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Magnesium and calcium concentrations in limestone groundwaters, Peninsular Malaysia

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Abstract: The discharge and solute concentrations of 217 groundwaters, draining the Kuala Lumpur Limestone, the Kinta Limestone, and limestones of the Setul Formation, were monitored over a 1-year period. The mean molar Mg: Ca+Mg ratio of the groundwaters (12.8%) is very similar to that of the bedrock (13.3%), indicating the dissolution of calcium and magnesium to be broadly congruent. Extremely low (<2.5%) or high (>35%) ratios are notably less common in groundwaters than bedrock, a feature attributed to: (i) heterogeneity in bedrock mineralogy within the catchments drained by individual groundwaters; (ii) differences in the relative solubilities of calcium and magnesium in magnesian calcites and dolomites; and (iii) preferential precipitation of calcium in secondary carbonate deposits. Where groundwaters have variable discharges, their Mg: Ca+Mg ratio tends to correlate negatively with discharge, as less calcium per unit volume of water is deposited on speleothems at higher flows. The possibilities of using groundwater survey data to locate areas of dolomitization and to make specific inferences about the mineralogy of limestone formations are discussed.

Because the soil cover in the Setul Boundary Range is generally deeper and more extensive than in the steeper tower karsts of the Kuala Lumpur and Kinta Limestones, groundwater recharge has almost twice the chemical weathering potential. However, net chemical denudation rates are similar in all three limestone formations (range, 56.6-70.9 $m^3/km^2/yr$) as the higher effective rainfall in the tower karst regions compensates for their lower solute concentrations.

INTRODUCTION

The proportions of magnesium and calcium in limestone often differ widely both within a single rock formation and between formations. 'True limestone' has a molar Mg: Ca+Mg ratio, expressed as a percentage, of less than 5% (Leighton and Pendexter, 1962). In these, any magnesium is usually present as magnesian calcite, which comprises magnesite ($MgCO_3$) dispersed in solid solution within a calcite lattice. As the concentration of magnesium increases, the limestone gives way to dolomitic limestone (Mg: Ca+Mg, 5-25%), calcareous dolomite (25-45%) and dolomite (>45%). As much as 6% magnesium may be present as magnesite in solid solution, but magnesium in excess of this usually occurs as dolomite ($CaMg(CO_3)_2$) mixed with calcite (Graf and Lamar, 1955). Magnesian calcite may have been present in the original carbonate deposits, whereas dolomite results from slow postdepositional alteration of calcium carbonate by magnesium-rich waters. Entire beds may be affected if dolomitization follows shortly after deposition. Commonly, however, transformation takes place later. Magnesium-rich solutions then tend to be confined along bedrock fractures, and the effects are more localized (Krauskopf, 1967). The magnesium content and the nature and degree of dolomitization therefore provide considerable insight into the evolution of a particular limestone formation. Furthermore, because magnesium affects both the equilibrium solubility and rate of solution of carbonates (see reviews by Jennings, 1985; Trudgill, 1985), variations in bedrock chemistry directly affect contemporary denudation and long-term landform development in karst terrain.

The karst outcrops in Peninsular Malaysia provide ideal sites for investigating the relationships between carbonate composition (bedrock and secondary deposits), groundwater chemistry, and chemical weathering rates, for two reasons. First, the limestones vary widely in their magnesium concentration (Hutchison, 1966, 1968). Secondly, extensive cave networks allow ready access to underground seepages. The present paper reports on a detailed chemical investigation of more than 200 cave seepages, cave streams and springs, focusing in particular upon spatial and temporal variations in the Mg: Ca+Mg ratio, and on chemical denudation rates. Consideration is also given to the possibility of using groundwater survey data as a means of locating areas of dolomitization and as a basis for making more specific inferences about the mineralogy of limestone formations.

FIELD AREAS

Three of the major limestone formations in the peninsula were studied: the Kuala Lumpur Limestone (Silurian age) in Selangor, the Kinta Limestone (Ordovician-Permian) of the Kinta Valley, Perak, and the limestones of the Setul Formation (Ordovician-Silurian) in Perlis (Fig. 1). Of 187 specimens, 60% are true limestone, 17% calcareous dolomite, 7% dolomitic limestone and 16% dolomite (Fig. 2). The Mg: Ca+Mg ratio averages 13.3% (range, 0.00-56.3%; Table 1).

The Kuala Lumpur and Kinta Limestones mostly comprise very pure, massive crystalline marble (Gobbett, 1964; Ingham and Bradford, 1960), with mean Mg: Ca+Mg ratios of 11.0 and 17.5%, respectively. Both are exposed as residual tower karst hills, which rise precipitiously from broad alluviated karst plains. Because of the characteristically steep relief and the purity of the bedrock (mean acid-insoluble residue content, 1.72 and 1.61%, respectively), the soil cover on the towers is mostly thin and patchy. Thus, while the soil in isolated pockets may exceed 2 m in thickness, average depths typically range from 1-6 cm on the rocky hilltops to 23-38 cm on the ramp-like, 30°-45° footslopes that fringe sections of the tower perimeters (Jennings, 1976; Crowther, 1984a). Virtually all the effective rainfall (i.e. rainfall minus losses due to evaporation and evapotranspiration) is absorbed by the highly permeable soils and bedrock, and direct surface runoff from the outcrops is negligible. Groundwater flow is mostly confined to vertical and near-vertical joints and faults (Crowther, 1983a). As a

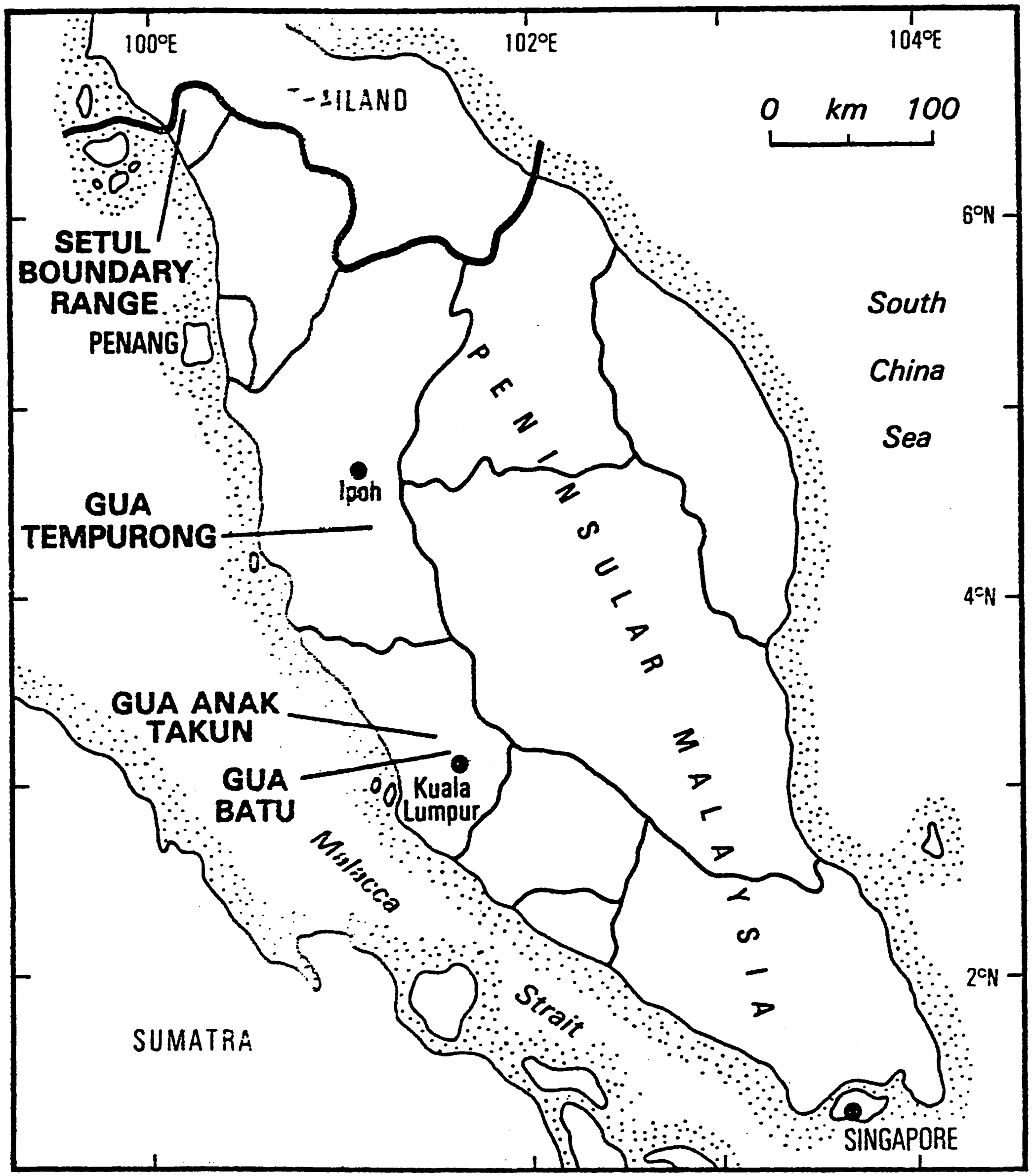

Figure 1 : Location of the principal study areas

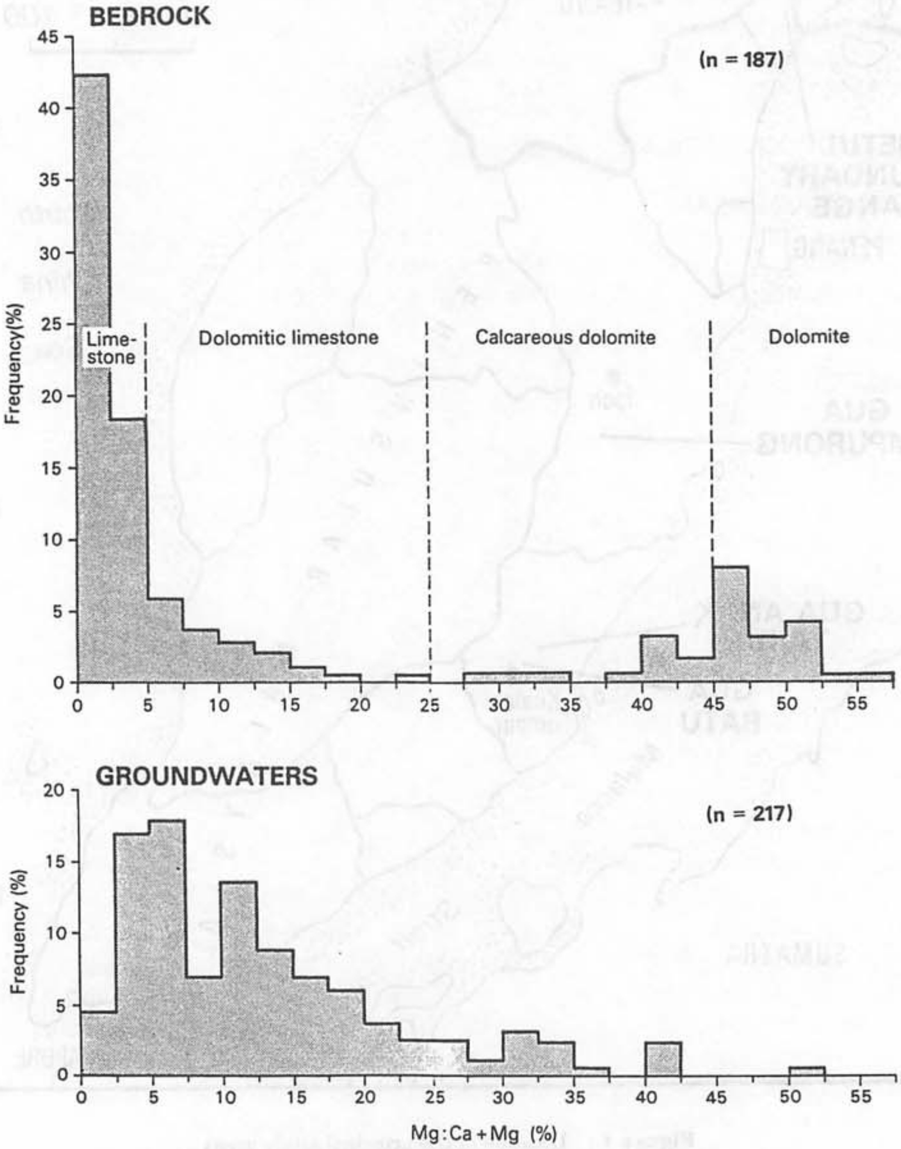

Figure 2 : Frequency distribution of Mg:Ca+Mg (%) in bedrock and groundwaters

Table 1 : Molar Mg : Ca+Mg (%) Ratio of Bedrock and Speleothems*

	n	Mean	Minimum	Maximum	Standard deviation
LIMESTONE FORMATIONS					
Kuala Lumpur Limestone	62	11.0	0.00	50.6	17.4
Kinta Limestone	83	17.5	0.00	56.3	20.7
Setul Formation	42	8.51	0.00	51.1	11.4
ALL BEDROCK SAMPLES	187	13.3	0.00	56.3	18.2
MAIN STUDY AREAS					
Gua Anak Takun	7	1.13	0.00	2.87	1.00
Gua Batu	12	16.2	0.83	46.2	17.6
Gua Tempurong	7	15.4	0.41	48.6	22.2
Perlis Mine/Subway	6	14.8	1.61	41.6	16.4
SPELEOTHEMS	46	0.84	0.05	2.42	0.60

* Based on Alexander *et al.* (1964), unpublished data from Hutchison (1966) and present study.

consequence,very few springs or cave streams emerge at the margins of the towers, and the bulk of the water that enters the outcrops ultimately feeds into the limestone aquifer beneath the adjacent plains. Narrow conduits may be present in the uppermost 40 m or so of bedrock, but otherwise flow is predominantly through tight rock fractures (i.e. diffuse flow). Seepages in the tower karst caves therefore tend to be closely spaced and of low discharge (Crowther, 1983a), with groundwater-residence times in the order of 60-80 days (Crowther, 1980).

By comparison, the Setul limestones are less pure (mean acid-insoluble residue concentration, 9.60%; range, 0.97-42.3%), have not been so strongly affected by metamorphism, and contain a notably smaller proportion of magnesium (mean Mg: Ca+Mg, 8.51%). In fact, only 1 of the 42 specimens is dolomite. These limestones form the Setul Boundary Range, an extensive, plateau-like outcrop that contains several large, steep-sided depressions ("wangs"). Generally, the terrain is less rugged than that of the tower karst hills, and the soil cover is correspondingly deeper and more continuous. Thus, even at gradients above 30° the average soil depth on beds of particularly impure limestone exceeds 40 cm (Crowther, 1984a). Here too, effective rainfall is almost entirely absorbed by the bedrock. In this case, however, the geohydrological character of the limestone is strongly influenced by the presence of near-horizontal bedding planes, which favour lateral groundwater movement and the development of integrated flow networks. As a result, groundwater-residence times tend to be shorter than in the tower karst limestones, and underground seepages are more widely spaced, with higher and more variable discharges (Crowther, 1983a). Springs and vadose cave streams are also much more numerous.

EXPERIMENTAL DESIGN AND METHODS

A total of 217 groundwaters were sampled, 202 of which are seepage points (drips and flows) in four cave systems. Gua Anak Takun and Gua Batu in Selangor and Gua Tempurang in the Kinta Valley (Figrue 2), the three tower karst caves investigated, lie 30-40 m, 60-140 m, and 200-400 m, respectively, below the ground surface. As the thickness of the overlying limestone increases, groundwater-residence times tend to increase, with a consequent reduction in the temporal variability of flow rates at individual seepage points. Sampling in Gua Batu was confined to Gua Gelap. Seventeen seepages in Gua Anak Takun and eleven in Gua Batu were found to be contaminated with bat guano (Crowther, 1981) and are excluded from the present discussion. The underground seepages investigated in the Setul Boundary Range are located in the main cave at the southeastern corner of Wang Tangga (owned by Perlis Mines Ltd.) and in the adjacent subway that connects the village of Kaki Bukit and Wang Tangga. For convenience, these sites are grouped together as the "Perlis Mine/Subway" cave system. Surveys and full descriptions of these caves have been published elsewhere (Gua Anak Takun - Dunn (1965), Crowther (1981), Gale (1986); Gua Batu - Heynes-Wood and Dover (1929), Soepadmo and Ho (1971); Gua Tempurong - Crowther (1978a,b); Perlis Mine/Subway - Jones (1965, 1978), Crowther (1982)). The bedrock in the four caves has a mean Mg: Ca+Mg ratio of 12.5% (range, 0.00-48.6%) and is therefore representative of the Malaysian limestones (Table 1). Fortunately for this study, however, the limestones of Gua Anak Takun contain exceptionally small proportions of magnesium (mean Mg: Ca+Mg, 1.13%), whereas the Perlis Mine/Subway system is located in a part of the Boundary Range that is relatively rich in magnesium (mean Mg:Ca+Mg, 14.8%).

The remaining sampling points were at Pinji fish farm borehole (Simpang Pulai-Lahat road), a deep groundwater borehole in the Kinta Valley aquifer; and at twelve cave streams and springs in the Bounday Range. The latter are located in Wang Tangga (including the main stream draining Perlis Mine Cave) and along the eastern front of the Range between Kangar and Kaki Bukit (Figure 3). Rainwater was also sampled in the three karst regions to assess the atmospheric input of calcium and magnesium.

In order to examine both spatial temporal variations in groundwater compostition a three-phase sampling strategy was adopted (Table 2). Initially, all 217 sites were sampled 2 or 3 days after a storm (Phase I). The majority were then monitored regularly at 3- to 6- week intervals over a 1- year period (Phase II), with storm hydrograph events being investigated at 26 of these (Phase III).

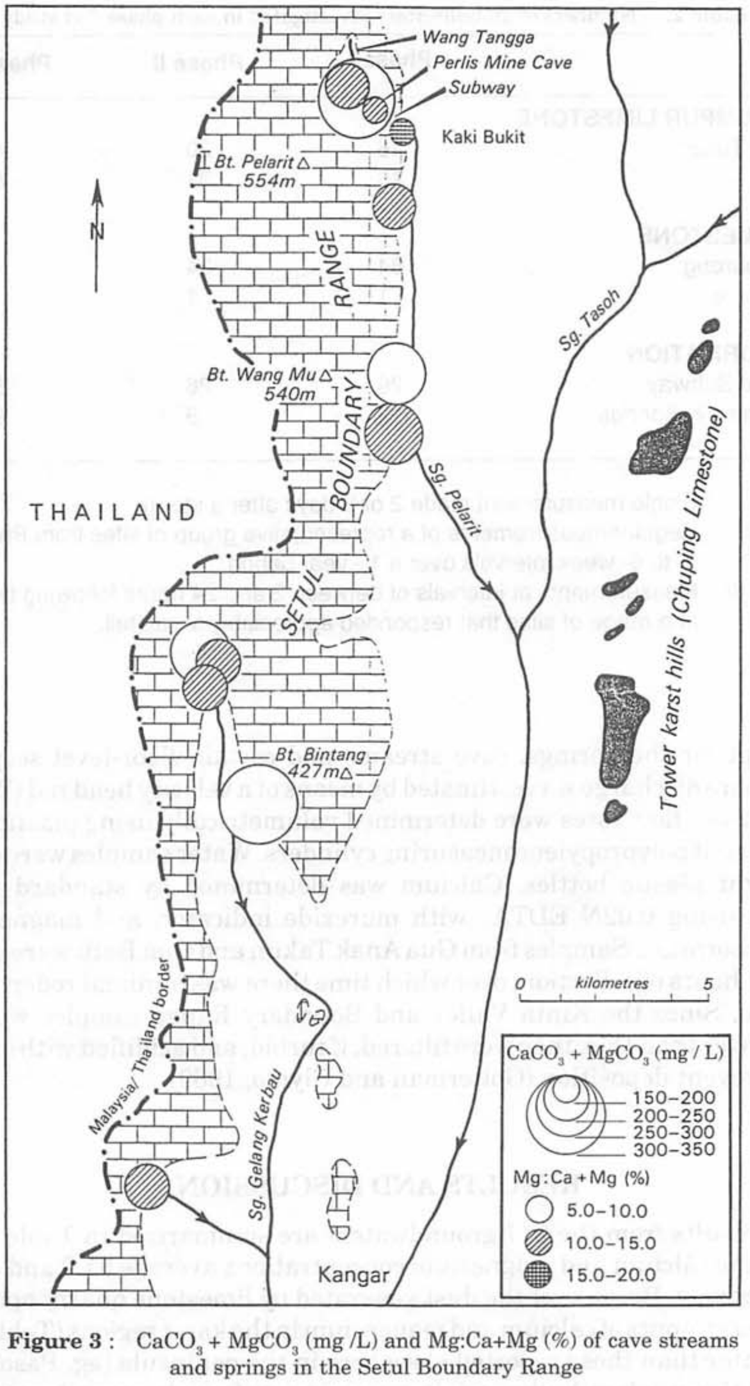

Figure 3 : $CaCO_3 + MgCO_3$ (mg /L) and Mg:Ca+Mg (%) of cave streams and springs in the Setul Boundary Range

Table 2 : Numbers of groundwaters investigated in each phase * of study

	Phase I	Phase II	Phase III
KUALA LUMPUR LIMESTONE			
Gua Anak Takun	46	20	4
Gua Batu	48	31	8
KINTA LIMESTONE			
Gua Tempurong	84	34	-
Pinji borehole	1	1	-
SETUL FORMATION			
Perlis Mine/Subway	26	26	5
Cave streams & Springs	12	9	9

* Phase I: Single measurement made 2 or 3 days after a storm.
Phase II: Regular measurements of a representative group of sites from Phase I at 3- to 6- week intervals over a 1 - year period.
Phase III: Measurements at intervals of between 2 and 24 hours following two storms at a range of sites that responded appreciably to rainfall.

Except for the springs, cave streams and certain floor-level seepages in caves, where discharge was estimated by means of a velocity head rod (Wilm and Storey, 1944), flow rates were determined volumetrically using plastic funnels and a range of polypropylene measuring cylinders. Water samples were collected in air-tight plastic bottles. Calcium was determined by standard titration methods, using 0.02N EDTA with murexide indicator, and magnesium by atomic absorption. Samples from Gua Anak Takun and Gua Batu were analysed within 24 hours of collection, over which time there was minimal redeposition of carbonate. Since the Kinta Valley and Boundary Range samples were often stored longer than this, they were filtered, if turbid, and acidified with sulphuric acid to prevent deposition (Golterman and Clymo, 1969).

RESULTS AND DISCUSSION

The results from the 217 groundwaters are summarized in Table 3 and 4. Overall, the calcium and magnesium concentrations average 51.3 and 4.80 mg/L, respectively. Because of the dust generated by limestone quarry operations, atmospheric inputs of calcium and mangesium in the karst regions (Table 5) tend to be greater than those reported elsewhere in the peninsula (eg. Pasoh Forest Reserve). Nonetheless, bulk precipitation accounts for only a small proportion of the solutes present in groundwaters. Impurities within the limestone provide a further possible source of calcium and magnesium. However, these generally comprise argillaceous, siliceous, or carbonaceous materials that not only contain much lower concentrations of these elements than carbonate minerals, but are also much less readily weathered. Thus, such sources can be discounted in the majority of the Malaysian limestones; even in the less pure strata of the Setul Formation, or where argillaceous facies occur in the Kinta Limestone, they are likely to be of minor significance. The bulk of the calcium and magnesium in groundwaters is therefore derived directly, or indirectly (eg. cations leached from the soil), from the dissolution of carbonate minerals. Attention here focuses upon spatial and temporal variations in the proportions of magnesium and calcium present in groundwaters and upon chemical denudation rates.

Table 3 : Average calcium and magnesium concentrations (mg/L) of groundwaters based on unweighted mean figures for each sampling point

	n	Calcium	Magnesium
KUALA LUMPUR LIMESTONE			
Gua Anak Takun	46	41.4 (25.5-69.3) *	1.86 (0.30-5.13)
Gua Batu	48	47.6 (26.8-78.1)	8.42 (2.77-17.8)
KINTA LIMESTONE			
Gua Tempurong	84	44.3 (23.6-74.9)	3.30 (0.70-15.0)
Pinji borehole	1	80.6	3.82
SETUL FORMATION			
Perlis Mine/Subway	26	80.2 (32.8-130)	7.66 (2.88-22.3)
Cave streams & springs	12	87.5 (60.3-126)	6.00 (3.67-7.83)
ALL GROUNDWATERS	217	51.3 (23.6-130)	4.80 (0.30-22.3)

* Range in parentheses.

Table 4: Mg:Ca+Mg ratios (%) of groundwaters based on unweighted mean figures for each sampling point

	n	Mean	Minimum	Maximum	Standard deviation
KUALA LUMPUR LIMESTONE					
Gua Anak Takun	46	6.93	0.96	19.00	4.71
Gua Batu	48	22.90	10.40	52.20	9.14
KINTA LIMESTONE					
Gua Tempurong	84	10.20	2.42	34.90	6.95
Pinji borehole	1	7.24	-	-	-
SETUL FORMATION					
Perlis Mine/Subway	26	14.40	5.62	40.40	11.60
Cave streams & springs	12	10.70	5.64	17.60	3.63
ALL GROUNDWATERS	217	12.80	0.96	52.20	9.55

Table 5: Average concentrations of calcium and magnesium in bulk precipitation * and estimated atmospheric inputs

	Rainfall (mm/ yr)	Concentration (mg/L)		Atmospheric input (kg/ha/yr)	
		Calcium	Magnesium	Calcium	Magnesium
KARST REGIONS					
Selangor	2446	1.48	0.14	36.10	3.40
Kinta Valley	2847	0.40	0.05	11.40	1.40
Boundary range	2089	1.02	0.09	21.30	1.90
GRANITE & SHALE TERRAIN					
Pasoh Forest Reserve, Negeri Sembilan**	2054	0.18	0.03	4.20	0.68

* The gauges were exposed between storms and the rainwater therefore includes both wet deposition and the soluble fraction of dry deposition.

** Manokaran (1980).

Spatial variations in the Mg: Ca+Mg ratio

The average Mg: Ca+Mg ratio of the groundwaters (12.8%) is so close to that of the bedrock (13.3%) as to indicate that the dissolutional loss of calcium and magnesium from the outcrops is broadly congruent. The groundwater values are however much less variable than those of the limestone, with very few being less than 2.5% or greater than 35% (Figure 1). Thus, the close correspondence in mean values belies quite a complex relationship between groundwater and bedrock composition. Three factors appear to be important in interpreting the results: the equilibria and kinetics of carbonate dissolution reactions, local heterogeneity in bedrock composition, and incongruent precipition of calcium and magnesium in secondary carbonate deposits. To facilitate discussion, these are considered separately. It must be stressed however that the precise effects of individual factors are difficult to isolate in natural groundwaters and that complex interactions must be anticipated.

1. **Chemistry of carbonate dissolution.** The dissolution chemistry of calcite and dolomite is well understood. Both have almost identical solubility products: $10^{-8.4}$ and $10^{-8.5}$ molar at 25 °C, respectively. Dolomite dissolves congruently (Berner, 1967) but much more slowly than calcite. Indeed, it may well take several years for groundwaters to equilibriate with dolomite (Herman, 1982; White, 1984). Consequently, in the case of dolomitic limestones, which contain both minerals, the calcite dissolves preferentially and the resulting groundwaters are incongruent with respect to calcium and magnesium. For example, in a 400-hour simulation experiment on dolomitic limestone (Mg: Ca+Mg, 38.0%) the proportion of dissolved magnesium remained below 30% (Trudgill *et al.*, 1980). The micromorphological effects of differential weathering are clearly revealed in exposures of the Kuala Lumpur Limestone. Gobbett (1964), for instance, cites cases where calcite has been etched out to leave a highly vesicular, pale yellow dolomite.

Dissolution of carbonates is usually further complicated by the fact that pure calcite and dolomite are extremely rare. For example, 79 of the Malaysian specimens have Mg: Ca+Mg ratios below 2.5%, but 73 of these contain traces of magnesium in solid solution as $MgCO_3$. Magnesite has a higher solubility product ($10^{-5.1}$ at 25 °C) than calcite (Siedell, 1958; Krauskopf, 1967). Furthermore, carbonates containing up to about 14% magnesium (estimated from Rauch and White, 1977) dissolve more rapidly than pure calcite. Magnesian calcite therefore dissolves incongruently, and this may explain why so few groundwaters have Mg: Ca+Mg ratios below 2.5%. The results from Gua Anak Takun are noteworthy in this respect. Here the bedrock specimen with the highest proportion of magnesium has a Mg: Ca+Mg ratio of only 2.87%, yet as few as nine of the 46 seepages investigated have ratios as low as this (Figure 4). These results parallel those from the Arthur Marble, New Zealand, where the groundwater value is 3.25%, compared with 1.37% for the bedrock (Williams and Dowling,

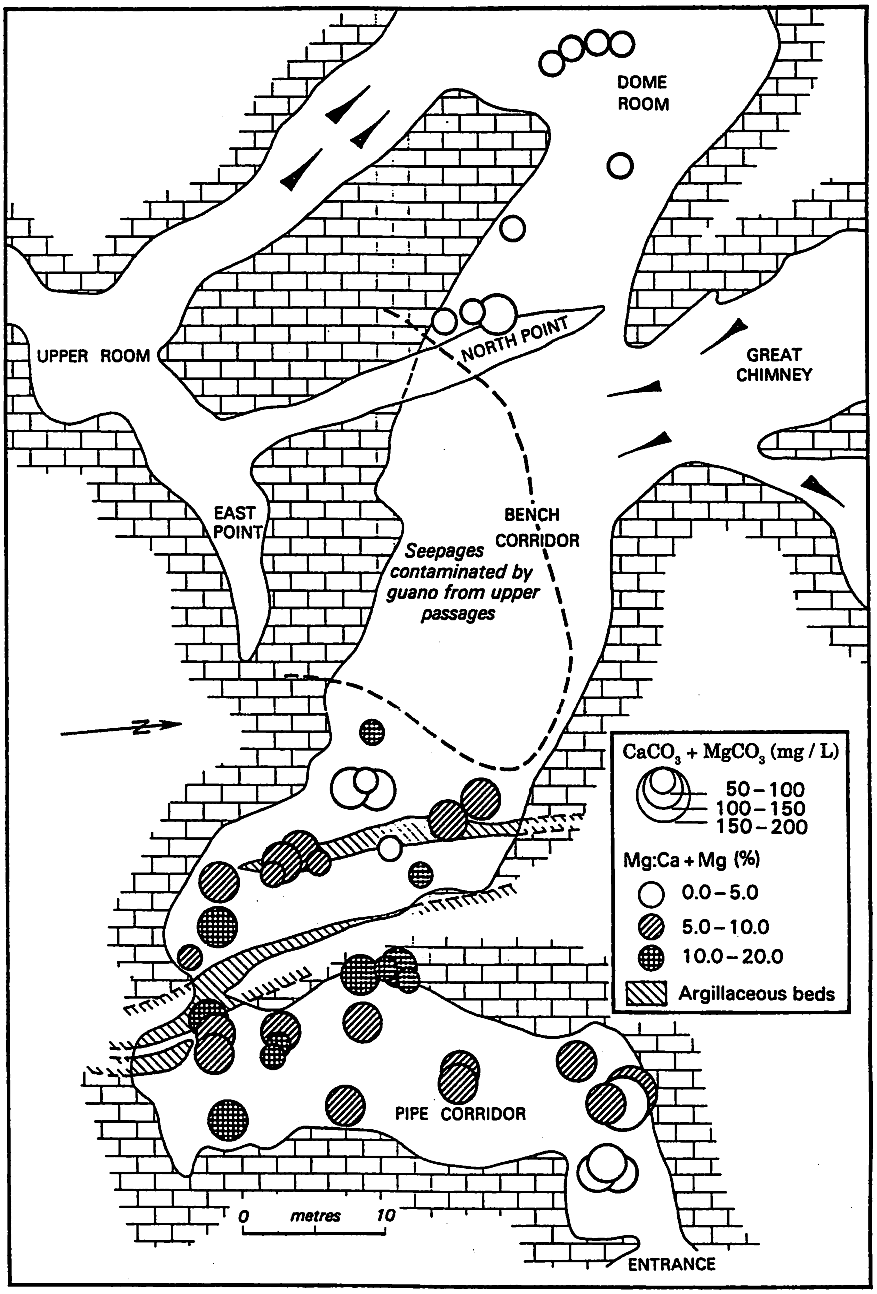

Figure 4: $CaCO_3 + MgCO_3$ (mg/L) and Mg:Ca+Mg (%) of seepages in Gua Anak Takun, Selangor.

1979). Although these findings appear to support the theory of incongruent dissolution, two notes of caution must be emphasised. First, without detailed knowledge of vertical variations in bedrock composition from accessible cliff/ quarry sections or drilling, it will always be uncertain as to how representative the rock samples are of the entire body of limestone through which groundwaters percolate. Secondly, while freshly exposed magnesian calcite dissolves incongruently, as weathering proceeds this effect will tend to be nullified by the progressively smaller proportion of magnesium (at the molecular scale) that is actually exposed at crystal surfaces.

Naturally occurring dolomite, on the other hand, often contains unequal proportions of calcium and magnesium. Thus, only five of the 30 specimens in the dolomite range (Figure 1) have a Mg: Ca+Mg ratio between 49.0 and 51.0%. Slight excess of calcium or magnesium may increase the solubility product of dolomite to $10^{-7.5}$ molar (Bricker and Garrels, 1967), but the effects on the rate and congruence of dissolution are not well established. However, the more disproportionate the composition, the more likely will calcite or magnesite occur within the dolomite matrix, thereby favouring incongruent dissolution. Since the majority of Malaysian dolomites fall within the 45-49% range, preferential dissolution of calcium would be anticipated, and this may partly explain the scarcity of groundwaters with high Mg: Ca+Mg ratios.

2. **Heterogeneity of bedrock composition.** It is apparent even from the small numbers of samples taken from the cave walls that there is as much variability in bedrock composition within areas as small as one hectare as is present within entire limestone formations (Table 1). In Gua Tempurong, for example, five of the seven specimens are true limestone, whereas the other two are dolomite. Whether or not a given groundwater is able to establish and maintain chemical equilibrium through a sequence of carbonates of differing composition depends upon several factors, including: bedrock mineralogy, the order in which the various carbonate rocks are encountered, the duration of water-rock contact, and the readiness with which secondary carbonates precipitate from supersaturated solutions (for fuller discussion see Freeze and Cherry, 1979). In the present study the mineralogy of the bulk of the limestone outcrops and the duration of contact with beds of different composition are unknown. Consequently, it is impossible to establish exactly how a given groundwater has evolved. What is clear, however, is that the chances of any groundwater in the Malaysian limestones being exclusively derived from either magnesium-rich or magnesium-poor carbonates are small, and this is undoubtedly a further reason why so few groundwaters display extreme Mg: Ca+Mg ratios.

Despite this tendency towards homogeneity in groundwater composition, quite wide variations in the Mg: Ca+Mg ratio were recorded in all three rock formations. Marked differences were observed, for example, between certain closely-spaced seepages or groups of seepages in the tower karst caves. This is well illustrated in one 85-m section of Gua Tempurong (Figure 5). Here, the Mg: Ca+Mg ratio increases from the western group of sites (typically, 3-8%) to the eastern group (8-20%), but superimposed upon this general trend are two seepages with exceptionally high ratios of 33.2 and 34.9%. Although bedrock composition cannot be inferred directly from groundwater chemistry, these patterns suggest very localized (i.e. post-depositional) dolomitization. In Gua Anak Takun (Figure 4) the Mg: Ca+Mg ratio rises close to the steeplydipping argillaceous bed. Some magnesium may be derived directly from the noncarbonate strata. Alternatively, the limestones immediately adjacent to the argillaceous beds may be richer in magnesium than the bulk of the outcrop, either as a result of original differences in the composition of the carbonate sediments or from subsequent, localized dolomitization. Variations in bedrock composition in this section of the cave certainly merit further investigation. Differences in groundwater composition of these magnitudes over such short distance firmly support the model of discrete, vertical groundwater flow paths through the Kuala Lumpur and Kinta Limestones (Crowther, 1983a).

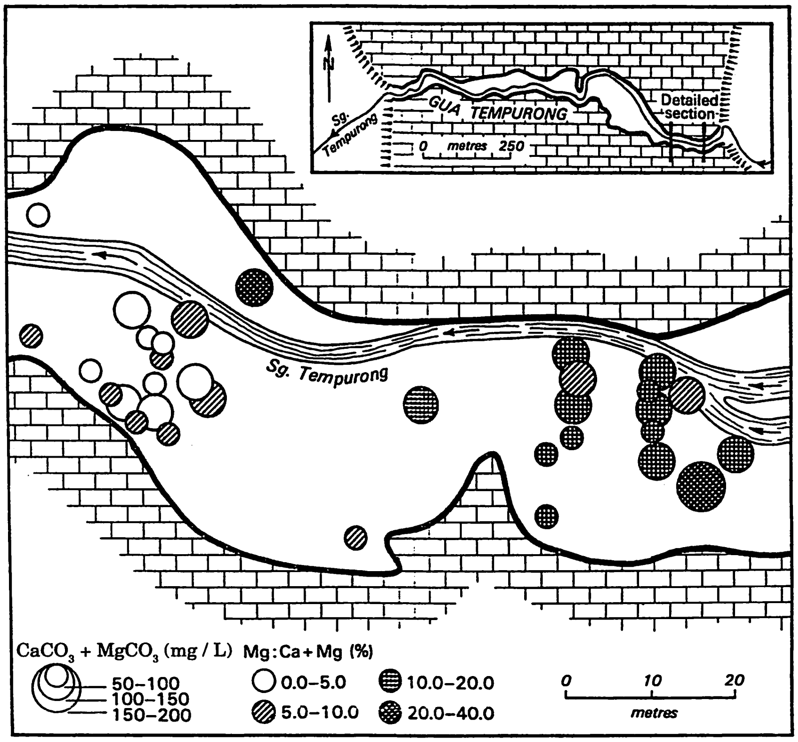

Figure 5: $CaCO_3$ + $MgCO_3$ (mg/L) and Mg:Ca+Mg (%) of seepages in a section of Gua Tempurong.

Although individual seepages in the Perlis Mine/Subway system drain larger catchments than those in the tower karst, inter-seepage variability in the Mg: Ca+Mg ratio is actually greater (standard deviation, 11.6%; Table 4). In fact, five of the 26 seepages investigated have Mg: Ca+Mg ratios in the range 30-42.5%, which indicates the presence of somewhat larger bodies of dolomite or dolomitic limestone. On the other hand, from the low Mg: Ca+Mg ratios (5.64-17.6%) of the springs and cave streams, and their highly irregular distribution (Figure 3), no major areas of dolomitization can be identified.

3. **Incongruent deposition of secondary carbonates.** Secondary deposition occurs when carbonate-saturated waters encounter circulatory cave air in vadose passages. High groundwater temperatures of about 24 °C in the peninsula (Crowther, 1982) favour high rates of deposition (Picknett *et al.,* 1976). Indeed, the exceptionally large speleothems that adorn many of the Malaysian caves bear witness to the effectiveness of this process. The actual concentration of magnesium in the majority of Malaysian groundwaters is so low that supersaturation with respect to dolomite (or magnesite) is unlikely and, in any case, precipitation of dolomite is extremely slow (Fyfe and Bischoff, 1965). Thus, while there are traces of magnesium in all the speleothem specimens that were analysed (Figure 6), and the Mg: Ca+Mg ratio of the secondary deposits correlates closely with groundwater composition (Figure 7), precipitation is incongruent. As a consequence, the relative proportion of magnesium in groundwater increases as precipitation proceeds, and variations in the Mg: Ca+Mg ratio of cave seepage waters must to some extent reflect differences in deposition rate between one speleothem and the next. Observations of temporal fluctuations in groundwater composition provide some insight into the factors that affect deposition rates.

Temporal fluctuations in Mg: Ca+Mg

At sites where six or more measurements were made in Phase II of the study, the coefficient of variation (C.V. = standard deviation x 100/mean%; Spiegel, 1972) of the Mg: Ca+Mg ratio is used as a measure of temporal variability. Temporal fluctuations are generally quite small, the average C.V. being 9.26% (Table 6). Indeed, calcium and magnesium concentrations both vary so little in 47 of the 113 groundwaters that fluctuatoins in Mg: Ca+Mg lie within the likely range of analytical error (Table 7), and the ratio is regarded as constant. There is a striking increase in the proportion of such seepages from 30% in Gua Anak Takun, through 47% in Gua Batu, to 89% in Gua Tempurong. This closely reflects the reduction of discharge variablity in the tower karst caves as the thickness of the overlying limestone increases. In fact, variations in calcium and magnesium of as little as 0.8 and 0.1 mg/L, respectively, were recorded at certain seepage points in Gua Tempurong over the study period. There is a notable absence of such groundwaters in the Perlis Mine/Subway system, where all the seepages have high and quite variable flow rates.

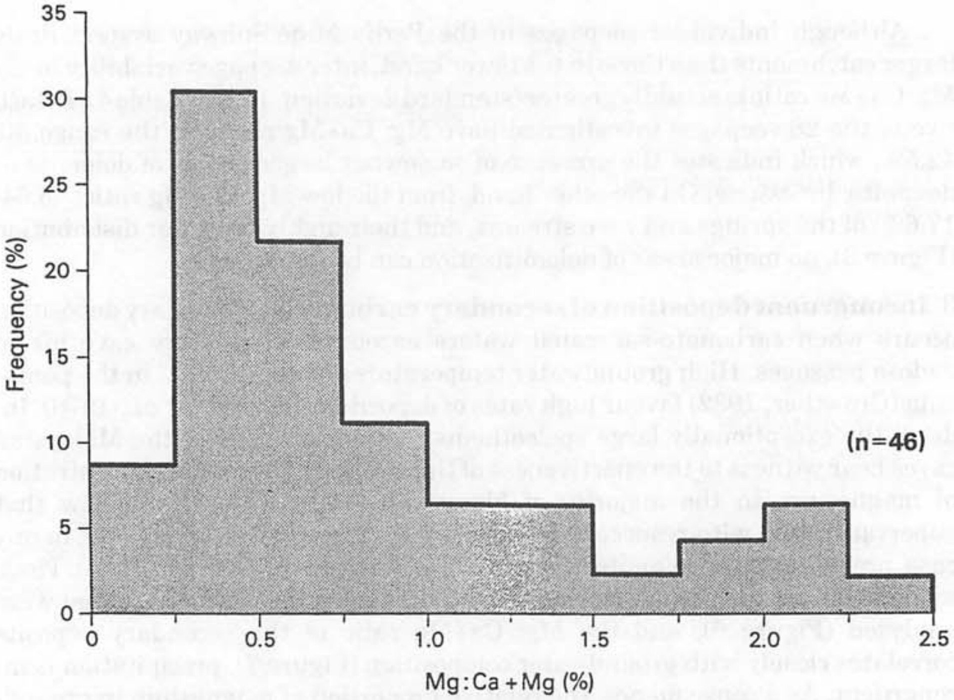

Figure 6 : Frequency distribution of Mg:Ca+Mg (%) in speleothems.

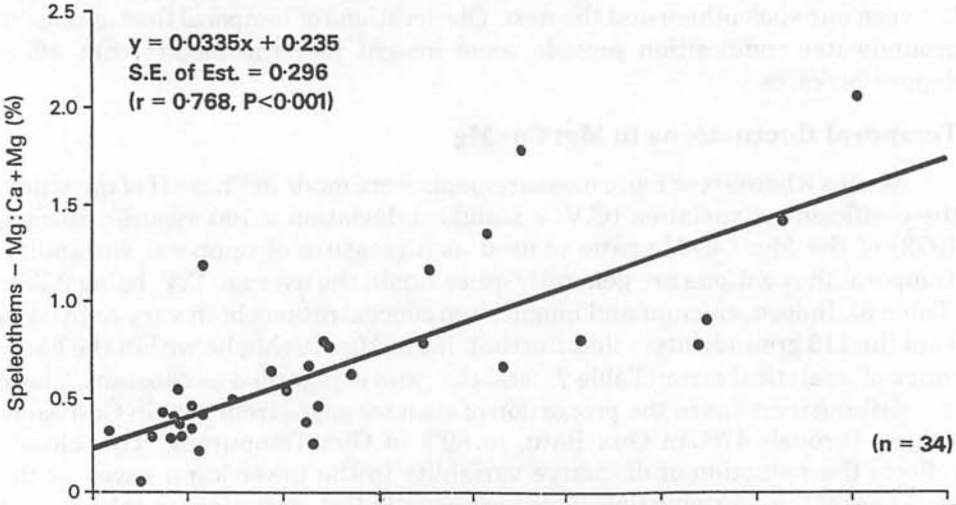

Figure 7 : Relationship between the Mg:Ca+Mg ratios of speleothems and groundwaters.

Table 6 : Coefficient of variation (%) Mg:Ca+Mg ratio for those groundwaters for which 6 or more samples were analysed

	n	Mean	Minimum	Maximum	Standard deviation
KUALA LUMPUR LIMESTONE					
Gua Anak Takun	20	13.90	5.17	34.00	7.84
Gua Batu	30	6.69	2.04	15.20	3.40
KINTA LIMESTONE					
Gua Tempurong	28	7.98	1.61	17.40	4.29
Pinji borehole	1	7.88	-	-	-
SETUL FORMATION					
Perlis Mine/Subway	25	10.40	3.89	22.7	5.51
Cave streams & Springs	9	8.42	3.86	26.2	7.00
ALL GROUNDWATERS	113	9.26	1.61	34.0	5.85

Table 7 : Numbers of groundwaters exhibiting particular relationships between Mg:Ca+Mg and discharge

	Mg:Ca +Mg constant*	Positive correlation ($p<0.05$)	Negative Correlation ($p<0.05$)	No Correlation ($p>0.05$)
KUALA LUMPUR LIMESTONE				
Gua Anak Takun	6	0	12	2
Gua Batu	14	1	9	6
KINTA LIMESTONE				
Gua Tempurong	25	0	3	0
Pinji borehole**	1	-	-	-
SETUL FORMATION				
Perlis Mine/Subway	0	1	11	13
Cave streams & springs	1	1	2	5
ALL GROUNDWATERS	47	3	37	26

* Sites with such small variations in both magnesium (standard deviation <1.0 mg/L) and calcium (standard deviation <2.0 mg/L) that the magnitude of temporal variation lies within the possible range of analytical error.

** Included only for comparative purposes, as no discharge measurements were made at this site.

For each of the remaining groundwaters, the correlation coefficient was calculated for the relationship between the Mg: Ca+Mg ratio and discharge. Forty exhibited a statistically significant relationship ($P < 0.05$), of which 37 were negative. Seepages 13 (Figure 8A) and 26 (Figure 8B) in Gua Batu illustrate the types of relationship observed. Calcium (mean standard deviaiton, 4.39% mg /L) fluctuates much more than magnesium in groundwaters (0.538 mg/L; Table 8) and is therefore the main determinant of temporal fluctuatoins. This is well illustrated by the results obtained during hydrograph events at many of the cave seepages (investigated in Phase III) that responded to individual storms. Figure 8C, for example, shows the hydrograph produced by a 65 mm downpour at Seepage 1 in the Perlis Mine/Subway system. In this case the rise in discharge from 0.68 L/min to a peak of well over 15 L/min was closely parallelled by an increase in calcium from 51.3 to more than 80 mg/L. In contrast, there was a slight dilution in magnesium at peak discharge, with concentrations during the hydrograph event varying by only 0.3 mg/L (range, 2.7-3.0 mg/L). As there is no apparent reason why calcium should dissolve incongruently under stormflow conditions, these results must reflect differences in rates of secondary calcite deposition. With an increase in discharge, water is not only transmitted more rapidly through the limestone system, but the ratio of water volume to surface area of contact with bedrock or speleotherms is also increased. Consequently, the rate of deposition per unit volume of water will decrease, thereby reducing the Mg: Ca+Mg ratio. Similar results have been reported from several caves in the United States (Holland *et al.*, 1964; Thraikill and Robl, 1981).

Chemical Denudation Rates

The mean discharge-weighted calcium and magnesium concentrations used in estimating rates of chemical denudation are summarized in Table 9. The most striking feature of these results is that the calcium concentrations ingroundwaters draining the limestones of the Setul Formation (72.6-81.7 mg/L) are almost twice as high as those recorded in caves in the Kuala Lumpur and Kinta Limestones (40.6-46.5 mg/L). Carbonic acid (derived largely from biogenic carbon dioxide in the soil) is the principal agent of chemical weathering in limestone terrain, and a 1 year study of six representative limestone soils in the Malay Peninsula has shown that the carbon dioxide concentration at the base of soil profiles increases with soil depth (Crowther, 1983b, 1984b). For example, the average concentration of carbon dioxide in the soil atmosphere increased from 0.67% at 15 cm to 1.98% at 60 cm. Since the soil cover in the Boundary Range is generally deeper and more extensive than on the tower karst hills (Crowther, 1984a), recharge waters entering the limestone of the Setul Formation encounter higher carbon dioxide concentrations and consequently have a greater weathering potential. Indeed, on certain tower karst hilltops the soil cover is so thin and patchy that as much as two-thirds of the groundwater recharge

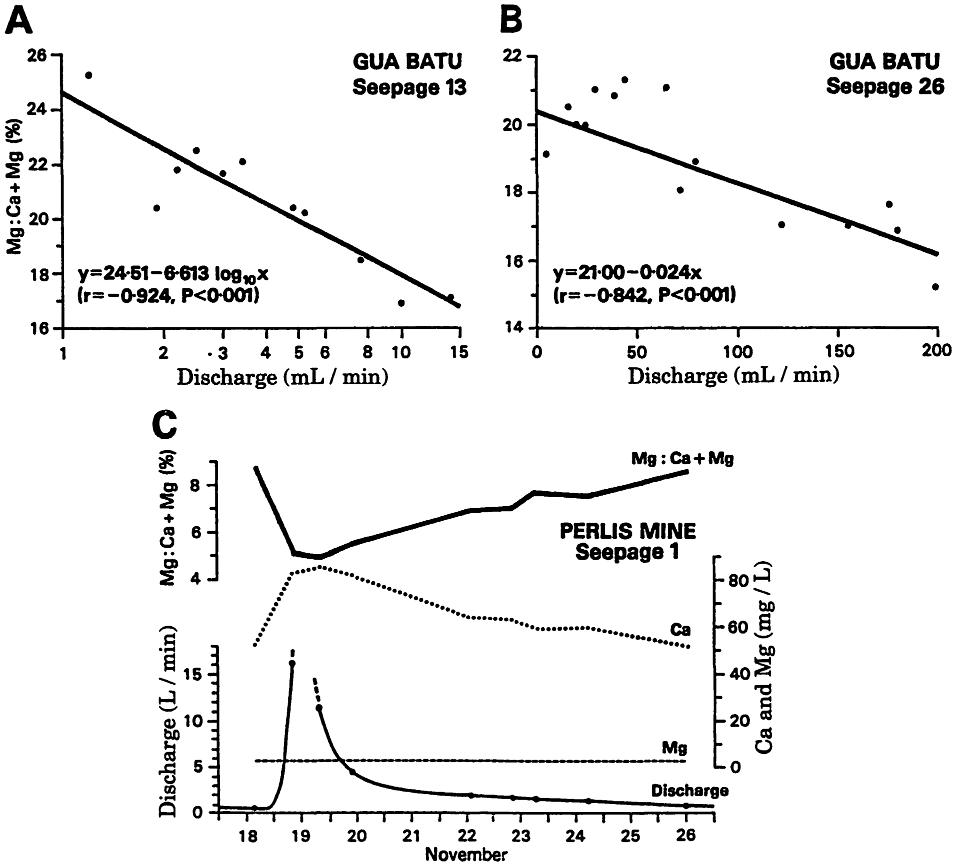

Figure 8 : Relationships between the Mg:Ca+Mg ratio of groundwaters and discharge at selected sites.

Table 8 : Standard deviations of calcium and magnesium concentrations (mg/L) at individual sampling points

	n	Calcium	Magnesium
KUALA LUMPUR LIMESTONE			
Gua Anak Takun	20	4.88 (0.47-15.6)*	0.170 (0.04-0.32)
Gua Batu	30	3.04 (0.77-9.63)	0.791 (0.18-3.98)
KINTA LIMESTONE			
Gua Tempurong	28	1.54 (0.36-6.47)	0.229 (0.03-1.62)
Pinji borehole	1	1.04	0.350
SETUL FORMATION			
Perlis Mine/Subway	25	7.48 (2.79-20.4)	0.803 (0.12-3.43)
Cave streams & Springs	9	8.44 (2.95-21.0)	0.760 (0.13-2.09)
ALL GROUNDWATERS	113	4.39 (0.36-21.0)	0.538 (0.03-3.98)

* Range in parentheses.

Table 9 : Chemical Denudation Rates

	Discharge-weighted mean concentrations* (mg/L)		Net solutional loss** (t/km^2/yr)		Net denudation loss $
	Calcium	Magnesium	$CaCO_3$	$MgCO_3$	(m^3/km^2/yr)
KUALA LUMPUR LIMESTONE					
Gua Anak Takun	46.5	1.33	145	5.6	56.6
Gua Batu	43.1	6.78	135	29.5	62.0
KINTA LIMESTONE					
Gua Tempurong	40.6	4.87	161	26.8	70.9
SETUL FORMATION					
Perlis Mine/Subway	81.7	6.75	168	19.2	70.8
Cave streams & Springs	72.6	5.80	149	16.5	62.6

* Determined by calculating the discharge-weighted cation concentration of individual sampling sites, and then weighting these according to the mean discharge of each sampling sites in the field area.

**Based on: (i) effective rainfall estimates of 1254, 1264, 1603 and 830 mm, respectively, for Gua Anak Takun, Gua Batu, Gua Tempurong and the two groups of sites from the Setul Formation, and (ii) atmospheric inputs in bulk precipitation equivalent to 0.18 mg/L calcium and 0.03 mg/L magnesium (see text).

$Rock density 2.65 g/cm^3.

comprises direct runoff from bare rock surfaces (Crowther, 1984b). The only sampling site in the tower karst terrain that yielded calcium concentrations in excess of 80 mg/L was the Pinji borehole in the Kinta Valley (Table 3). In this case the recharge waters percolate through the much deeper alluvial soils and sediments of the karst plain before entering the limestone, and are known to have a high chemical weathering potential, equivalent to about 100 mg/L calcium (Crowther, 1986).

A considerable proportion of the atmospheric input of calcium and magnesium in the karst regions is thought to originate from quarry operations. Under these circumstances, the bulk precipition concentrations of 0.18 mg/L calcium and 0.03 mg/L magnesium reported from the Pasoh Forest Reserve (Manokaran, 1980) are probably more representive of externally-derived atmospheric inputs in the karst regions, and they have been used in estimating net solutional losses from the limestone outcrops. Studies in forested granite catchments in Selangor have shown evapotranspiration rates to be about 17% less than evaporation measurements (Douglas, 1971; Low and Goh, 1972). It is also known that in the vicinity of the Boundary Range, soils with a water holding capacity of 150 mm experience and average moisture deficit of 107 mm during the January-February dry season (Nieuwolt, 1965). These corrections have been applied to the available rainfall (Table 5) and evaporation data in order to estimate the mean annual effective rainfall (see footnote, Table 9). In the absence of specific water-balance data for the limestone hills, effective rainfall provides the best estimate of the volume of groundwater flow. It must be noted, that because the shallow limestone soils have quite a low water-holding capacity, volumes of flow and, hence, solute and denudation loss (Table 9) are probably slightly underestimated in the present study.

The estimated rates of chemical denudation are similar in all three limestone formations (range, 56.6-70.9 $m^3/km^2/yr$), with the higher effective rainfall in Selangor and the Kinta Valley compensating for the lower solute concentrations. These rates are low compared with some other humid tropical karst terrains. Typically, many areas have solute concentrations in the range recorded in the Boundary Range, but have an effective rainfall similar to Selangor or the Kinta Valley; examples include Kalapanungal, western Java, 99 $m^3/km^2/yr$ (Balázs, 1971) and Madagascar, 109-135 $m^3/km^2/yr$ (Rossi, 1976). Elsewhere, however, as in the Mulu National Park, Sarawak (150 $m^3/km^3/yr$), average solute concentrations lower than any recorded in the present study are compensated by a high annual rainfall of over 5000 mm (Laverty, 1980).

CONCLUSIONS

This study has demonstrated that there is a broad measure of congruence in the Mg: Ca+Mg ratios of carbonate bedrock and groundwaters in Peninsular Malaysia, thus supporting Hem's (1970) suggestion that in areas of known bedrock composition the proportion of calcium and magnesium in karst groundwaters may provide a guide to their origin. The corollary, namely that much insight into bedrock composition may be gained from an analysis of groundwaters, is perhaps of greater significance from a geological viewpoint, for two reasons. First, the composition of groundwaters can be determined directly and, hence, more readily than that of bedrock. Secondly, individual groundwaters drain a large body of bedrock, much of which is inaccessible without expensive drilling. Bedrock specimens, by comparison, are very small and their representativeness is often doubtful. Sampling problems are particularly acute where, as in Peninsular Malaysia, dolomitization is sporadic and extremely localized. For example, none of the 17 specimens analysed by Hutchison (1968) from the Setul Formation was dolomitic, and it appeared that this limestones was free of dolomitization. However, two of the cave seepages investigated in the Perlis Mine/Subway system have Mg: Ca+Mg ratios above 40%, and a bedrock specimen from one of these locations was found subsequently to be dolomitic. The very marked local variations in groundwater composition reported from Gua Anak Takun (Figure 3) and Gua Tempurong (Figure 4) further demonstrate the potential of groundwater surveys in identifying possible areas of dolomitization.

When the present results are examined more closely, the relationship between bedrock and groundwater composition is found to be quite complex. Extremely low or high Mg: Ca+Mg ratios, for example, are much less common in groundwaters than bedrock. This in part reflects the heterogeneity of bedrock composition within the catchments drained by individual groundwaters, but it is also a result of the different solubilities of calcium and magnesium in magnesian clacites and dolomites, and their incongruent precipitation in secondary carbonate deposits. The situation is further complicated where groundwaters have strongly variable discharges, for under those cirumstances temporal variations in the rate of secondary deposition cause fluctuations in the Mg: Ca+Mg ratio. In the majority of cases Mg: Ca+Mg correlates negatively with discharge, as less calsium per unit volume of water is deposited on speleothems at higher flows. Thus, while groundwater surveys can undoubtedly shed some light on the mineralogy of limestone formations, caution must be exercised when making detailed geological inferences.

Because the soil cover in Setul Boundary Range is generally deeper and more extensive than in the steeper tower karsts of the Kuala Lumpur and Kinta Limestones, groundwater recharge has almost double the chemical weathering potential. However, net chemical denudation rates are similar in all three limestone formations (range, 56.6-70.9 $m^3/km^2/yr$), because the higher effective rainfall in Selangor and the Kinta Valley compensates for the lower solute concentrations.

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REFERENCES

ALEXANDER, J.B., HARRAL, G.M. and FLINTER, B.H., 1964. Chemical analysis of Malayan rocks, commercial ores, alluvial mineral concentrates 1903-1963. *Prof. Pap. Geol Surv. Dep. W. Malaysia*, E 64.1c, 295p.

BALÁZS, D., 1971. Intensity of the tropical karst development based on cases of Indonesia. *Karszt- és Barlangkutatás*, 6, 33-67.

BERNER, R.A., 1967. Comparative dissolution characteristics of carbonate minerals in the presence and absence of aqueous magnesium ion. *Am. J. Sci.*, 265, 45-70.

BRICKER, O.P. and GARRELS, R.M., 1967. Mineralogical factors in natural water equilibria. *In* Faust, S.D. and Hunter, J.V. (Eds), *"Principles and applications of water chemistry"*, Wiley, New York, 449-68.

CROWTHER, J., 1978a. Karst regions and caves of the Malay Peninsula, west of the Main Range. *Trans. Br. Cave Res. Assoc.*, 5, 199-214.

CROWTHER, J., 1978b. The Gunong Gajah-Tempurong Massif, Perak, and its associated cave system, Gua Tempurong. *Malay. Nat. J.*, 32, 1-17.

CROWTHER, J., 1980. *Karst water studies and environment in West Malaysia*. Unpub. Ph.D. Thesis, University of Hull, U.K.

CROWTHER, J., 1981. Small-scale spatial variations in the chemistry of diffuse-flow seepages in four West Malaysian caves. *Trans. Br. Cave Res. Assoc.*, 8, 168-77.

CROWTHER, J., 1982 Temperature characteristics of seepages in four West Malaysian caves. *Trans. Br. Cave Res. Assoc.*, 9, 38-46.

Crowther, J., 1983a. Hydrology of autogenic percolation systems in some tropical karst outcrops, West Malaysia. *J. Hydrol.*, 60, 227-42.

CROWTHER, J., 1983b. Carbon dioxide concentrations in some tropical karst soils, West Malaysia. *Catena*, 10, 27-39.

CROWTHER, J., 1984a. Meso-topography and soil cover in tropical karst terrain, West Malaysia. *Z. Geomorph., N.F.*, 28, 219-34.

CROWTHER, J., 1984b. Soil carbon dioxide and weathering potentials in tropical karst terrain, Peninsular Malaysia: a preliminary model. *Earth Surf. Processes & Landforms,* 9, 397-407.

CROWTHER, J., 1986. Chemical erosion in tower karst terrain, Kinta Valley, Peninsular Malaysia. *In* Paterson, K. and Sweeting, M.M. (Eds), *"New directions in Karst"*. Geo Books, Norwich, 427-41.

DOUGLAS, I., 1971. Aspects of the water balance in the Main Range near Kuala Lumpur. *In* Flenley, J.R. (Ed), *"Trans. 1st Aberdeen-Hull symposium on Malesian ecology"*, University of Hull, Department of Geography, Miscellaneous Series, No. 11, 23-48.

DUNN, F.L., 1965. Gua Anak Takun: ecological observations. *Malay. Nat. J.*, 19, 75-87.

FREEZE, R.A. and CHERRY, J.A.,1979. *Groundwater*. Prentice Hall.

FYFE, W.S. and BISCHOFF, J.L., 1965. The calcite-aragonite problem. *Society of Economic Palaeontologists and Mineralogists, Special Pub.*, No. 13, 3-13.

GALE, S.J., 1986. The hydrological development of tropical tower karst: an example from Peninsular Malaysia. *In* Paterson, K. and Sweeting, M.M. (Eds), *"New directions in karst"*. Geo Books, Norwich, 443-59.

GOBBETT, D.J., 1964. The Lower Palaeozoic rocks of Kuala Lumpur, Malaysia. *J. Fed. Malay St. Mus.*, 9, 67-79.

GOLTERMAN, H.L. and CLYMO, R.S., 1969. *Methods for the chemical analysis of fresh waters.* International Biological Programme Handbook, No. 8, Blackwell Scientific Pub., Oxford.

GRAF, D.L. and LAMAR, J.E.,1955. *Economic Geology*. 50th Anniversry Vol., 639-713.

HEM, J.D., 1970. *Study and interpretation of the chemical characteristics of natural water.* Water-Supply Paper, U.S. Geol. Surv., 1473, U.S. Govt Printing Office, Washington.

HERMAN, J.S., 1982. *The dissolution kinetics of calcite, dolomite and dolomitic rocks in the CO2-water system.* Unpub. Ph.D. Thesis, Pennsylvania State University, U.S.A.

HEYNES-WOOD, M. and DOVER, C., 1929. Fauna of the Batu Caves, Selangor, J. Fed. *Malay St. Mus.*, 14, 325-87.

HOLLAND, H.D., Kirsipu, T.V., Huebner, J.S. and Oxburgh, U.M., 1964. On some aspects of the chemical evolution of cave waters. *J. Geol.*, 72, 36-67.

HUTCHISON, C.S., 1966. *Tectonic and petrological relations within three rock associations of orogenic zones in Malaysia.* Unpub. Ph.D. Thesis, University of Malay.

HUTCHISON, C.S., 1968. Physical and chemical differentiation of West Malaysian limestone formations. *Geol. Soc. Malaysia Bull.*, 1, 45-56.

INGHAM, F.T. and BRADFORD, E.F., 1960. *The geology and mineral resources of the Kinta Valley.* Federation of Malaya Geological Survey, District Memoir, No. 9.

JENNINGS, J.N., 1976. A test of the importance of cliff-foot caves in tower karst development. *Z. Geomorph., N.F., Suppl. -Bd.*, 26, 92-97.

JENNINGS, J.N., 1985. *Karst geomorphology*. Blackwell, Oxford.

JONES, C.R., 1965. The limestone caves and cave deposits of Perlis, North Kedah and the Langkawi Islands. *Malay. Nat. J.,* 19, 21-30.

JONES, C.R., 1978. T*he geology and mineral resources of Perlis, North Kedah and the Langkawi Islands.* Geological Survey, Malaysia, District Memoir, No. 17.

KRAUSKOPF, K., 1967. *Introduction to geochemistry*. McGraw-Hill, New York.

LAVERTY, M., 1980. Symposium on the geomorphology of the Mulu Hills: VI. Water chemistry in the Gunung Mulu National Park including problems of interpretation and use. *Geogrl J.*, 146, 232-57.

LEIGHTON, M.W. and PENDEXTER, C., (1962). Carbonate rock types. Amer. Ass. Petrol. *Geol. Mem.,* 1, 33-16.

LOW, K.S. and Goh, K.C., 1972. The water balance of five catchments in Selangor. *J. trop. Geog.*, 35, 60-66.

MANOKARAN, N., 1980. The nutrient contents of precipitation, throughfall, and stemflow in a lowland tropical forest in Peninsular Malaysia. *Malay. Forester*, 43, 266-289.

NIEUWOLt, S., 1965. Evaporation and water balances in Malaya. *J. trop. Geog.*, 20, 34-53.

PICKNETT, R.G., BRAY, L.G. and STANNER, R.D., 1976. The chemistry of cave waters. *In* Ford, T.D. and Cullingford, C.H.D. (Eds), *"The science of speleology"*, Academic Press, London, 213-66.

RAUCH, H.W. and WHITE, W.B., 1977. Dissolution kinetics of carbonate rocks: 1. Effects of lithology on dissolution rate. *Water Resour. Res.,* 13, 381-94.

ROSSI, M.G., 1976. Karst et dissolution des calcaires en milieu tropical. *Z. Geomorp., N.F., Suppl. -Bd.*, 26, 124-52.

SIEDELL, A., 1958. *Solubilities of inorganic and metal-organic compounds,* Vol. 1, 4th edn, Norstrand Co. Inc., New York.

SOEPADMO, E. and HO, T.H. (Eds), 1971. *A guide to Batu Caves*. Malayan Nature Soc. and Batu Cave Protection Assoc., Kuala Lumpur.

SPIEGEL, M.R., 1972. *Theory and problems of statistics.* McGraw-Hill, New York.

THRAILKILL, J. and ROBL, T.L., 1981. Carbonate geochemistry of vadose water recharging limestone aquifers. *J. Hydrol.*, 54, 195-208.

TRUDGILL, S.T., 1985. *Limestone geomorphology*. Longman, London.

TRUDGILL, S.T., LAIDLAW, I.M.S. and SMART, P.L., 1980. Soil water residence times and solute uptake on a dolomite bedrock - preliminary results. *Earth Surf. Processes*, 5, 91-100.

WHITE, W.B., 1984. Rate processes: chemical kinetics and karst landform development. *In* LaFleur, R.G. (Ed), *"Groundwater as a geomorphic agent"*, Allen & Unwin, 227-48.

WILLIAMS, P.W. and DOWLING, R.K., 1979. Solution of marble in the karst of the Pikikiruna Range, Northwest Nelson, New Zealand. *Earth Surf. Processes,* 4, 15-36.

WILM, H.G. and STOREY, H.C., 1944. Velocity-head rod calibrated for measuring streamflow. *Civil Engng*, 14, 475-76.

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