22	0.28	1.07

What there is to show for it all

All of these complex things have been going on, but there is surprisingly little to show for it. Compared with the Florentine, Exit Cave or Mt Anne, the magnesite karsts can hardly be described as spectacular. However, what they lack in spectacularity [a neologism] they more than compensate for in interest.

Although at least one of the warm springs at the Lyons River is quite large and very pleasant, most of them are small in comparison with other karst springs such as Junee or Exit, and range between 15 and 20°C, so are hardly hot. Many springs are actively depositing iron oxides. The most likely source for this is, again, the pyrites common in surface and underground catchments. Perhaps the most important of these warm springs is one that has deposited an extensive ferricrete in Tertiary(?) gravels, progressively abandoning upper levels as the stream cuts into its bed. At first the ferricrete was assumed to be a gossan (a deeply weathered mineralized area) casting some doubt on the origin of other large 'gossans' mapped in the area.

Caves are restricted to a few tens of metres in extent, but contain many of the more common speleogens found in limestone or dolomite karsts. Pendant Cave at Main Creek (named by Arthur Clarke), is developed on three distinct horizontal levels, although the rock structure is

steeply dipping. Impressive phreatic tubes and pendants are found but there are almost no speleothems other than some hydromagnesite moonmilk and cave coral (not yet analyzed). Some large, naturally formed, soil pipes (enterable and containing cave adapted invertebrates) are found adjacent to magnesite pinnacles at Lyons River, associated with pseudokarst sinkholes, blind valleys and springs.

Niall Doran has made a preliminary inventory of cave fauna in the magnesites, finding many invertebrates common to limestone and dolomite karsts, but (as always seems to be the case) a few new beasts will require formal description. Given the extensive cavities intersected by the drilling there is also the possibility that a thermophillic (heat loving) invertebrate fauna exists in some of the larger, deeper caves, but we have not sampled for these.

Surface karst features are impressive, but again subdued in comparison with similar forms in more soluble rock. The most spectacular are pinnacles up to 10 m high at Central Creek and BA Creek near Lyons River. These appear to be exhumed rather than dissolved by rainwater. Pinner Quarry is a very instructive site excavated near the contact of the magnesite with overlying Tertiary gravels and basalt, called the Magnesite pinnacles are exposed, surrounded in some cases by ochres which appear to be magnesite weathering products, by Tertiary

gravels, sands and transported tuffs which also fill some small caves, and by Pleistocene slope deposits which have filled depressions in the Tertiary material. Pinnacles are gradually being exposed by surface erosion, as they are at Central Creek, Lyons River and Main Creek.

The pinnacles do not have any karren developed on them. The most common small scale solution feature are interlinked solution pans, and a form of rundkarren, apparently developed beneath a thick moss cover, with pans and moss self perpetuating. It seems that the small amount of CO₂ in rainfall just doesn't produce enough carbonic acid to drive magnesite solution on the surface. Extensive ochre deposits fill Tertiary-aged sinkholes at Bowry Creek, which contain carbon-rich beds, possibly suitable for pollen analysis (Shannon 1993). A sinkhole lake about 60 metres in length is found near Lyons River. Filled solution pipes, small arches and minor pinnacles dotted throughout the horizontal scrub in swampy karst valleys complete the inventory of surface features.

The general impression given by these karsts is that their overall form developed in warmer, more humid conditions in the Tertiary, along with an ongoing hydrothermal influence. Much is inherited, having been buried by Tertiary and Pleistocene deposits and is now gradually being exhumed by fluvial processes. This exhumation is the most active process occurring today, although the warm springs are highly charged with calcium, magnesium, bicarbonate and sulphate, indicating ongoing solution at depth.

REFERENCES

- AHARON, P. 1988. A stable isotope study of magnesites from the Rum Jungle uranium field, Australia: Implications for the origin of strata-bound massive magnesites. *Chem. Geol.* 69 127-145.
- BAKER, W.E. 1986. Humic substances and their role in the solubilization and transport of metals. In: CARLISLE, D., BERRY, W.L., KAPLAN, I.R. and WATTERSON, J.R. (eds.) *Mineral exploration: Biological systems and organic matter*. Rubey Volume5, Prentice-Hall.
- BUSENBERG, E. and PLUMMER, L. N., 1982. The kinetics of dissolution of dolomite in CO₂ - H₂O systems at 1.5 to 65°C and 0 to 1 atm pCO₂. *Am. J. Sci.* 282: 45 - 78.
- FORD, D. C. AND WILLIAMS, P. W. 1989. Karst geomorphology and hydrology. Chapman and Hall.
- GILLIESON, D.S. and SMITH, D.I. (EDS), 1989. Resource Management in limestone landscapes: international perspectives, *Special Publication No. 2, Dept. of Geography and Oceanography, University College, Australian Defence Force Academy, Canberra*
- HARMON, R. S., ATKINSON, T. C. and ATKINSON, J. J. 1983. The mineralogy of Castleguard Cave, Columbia icefields, Alberta, Canada. *Arctic and Alpine Research* 15(4): 503-16.
- LEE, J. D. 1991. *Concise inorganic chemistry, 4th edition*. Chapman and Hall.
- Mc CALLUM, W. S. 1990. Magnesite deposits in South Australia. In: HUGHES, F. E. (ed) *Geology of the mineral deposits of Australia and Papua New Guinea*. Aust. Inst. Mining and Metallurgy, Melbourne.

What to do about it?

The scientific significance of these karsts is high. They will be invaluable in documenting the field processes related to magnesite (and also dolomite) solution. The influence of carbonic, sulphuric and humic acids could be investigated, along with an extensive cool and warm karst hydrology. The palaeokarst features and their relationships with Tertiary and older rocks will add to our knowledge of geological, geomorphological and environmental history of the area. Whilst the surface karst features, caves, and hydrology are probably the best developed in Australian magnesites, they may also compare with magnesite karst on an international scale. Literature suggests that the extent of Tasmanian magnesite deposits is comparable with overseas bodies, however the international literature is almost totally devoid of any description of features and there has been no research into karst processes.

The magnesites are also of undoubted economic importance. Two companies have indicated their intention to develop mines at the Keith-Arthur and Main Creek deposits and hundreds of jobs have been promised. There is now a great expectation that a mine will proceed. Following the closure of the Burnie pulp mill there is very little left in the way of industry to provide employment.

A decision on if or where to mine will ultimately rest on a compromise between scientific and economic values.

- MARKER, M. E. 1973. Some aspects of the magnesium problem in karst weathering, with special reference to the northeastern Transvaal, South Africa. *Trans. Cave Res. Group Grt. Britain* 15(1): 9-17.
- PICKNETT, R. G. 1972. The pH of calcite solutions with and without magnesium carbonate present, and the implications concerning rejuvenated aggressiveness. *Trans. Cave Res. Group Grt. Britain* 14(2): 141-150.
- PICKNETT, R. G. and STENNER, R. D. 1978. Enhanced calcite solubility in dilute magnesium carbonate solutions. *Trans. British Cave Research Assn.* 5(1):47 - 54.
- SHANNON, C. H. C. 1993. Karst values of the proposed mining sites for ochre extraction and their environs, Savage River, Tasmania. In: SAVAGE RESOURCES 1993. *Development proposal and environmental management plan to operate a mine and beneficiation plants for the production of pigment at Savage River and on the northwest coast.* Unpub. rept. Savage Resources Ltd.
- SHARPLES, C. 1997. *Karst geomorphology and values of the Tarkine. Limestone, dolomite and magnesite karst systems of the Arthur-Pieman region of Tasmania.* Rept. to Aust. Heritage Commission and the Tasmania. Conservation Trust Inc.