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Overseas Geology Series

PROCEDURES FOR THE RAPID ASSESSMENT OF LIMESTONE RESOURCES

D J Harrison[1], S D J Inglethorpe[1], C J Mitchell[1], S J Kemp[1], P Chaodumrong[2] and
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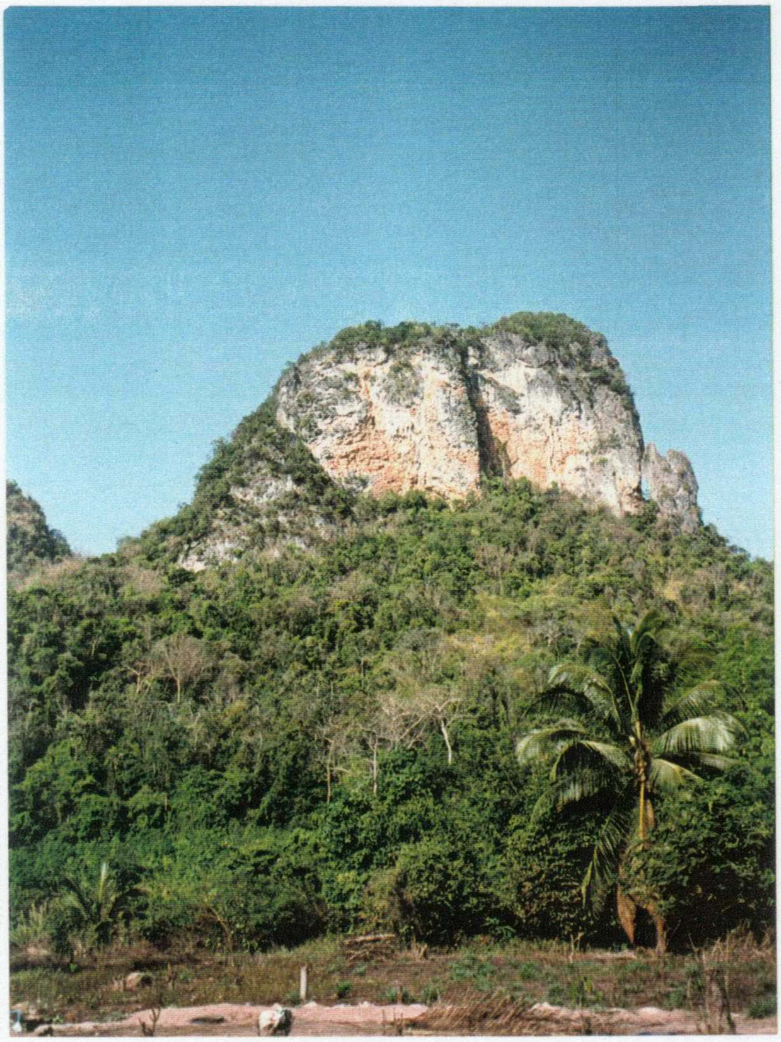

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Responsibilities for production of the report have been as follows:

S D J Inglethorpe	-	Laboratory chemical and mineralogical analysis, Lime burning trials
C J Mitchell	-	Density trials, Brightness determination
S J Kemp	-	Portable Infrared Mineral Analyser (PIMA)
D J Harrison (Project Leader)	-	all other sections

In addition to the named authors, the report draws on the pool of expertise in the Mineralogy and Petrology Group of BGS. In particular, Ellie Evans is thanked for her invaluable laboratory support.

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SUMMARY

Limestone is an extremely valuable raw material and is one of the most versatile of all industrial rocks and minerals. Its main use, however, is in the construction industry, as an essential raw material for cement manufacture, as crushed rock aggregate and also as a source of building and ornamental stone. Limestone is therefore widely extracted, often by poorly-regulated open-pit quarrying in many developing countries. There is an increasing awareness of the environmental impact of limestone quarrying and of the need for geological resource studies to guide strategic mineral planning and development plans. In many developing countries there is often no factual basis to assess either potential total or workable stone resources, nor their quality, to inform the planning process.

The work summarised in this report was carried out under the Department for International Development Technology Development and Research Programme as part of the British Government's programme of aid to the developing countries. The project was formulated to develop and apply cost effective field and laboratory procedures for rapid assessment of limestone resources in developing countries based on appropriate technologies. The project was undertaken in collaboration with the Department of Mineral Resources, Thailand who carried out project field mapping, and assisted in field trials and in the generation of resource assessment data.

An area near Surat Thani in southern Thailand was selected for project fieldwork and this area was geologically surveyed at the 1:50 000 scale applying rapid mapping techniques to identify mappable limestone units (formations) and geological structure. Each formation was sampled for laboratory studies of physical, mechanical and chemical properties.

During the limestone mapping and sampling, field trials were carried out on a range of techniques for determination of dolomite and also for rock strength testing. Density determination, using a sodium polytungstate (heavy liquid) method developed during the project, proved to be a rapid, reliable method for determining dolomite content and was routinely used in the field to rapidly map the main zones of dolomitisation. A portable spectrometer (PIMA) was also investigated for dolomite discrimination and proved to be a potentially useful tool for field reconnaissance. In order to assist field assessments of the aggregate properties of limestones two techniques, the Schmidt hammer and the Point Load Tester, were investigated and the Schmidt hammer was routinely used during fieldwork to estimate rapidly rock strengths.

A further objective of the project was to investigate rapid techniques for laboratory analysis of limestones and dolomites. To achieve this aim the range of available techniques were reviewed and laboratory trials were carried out using several methods for determination of carbonate content. Laboratory techniques for testing aggregate properties, brightness and lime burning were also investigated with the emphasis on the development of simple, rapid procedures.

The field and laboratory data generated during the project have been used to assess the limestone resources of the project's study area in Surat Thani, Thailand and to generate a limestone resource map which categorises the limestone quality in terms of physical and chemical properties.

It is anticipated that the resource assessment methodologies so developed will be applicable to other regions and countries. Overall, the results presented in the report are aimed to be of benefit not only to geologists, but also to planners, environmentalists and engineers.

1. INTRODUCTION

Limestone is an essential raw material for commerce and industry and is widely extracted, often by poorly-regulated open-pit quarrying in many developing countries. If limestone deposits are to be developed wisely there is a need for geological resource studies to provide the framework for land use planning policies to secure supplies of stone of a certain quality, to ensure that scarce resources of high purity limestone are not widely extracted for low grade uses, and to ensure that information is available to allow the resources to be developed in a regulated and sustainable manner. In many developing countries this fundamental resource inventory has not been systematically carried out, partly due to the high costs and lengthy duration of conventional geological and resource surveys.

In order to resolve these problems a project was formulated by the British Geological Survey (BGS) in collaboration with the Department of Mineral Resources (DMR), Thailand, to develop and apply appropriate field and laboratory procedures for rapid assessment of limestone resources in developing countries. The research project commenced in 1995. BGS participation was funded by the United Kingdom's Department for International Development (DFID) under the Technology Development and Research (TDR) Programme project 'Procedures for the rapid assessment of limestone resources' (Project No R6225). Particular emphasis was given to the development of simple, but rapid field and laboratory techniques for determination of dolomite content in limestone, as this is a fundamental constraint on limestones used in cement manufacture. A further project objective was to develop appropriate techniques for the systematic determination of carbonate content, to reduce the requirement for costly detailed chemical analyses. In addition, emphasis was given to the development of appropriate geological surveying strategies and sampling and testing programmes.

The field study area selected for the project was near Surat Thani in southern Thailand and is characterised by isolated steep sided hills of tower karst Ordovician and Permian limestones in a coastal lowland setting. These limestones had not been previously geologically surveyed in any detail but were actively quarried for aggregate and lime production. The area was also under consideration as a source of raw materials for cement production. Certain laboratory work (mainly sample preparation and chemical analysis) was undertaken at DMR laboratories in Bangkok, but most laboratory research and development was done at BGS, Keyworth in the UK. Additional supporting field trials were also undertaken in the UK on areas of Carboniferous limestones in the Peak District and in South Wales, which had previously been well characterised in earlier BGS studies.

This report presents the results of the field and laboratory investigations carried out in Thailand and in the UK between May 1995 and October, 1997, emphasising the methodologies for rapid assessment of limestone resources. It is envisaged that the project's methodologies can be used for addressing similar limestone resource assessment problems elsewhere in the developing world.

2. CLASSIFICATION OF LIMESTONES

2.1 Pure Carbonates

There are several systems developed for the description and classification of carbonate rocks. The two classifications most widely used are those of Folk (1959, 1962) and Dunham (1962). Both of these classifications subdivide limestones according to descriptive and genetic parameters, so knowing the name of a particular limestone gives some idea of how it was formed, its characteristics and likely properties.

Folk (Figure 1) bases his classification on the fact that limestones are composed of three end members - allochems (fossils, oolites, pellets, intraclasts), sparry calcite cement (spar) and fine grained lime mud cement (micrite). The classification is based on the proportion of the allochem components. Folk's classification is useful for investigating past depositional environments, but requires detailed studies of thin sections or peels to differentiate limestone lithologies. For this reason it is not widely used in limestone resource surveys.

Dunham's classification (Figure 2) is based on depositional texture. The fundamental criterion of subdivision is the grain-to-matrix relationship: i.e. whether the grains or the matrix form the supporting framework. The only size distinction is between mud (<0.03 mm) and grains (>0.03 mm). The presence or absence of mud differentiates muddy carbonates from grainstone. The relative abundance of grains allows muddy carbonates to be subdivided into 'mudstone', 'wackestone' and 'packstone', and the presence of signs of binding during deposition characterises 'boundstone'. The degree of packing differentiates 'packstone' from 'wackestone'. The former is composed of grains in close contact with each other, whereas the latter consists of a relatively small amount of grains 'floating' in a mud matrix. Dunham's classification is highly suited for fieldwork as the textural parameters of lithified carbonates can generally be easily recognised by eye or with a hand lens. Unlike Folk's scheme, it does not depend on the almost exclusive use of the petrological microscope to identify the important parameters.

A defect in Dunham's classification, however, is the lack of grain size differentiation; all organically bound limestones are grouped into one term - 'boundstone'. Embry and Klovan (1971) modified Dunham's classification in order to differentiate organically bound (autochthonous) limestones into meaningful categories (Figure 3). A third size division, >2 mm components, has been introduced to recognise 'carbonate conglomerates'. 'Floatstone' and 'mudstone' are terms which describe rocks containing more than 10 percent >2 mm components. The difference between the two types is that in a 'mudstone' the coarse particles form the supporting framework, whereas in a 'floatstone' they 'float' in the fine grained matrix. This classification scheme is useful for carbonate rock bodies which contain organic build-ups, such as reef limestones. The Ratburi Limestone of Thailand is of this type and hence the classification scheme of Embry and Klovan was used to describe the carbonates in the project's field study area.

Figure 1. **Classification of limestones (based on Folk, 1959)**

<table>
<tr><td colspan="5" rowspan="3"></td><td colspan="5">LIMESTONES</td></tr>
<tr><td colspan="2">>10% Allochems
Allochemical Rocks</td><td colspan="3"><10% Allochems
Microcrystalline Rocks</td></tr>
<tr><td>Sparry calcite cement> microcrystalline ooze</td><td>Microcrystalline ooze> sparry calcite cement</td><td colspan="2">1-10% allochems</td><td><1% allochems</td></tr>
<tr><td rowspan="5">Volumetric allochem composition</td><td colspan="4">>25% Intraclasts</td><td>Intrasparite</td><td>Intramicrite (rare)</td><td rowspan="5">Most abundant allochem</td><td>Intraclasts: intraclastic micrite (rare)</td><td rowspan="5">Micrite</td></tr>
<tr><td rowspan="4"><25% intraclasts</td><td colspan="3">>25% oolites</td><td>Oosparite</td><td>Oomicrite (rare)</td><td>Oolites: oolitic micrite (rare)</td></tr>
<tr><td rowspan="3"><25% oolites</td><td rowspan="3">Volume ratio of fossils: pellets</td><td>>3:1</td><td>Biosparite</td><td>Biomicrite</td><td>Fossils: fossiliferous micrite</td></tr>
<tr><td>3:1 to 1:3</td><td>Biopelsparite</td><td>Biopelmicrite</td><td rowspan="2">Pellets: pelletiferous micrite</td></tr>
<tr><td><1:3</td><td>Pelsparite</td><td>Pelmicrite</td></tr>
</table>

Figure 2. **Classification of carbonate rocks according to depositional texture (Dunham, 1962).**

<table>
<tr><td colspan="5">Depositional Texture Recognisable</td><td rowspan="5">Depositional Texture Not recognisable</td></tr>
<tr><td colspan="4">Original components not bound together during deposition</td><td rowspan="4">Original components bound together during deposition</td></tr>
<tr><td colspan="3">Contains mud (clay and fine silt)</td><td rowspan="3">Lacks mud and is grain-supported</td></tr>
<tr><td colspan="2">Mud supported</td><td rowspan="2">Grain-supported</td></tr>
<tr><td>Less than 10% grains</td><td>More than 10% grains</td></tr>
<tr><td>Mudstone</td><td>Wackestone</td><td>Packstone</td><td>Grainstone</td><td>Boundstone</td><td>Crystalline carbonate</td></tr>
</table>

Figure 3. Classification of limestones according to depositional texture (after Embry and Klovan, 1971)

<table>
<tr><td colspan="6">Allochthonous limestones
Original components not organically bound during deposition</td><td colspan="3">Autochthonous limestones
Original components organically bound during deposition</td></tr>
<tr><td colspan="4">Less than 10% >2 mm components</td><td colspan="2">Greater than 10% >2 mm components</td><td rowspan="4">By organisms which act as baffles</td><td rowspan="4">By organisms which encrust and bind</td><td rowspan="4">By organisms which build a rigid framework</td></tr>
<tr><td colspan="3">Contains lime mud (<0.3 mm)</td><td>No lime mud</td><td rowspan="3">Matrix Supported</td><td rowspan="3">>2 mm component supported</td></tr>
<tr><td colspan="2">Mud supported</td><td colspan="2" rowspan="2">Grain supported</td></tr>
<tr><td>Less than 10% grains (>.03mm <2mm)</td><td>Greater than 10% grains</td></tr>
<tr><td>Mudstone</td><td>Wackestone</td><td>Packstone</td><td>Grainstone</td><td>Floatstone</td><td>Rudstone</td><td>Bafflestone</td><td>Bindstone</td><td>Framestone</td></tr>
</table>

A further classification scheme based solely on grain size (Table 1) has been developed by Fookes and Higginbottom (1975). This particle size classification is similar to that used in classifying clastic rocks, and has been adopted for use in engineering practice (British Standards, BS 5930).

In summary, the choice of classification schemes to describe and categorise carbonate rocks will be controlled by the aims and scale of individual investigations. Folk's classification is useful for detailed petrographical study of carbonate facies and depositional environments but for geological and resource mapping investigations Dunham's classification is more practicable. If the carbonate rocks contain reef associations, then it is recommended that Embry and Klovan's scheme is used for geological and resource mapping. Fookes and Higginbottom's simple scheme based on grain size terminology is widely used by engineering geologists, particularly for studies of recent unlithified or weakly lithified carbonates.

Table 1. Classification of limestones based on grain size (after Fookes and Higginbottom, 1975)

Grain size (mm)	Category	Alternative name
>2.00	Calcirudite	coarse grained limestone
0.06 - 2.00	Calcarenite	medium grained limestone
0.002 - 0.06	Calcisiltite	fine grained limestone
<0.002	Calcilutite	argillaceous limestone

2.2 Impure Carbonates

Carbonate rocks may contain mixtures of limestone, dolomite and non-carbonate components, such as quartz and clay minerals. The classification of impure limestones and dolomites according to composition is best demonstrated by the use of triangular diagrams, such as that proposed by Leighton and Pendexter (1962) (Figure 4). A similar classification of clay-bearing carbonate rocks is shown in Table 2. Carbonate rocks can also be subdivided mineralogically on the relative amounts of calcite and dolomite mineral content (Table 3). Such mineralogical terminology is, however, not always accurately or consistently applied; the term 'limestone' for example is often used to include rocks composed of dolomite. Also such classifications, although useful for rock descriptions, are usually not sufficient for industrial purposes which require analysis of chemical composition to indicate the rocks potential.

Table 2. Classification of clay-carbonate rocks (after Fookes and Higginbottom, 1975)

Percent $CaCO_3$

0 5 20 35 65 80 95 100

Pure claystone	Marly claystone	Clayey marlstone	Marlstone	Limey marlstone	Marly limestone	Pure limestone

100 95 80 65 35 20 5 0

Table 3. Classification of calcite-dolomite mixtures

Limestone	>90% calcite,	<10% dolomite
Dolomitic limestone	50-90% calcite,	10-50% dolomite
Calcitic dolomite	10-50% calcite,	50-90% dolomite
Dolomite	<10% calcite,	>90% dolomite

2.3 Classification of limestones for industrial purposes

Limestones can be classified by industrial use (Table 4) and this system can be simplified by user requirement into high purity and non-high purity groups. This classification, although useful for categorising the broad markets of limestone, does not allow categorisation of limestone resources based on specific rock properties.

In order to obtain a broad geological assessment of limestone purity BGS has developed a simple classification of limestone resources based on calcium carbonate content (Table 5). This system is used to establish various grades of limestone purity and has the advantage that the distribution of these grades can then be easily illustrated on resource maps.

Limestones (and other hard rocks) may also be classified in terms of their aggregate properties (Table 6). This classification scheme defines grades of aggregate resource which can be readily demonstrated on resource maps.

Table 4. **Classification of limestone resources based on industrial use (from Harrison and others, 1992)**

		Typical industrial uses	Typical important properties
NON-PURITY	Construction aggregates	roadstone, concrete fill, dimension stone	strength, porosity particle size and shape, freedom from clay, HIGH pyrite etc.
	Cement	concrete, mortars	freedom from MgO
	Low value powders	aglime, asphalt filter, mine dust	easy to pulverise
HIGH PURITY	Lime	steel, chemicals, water purification etc	high CaO content, reactivity
	Chemical reagent	glass, iron, FGD	high carbonate content, restrictions on specific impurities
	Medium value powders	animal feedstuffs, fertilisers, adhesives, rubbers, plastics, putties	particle size, whiteness, freedom from specific impurities
	High value powders	paper, paint	brightness, particle size, low abrasion

Table 5. **Classification of limestone by purity (Cox and others, 1977)**

Category	Percentage $CaCO_3$	Percentage CaO
Very high purity	>98.5	>55.2
High purity	97.0 - 98.5	54.3 - 55.2
Medium purity	93.5 - 97.0	52.4 - 54.3
Low purity	85.0 - 93.5	47.6 - 52.4
Impure	<85.0	<47.6

Table 6. **Classification of aggregates based on their physical and mechanical properties (based on Adlam, 1984, and Harrison, 1993)**

Group	Possible Uses	Description	Typical index test values
1	Road surfacing aggregates. Also suitable for most construction purposes	Durable, strong, low porosity aggregate	PSV >65, AIV <22, LAAV <24, AAV <8, Water Abs <0.8%
2	Base and sub-base roadstone. Concrete aggregate, railway ballast	Strong or moderately strong, durable aggregate. Low porosity	AIV <28, AAV <10, LAAV <30, Water Abs <1%
3	Generally only suitable for road sub-base or constructional fill	Weak aggregate with low durability. Moderate porosity	AIV <35, AAV <14, LAAV <40, Water Abs <3%

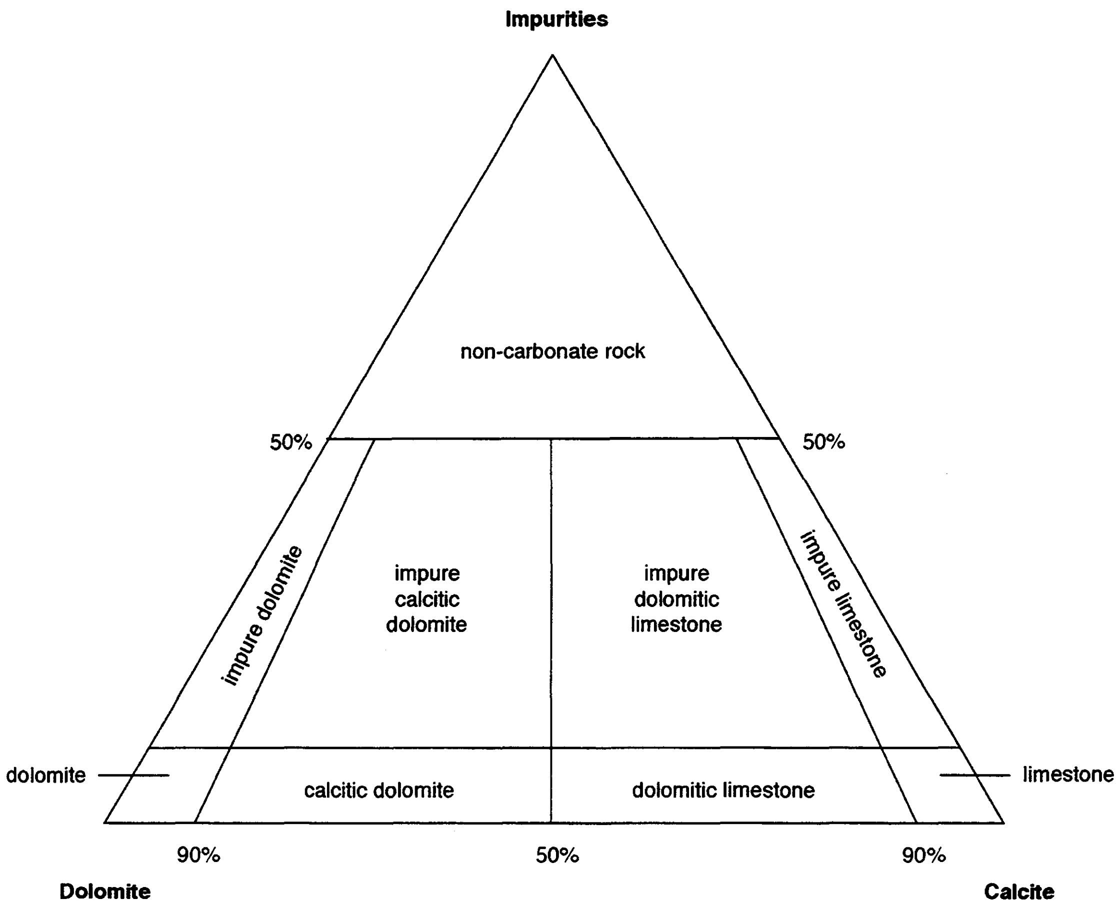


Figure 4 Mineralogical classification of carbonate rocks (after Leighton and Pendexter, 1962)

3. FIELD PROCEDURES

3.1 Geological Mapping

Evaluation of limestone resources is fundamentally based on adequate geological mapping to define the location, size, structure and general composition of the limestone deposits. From it the basic three-dimensional model, later to be refined by sampling or borehole drilling, will be developed. Structure includes the present attitude of the deposit and the extent to which it has been folded and faulted. The degree of fracturing and jointing of the rock is also important as it may affect the behaviour of the stone when quarried. Composition refers to the nature of the rock (eg limestone, dolomite, marble, chalk, carbonatite etc) and the degree of lithological variability which may result in separately mapped rock units (lithofacies, or more formalised formations and members) and the interrelationships of the differing rock types.

The scale of the mapping will vary depending on the degree of detail required. For example, evaluation of limestone prior to expansion of an existing quarry or development of a 'greenfield' site may require mapping at least at the 1:10 000 scale, although larger scale maps may be preferred. Detailed field mapping requires accurate base maps. In many less developed parts of the world large scale maps are not available and it may be necessary to prepare a contoured topographic map prior to geological mapping. Geologists in such areas therefore need to be able to undertake survey work, including the use of surveying techniques involving theodolites, compasses, abney levels and/or satellite-based Global Positioning Systems (GPS). Initial reconnaissance-scale geological mapping, however, can be, and often is, undertaken with the aid of small scale maps with scales between 1:50 000 and 1:250 000. In most countries, topographic base maps are available at these scales. It is recommended that geological mapping for reconnaissance scale limestone resource surveys should be carried out at the 1:50 000 scale, although 1:25 000 scale mapping may be more appropriate for more detailed surveys at the 'indicated' level (McKelvey, 1972) of resource appraisal.

Traditional field mapping aiming to provide a three-dimensional stratigraphical and structural interpretation of the rocks in a region is a time consuming and, in terms of manpower, a relatively expensive process. In order to provide regional geological survey maps for reconnaissance limestone appraisal at modest costs and within reasonable timescales, it is necessary to apply rapid mapping techniques (Wilson, 1989). These techniques differ from those traditionally used in systematic surveys in that they involve a mix of detailed surveying and accelerated phases of mapping to provide the regional coverage.

3.2 Geological Mapping of Limestones in Thailand

Rapid mapping techniques were used in the present project's trial study area in Surat Thani Province, Thailand. Mapping was carried out by staff from the Geological Survey Division, Department of Mineral Resources, Thailand with assistance from BGS project staff. The study area (Figure 5) is characterised by isolated steep sided hills (tower karst) of Ordovician and Permian limestones in a coastal lowland setting. These limestones had not been previously geologically surveyed in any detail but were quarried for aggregates

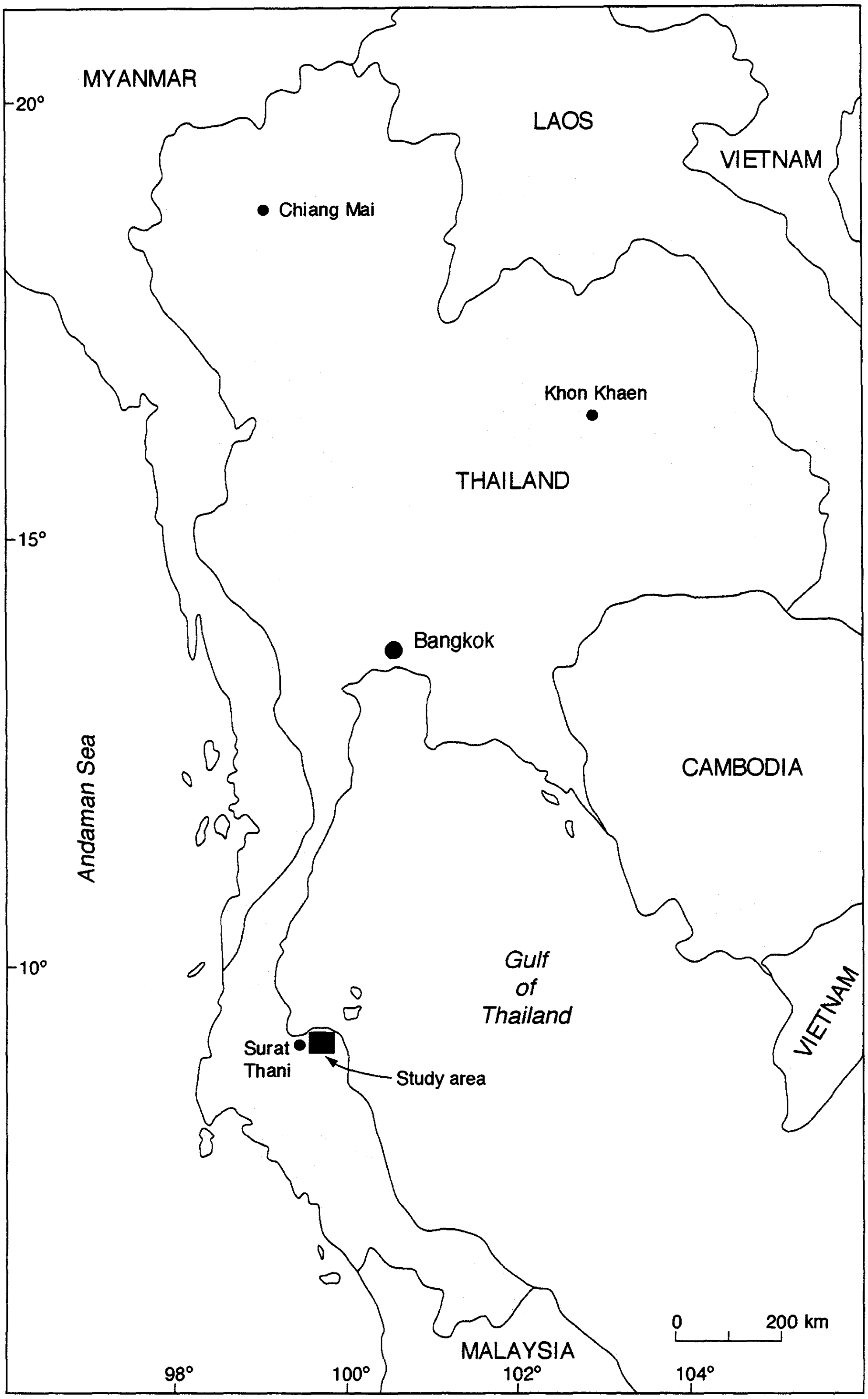


Figure 5 Location of study area, Surat Thani, Thailand

and lime production. The area was also under consideration as a source of raw materials for cement production.

The study area is covered by the Ban Pak Nam Tha Thong 1:50 000 scale topographic Sheet 4927-3. Mapping out the distribution of the limestones and dolomites involved detailed study of selected areas to erect a lithostratigraphy for the region and the application of this scheme to intervening deposits with only limited ground checking. Clearly the selection of areas for detailed study was critical, since these provided the framework upon which the accelerated phase of mapping could advance.

Initial visits to the area determined the broad lithologies of the limestones and established the likely range of carbonate facies present (Table 7). The range of characteristics (colour, bedding, biota, depositional textures, sedimentary structures etc) which define facies can be used to indicate particular sedimentary environments and processes of deposition. This approach has been used (Harrison and others, 1990) to facilitate mapping the distribution of limestones of high chemical purity in parts of the UK. This, however, was based on a wide range of research results. A similar approach to studying the limestone resources of the Surat Thani area in terms of facies models, depositional setting and potential quality could not be undertaken due to insufficient data and a lack of understanding of the detailed regional geology of the limestones and their structure.

The main aim of the limestone exploration in Surat Thani was to assess rapidly those aspects of the geology which are of potential economic importance. A working lithostratigraphy was identified, to be refined as surveying progressed. The sites chosen for detailed study combined good exposure with ease of accessibility. Many of the limestone hills, which rise to over 400 m above the surrounding alluvial plains, form steep sided scarps, surrounded by dense and often impassable thickets. Some of the outcrop could not be reached but traverses were made over almost all of the limestone hills. Binoculars were extremely useful for visually scanning and checking inaccessible outcrops and aerial photographs were also used to aid interpretation of the geology and structure across the area.

The reconnaissance field mapping was undertaken in 1995-97, involving several short periods of field survey totalling about 13 weeks for one, and sometimes two, DMR field geologists, supported by several short (2 week) visits by BGS staff to assist with mapping, sampling and field testing.

The limestones are folded and faulted and dips and strikes are variable, although on an outcrop scale there is little deformation, apart from near-vertical faults which are often obscured by karstic weathering.

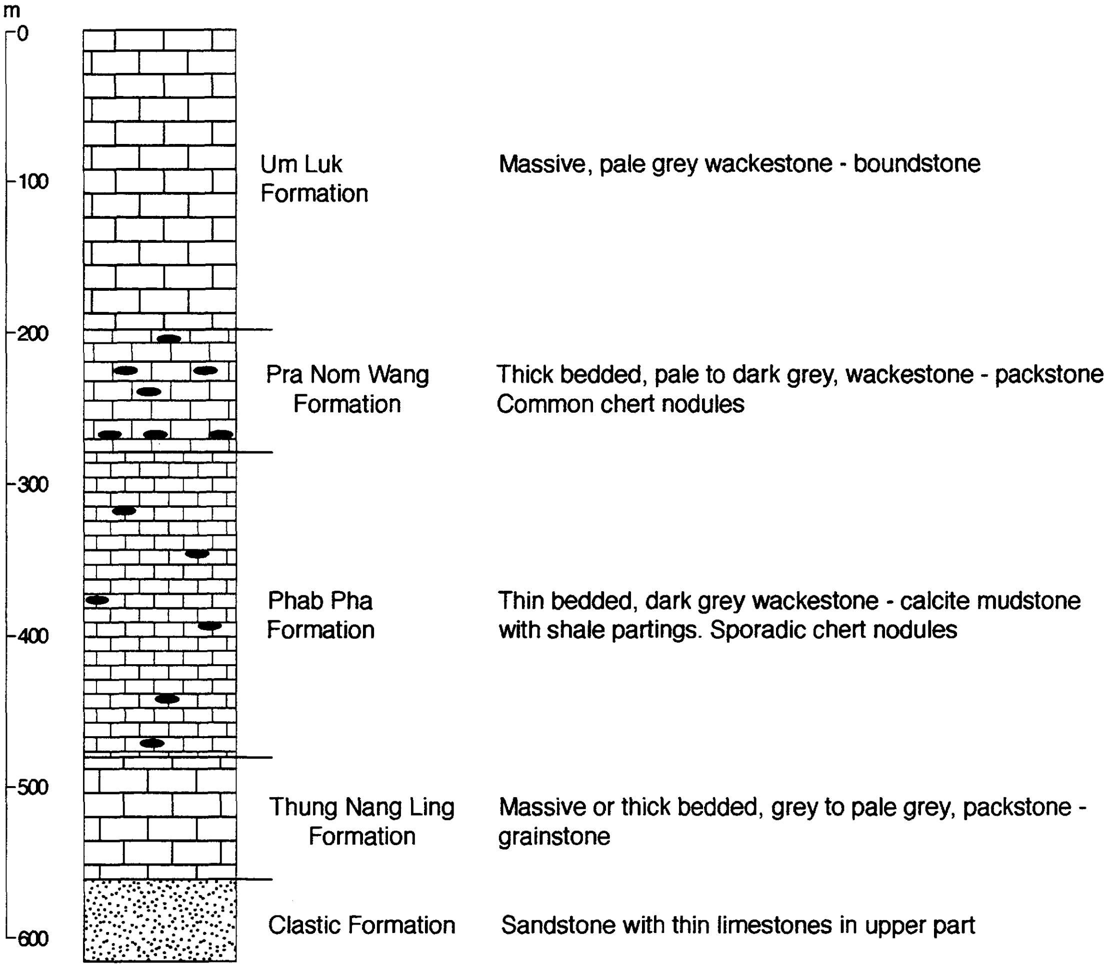
The limestones of the study area are mostly of Permian age (the Ratburi Limestone), although limestones of Ordovician age (the Chong Lot Formation of the Thung Song Group) occur in the east of the area. These two carbonate groups are separated by the SDC Formation consisting of fine grained clastic sediments. The limestones are overlain by Quaternary river and coastal deposits.

The Ratburi Limestone has been subdivided by the Department of Mineral Resources into five formations on the basis of their lithological composition (colour, bed thickness, facies type, presence of chert, dolomite, detrital sediments etc).

Table 7. Common limestone facies in the Ratburi Limestone of Surat Thani area, Thailand

BOUNDSTONE	-	massive or thick bedded, micritic with binding/encrusting elements (bryozoa, sponges, foraminifera, algae, Tubiphytes etc)
	-	form bioherms or patch reefs
	-	high energy environment
RUDSTONE	-	lensoid or planar bedded, grain supported, coarse grained (>10% clasts over 2 mm)
	-	high energy deposits
SKELETAL PACK/GRAINSTONE		
	-	massive, moderate sorting, finer than rudstones
	-	mainly high energy deposits
OOID PACK/GRAINSTONE		well bedded or massive, sometimes cross-bedded, well sorted, little micrite
	-	high energy ('sand shoal') deposits
FOSSILIFEROUS FLOAT/WACKE/MUDSTONE		
	-	thick bedded, organic micrite matrix, large fauna in life position, usually dark grey colour
	-	low energy deposits
UNFOSSILIFEROUS WACKE/MUDSTONE		
	-	thin to thick bedded, rare biota, variable colour
	-	low energy deposits
ALGAL MUDSTONE	-	thin bedded, algal laminated micrite
	-	peritidal environment of deposition
SEDIMENTARY BRECCIAS		
	-	debris flow or rock fall deposits

In ascending order these formations are known as the Clastic Formation, Thung Nang Ling Formation, the Phab Pha Formation, the Phra Nom Wang Formation and the Um Luk Formation (Figure 6). The basal Clastic Formation has a restricted outcrop (Figure 7) and is generally poorly exposed. It is more than 50 m thick and is composed, in the lower part, of medium to thick bedded, fine to medium grained, grey arkosic sandstones which grades to grey sandy mudstone with intercalated limestone in the upper part. The overlying Thung Nang Ling Formation, 80 m thick, comprises grey to pale grey crinoidal packstone and grainstone. It grades upwards into a monotonous sequence, 200 m thick, of thin to well bedded, mainly dark grey wackestones or calcite mudstone with thin shale interbeds. This unit, the Phab Pha Formation, is quarried at several sites for crushed rock aggregates. Chert nodules occur sporadically throughout the formation, but are more common in the overlying Pra Nom Wang Formation which is around 80 m in thickness and consists mainly



Um Luk Formation	Massive, pale grey wackestone - boundstone
Pra Nom Wang Formation	Thick bedded, pale to dark grey, wackestone - packstone Common chert nodules
Phab Pha Formation	Thin bedded, dark grey wackestone - calcite mudstone with shale partings. Sporadic chert nodules
Thung Nang Ling Formation	Massive or thick bedded, grey to pale grey, packstone - grainstone
Clastic Formation	Sandstone with thin limestones in upper part

Figure 6 Lithostratigraphy of the Ratburi Limestone in Surat Thani, Thailand

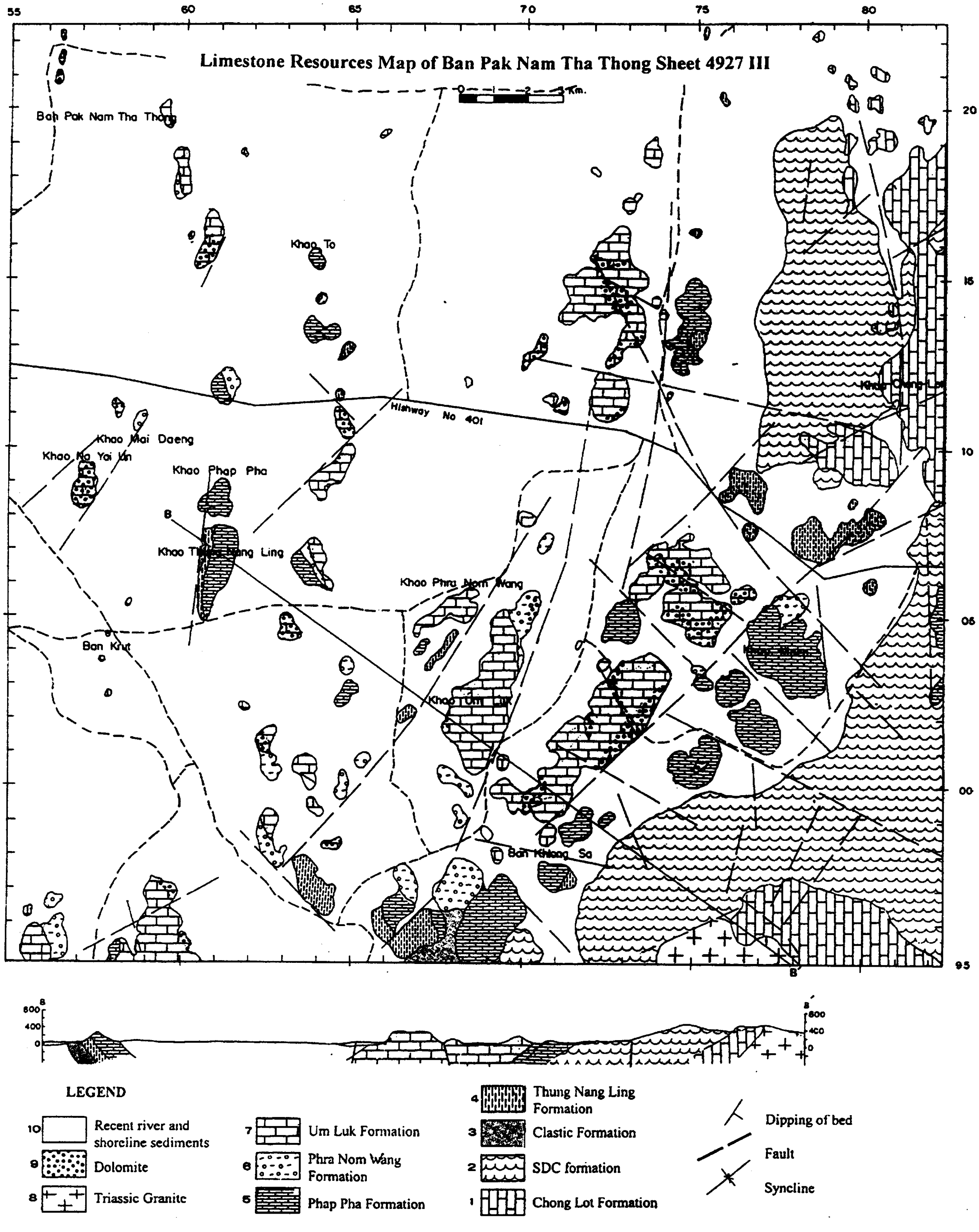


Figure 7. Limestone resources map of Kanchanadit district area, eastern part of Surat Thani province, map sheet Ban Pak Nam Tha Thong (4927 III), scale 1:50,000

of medium to thick bedded, dark grey to pale grey skeletal wackestones and packstones. The uppermost unit, the Um Luk Formation, is over 200 m thick and consists of massively bedded, pale grey wackestone, boundstone, rudstone and grainstone. Dolomite occurs patchily in all formations and is of secondary origin, replacing original limestone. As a result of late Triassic granite intrusion, limestones in some places, particularly in the southeast of the area, have been metamorphosed to marble.

3.3 Sampling

In order to provide an acceptable estimate of the overall properties of a limestone deposit, samples must be representative of the rock and its lithological variability. For a detailed resource survey aiming to assess resources at the 'indicated' level, large numbers of samples obtained from both cored boreholes and rock sections should be obtained (Cox and others, 1977). The boreholes should represent the complete limestone sequence and local facies variations. Exposed rocks can be used to provide supplementary information only, because even the best sections may be incomplete or inaccessible. This approach has been used by BGS in their resource assessments of limestone areas in central England (e.g. Cox and Harrison, 1980, Bridge and Kneebone, 1983) which led to the production of six detailed 1:25 000 scale resource maps. These were later summarised in a single report and 1:50 000 scale resource map (Harrison and Adlam, 1985) which provided a valuable tool for mineral planning in the region, most of which has National Park status. This detailed information on limestone resources was based on systematic geological mapping at the 1:10 000 scale and also on the collection and analysis of large numbers of samples (Table 8). It was therefore a costly and time consuming process.

Table 8. Summary of survey data for assessment of limestone resources of Peak District, UK

Survey area	-	approximately 600 sq km
Duration of survey	-	1972 to 1980
Effort	-	six man team (3 geologists, 3 assistants); totalling approximately 55 years man effort
Sampling	-	110 cored boreholes, totalling >7,000 m of core
	-	over 5,000 lump samples, mostly from measured natural or quarry sections
Logging	-	detailed lithological logging of all boreholes and sections
Testing	-	11,000 determinations of carbonate content
	-	over 1,600 chemical analyses (major and trace elements)
	-	over 1,000 aggregate property tests (mainly strength tests)
	-	around 10,000 brightness determinations
Output	-	six 1:25 000 scale resource maps with assessment reports
	-	one 1:50 000 scale summary resource map with report

A less expensive and more rapid approach is appropriate for reconnaissance survey investigations as carried out in the Surat Thani trial area. Similar reconnaissance studies had previously been carried out by BGS in the UK (Harrison and others, 1990, Harrison and others, 1992) and the experience was utilised to formulate suitable sampling strategies for the project in Thailand. The foundation for the work was the development of a field sampling programme to reliably link the identified lithostratigraphic parameters (from the field mapping) to rock properties. Lump samples were taken to provide material for thin section preparation and for laboratory mineralogical and chemical analysis. Larger samples (up to 20 kg) were also collected for investigation of aggregate properties and for lime burning trials. The sites for sampling were selected to provide maximum stratigraphic coverage and uniform geographic distribution of each formation at the reconnaissance level of appraisal. Most samples were taken from natural exposures, although some were taken in active or recently active quarries. Samples were only taken where the rock appeared to be unweathered or only slightly surface weathered. In total 215 samples were taken for laboratory petrographical/mineralogical/chemical analysis and physical tests, 30 bulk samples were collected for aggregate testing and 5 samples taken for estimation of lime burning properties.

During the limestone sampling and mapping, examinations were made of surface exposures to determine the degree to which key geological factors, other than general lithostratigraphy and structural features of the deposits, may affect resource potential (Table 9). Zones of dolomitisation were mapped out using a range of assessment techniques (as described below) and the relative amounts of chert nodules present in the sequence were estimated from measured sections. The purity (carbonate content) of most limestones is directly related to the amount of chert or clay or both in the rocks. Hence it is important to estimate accurately the amount of chert present as bias easily creeps into sampling of exposures and the sampling of cherty limestones may not be representative. Estimations of chert content can then be used to modify laboratory determinations of limestone purity and other assessment data (e.g. aggregate tests) where chert content may affect resource potential.

Table 9. **Geological factors affecting resource potential of limestones in Surat Thani, Thailand**

1. Degree and distribution of dolomitisation
2. Presence of chert and degree of silicification
3. Presence of caves, swallow holes
4. Presence of clay-filled karstic cavities
5. Staining by groundwater
6. Type and amount of overburden

3.4 Field Testing

Certain geophysical techniques may be applied to field exploration for limestone resources (Mathers, 1993). Electromagnetic, resistivity and ground radar surveys are useful in determining the distribution of poor quality rock or the presence of caverns and infilled solution features in areas designated for quarry development. Down-hole geophysical logging, particularly gamma logging, is useful for pinpointing clays and argillaceous units in limestone sequences and can enhance accurate borehole correlation (Harrison, 1982; Murray, 1983). Geophysical techniques are, however, mainly aimed at detailed site investigations or reserve determinations and are not appropriate for rapid appraisal of limestone resources.

Common problems in limestone assessment (Harrison, 1983) are the identification and quantification of dolomite in limestone sequences and the reliable determination of rock strength in the field to aid appraisal of aggregate quality. In order to address these problems a range of techniques have been investigated, both in the project's study area in Thailand and also in a trial area in the Peak District of Derbyshire, UK.

3.4.1 Rock Strength Testing

Limestones used as aggregates are required to be strong and durable and there are a number of laboratory tests to assess the physical and mechanical properties of roadstone and concreting aggregates (Harrison and Bloodworth, 1994). Such tests, however, require large samples (20-25 kg) which need to be processed to particles of a specified size prior to testing in a range of relatively sophisticated laboratory apparatus. This testing is necessarily expensive, in terms of labour and equipment costs, and is also time-consuming.

Simple determinations of the strength of rocks can be obtained in the field using techniques such as the Schmidt hammer (Deere and Miller, 1966; Al-Jasser and Hawkins, 1990) and the Point Load Tester (Broch and Franklin, 1972). Both techniques were investigated during the project and the Schmidt hammer (Plate 1) was routinely used during the field investigations in Thailand to estimate rock strengths.

The Schmidt hammer is lightweight, highly portable, robust and durable and is relatively cheap. It is simple to operate and a large number of tests can be carried out in a short period of time.

The Schmidt hammer measures the distance of rebound (R) of a controlled impact on a rock surface. Because elastic recovery depends upon the hardness of the surface, and hardness is related to strength, the distance of rebound (R) gives a relative measure of surface hardness or strength. An 'L' type Schmidt hammer was used in this study. It operates by releasing a spring loaded plunger which rebounds from the rock surface moving an index pointer up a scale numbered from 10 to 100, indicating the rebound number, R. This can be converted to unconfined compressive strength, by constructing a correlation curve (Figure 8). Recent research (West, 1994) indicates that aggregate strength properties can be estimated from unconfined compressive strength values (Figure 9), thus allowing aggregate properties to be inferred from Schmidt hammer values.

The relationship between Schmidt hammer values and Aggregate Impact Values from limestones tested in this project, as shown in Figure 10, reveals a relatively high degree of correlation, suggesting that the Schmidt hammer can be used to predict aggregate strength values. The accuracy and reproducibility of Schmidt hammer results are, however, affected by a wide range of factors (surface texture, mineralogy, porosity, fracturing, weathering etc), and test procedures (Appendix B) must be followed closely to obtain meaningful results.

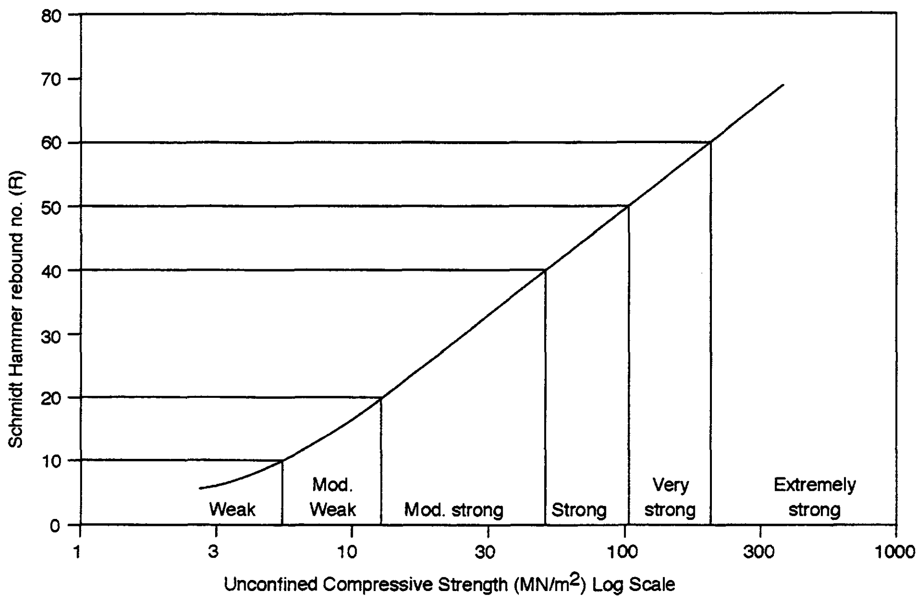


Figure 8 Correlation curve for Schmidt hammer used with Carboniferous rocks (after Carter and Mills, 1976)

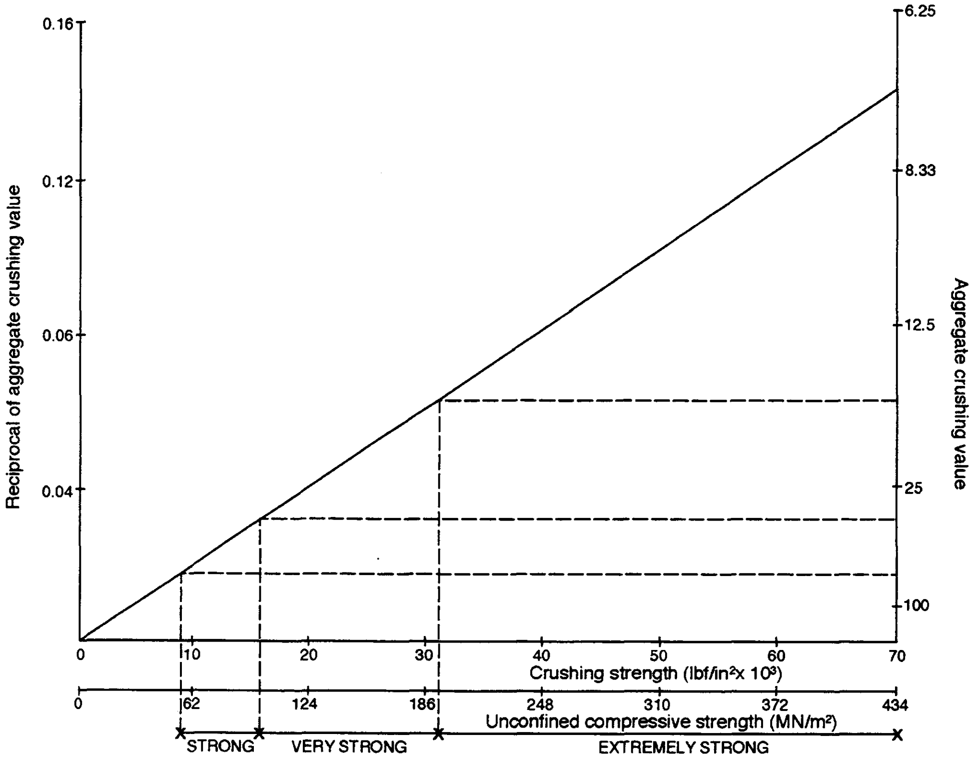


Figure 9 Chart for deriving aggregate crushing value from unconfined compressive strength (after West, 1994).

Schmidt hammer values were obtained at around 100 sites in the Surat Thani field area. In most cases the results (Appendix A) indicated that the rocks are of relatively high strength (R values of 50 to 60) but that there was little variation in strength between the various lithofacies. The testing experience, both in the UK and in Thailand, showed that the technique is insensitive to small changes in rock strength and also that the technique is not suitable for relatively soft or weak rocks. The test may therefore be unsuitable for classifying or zoning carbonate rock strengths in the field, particularly as the results are strongly influenced by variations in testing technique. Provided field testing procedures are carefully carried out, the Schmidt hammer can, nevertheless, be used to allow speedy and cost effective aggregate resource assessments.

A second method for determining rock strength in the field is the point load test which enables measurements to be made of the crushing strength of hand specimens or rock cores. The specimen, about 5 cm in size, is loaded to failure in the apparatus, using a hand-operated hydraulic pump. The hydraulic load at failure is recorded on a pressure gauge. The point load strength index (Is) is calculated by dividing the force at failure by the square of the distance between the loading points on the apparatus. The strength index gives a measure of tensile rock strengths and can be used to predict (Franklin and others, 1971) uniaxial compressive strengths.

The point load test is quick and simple to operate, but is is bulky and heavy and is not practicable to carry very far by hand. It could, however, be easily transported by vehicle to a convenient field testing station.

The point load method was applied to samples of Carboniferous Limestone from the Peak District in Derbyshire, England and also from South Wales (Table 10) whose aggregate properties had previously been thoroughly investigated (Harrison and Adlam, 1985). The results, however, showed that this method is generally insensitive to lithological variations and the test values have low reproducibility. This agrees with previous investigations (Harrison, 1983) using the point load tester in appraisals of sandstone, limestone and dolomite resources in several parts of the UK. Point load results are strongly affected by anisotropy (fractures and other planes of weakness) in the rock and also by moisture content (strength reduces with increasing water content). Testing must therefore be carried out using carefully controlled procedures (Anon, 1985).

The point load test is not considered sufficiently practical or reliable to be used as a field test for classifying the variability in the strengths of limestones and dolomites for resource mapping applications. It may, however, be suitable for supporting a laboratory-based aggregate resource assessment programme.

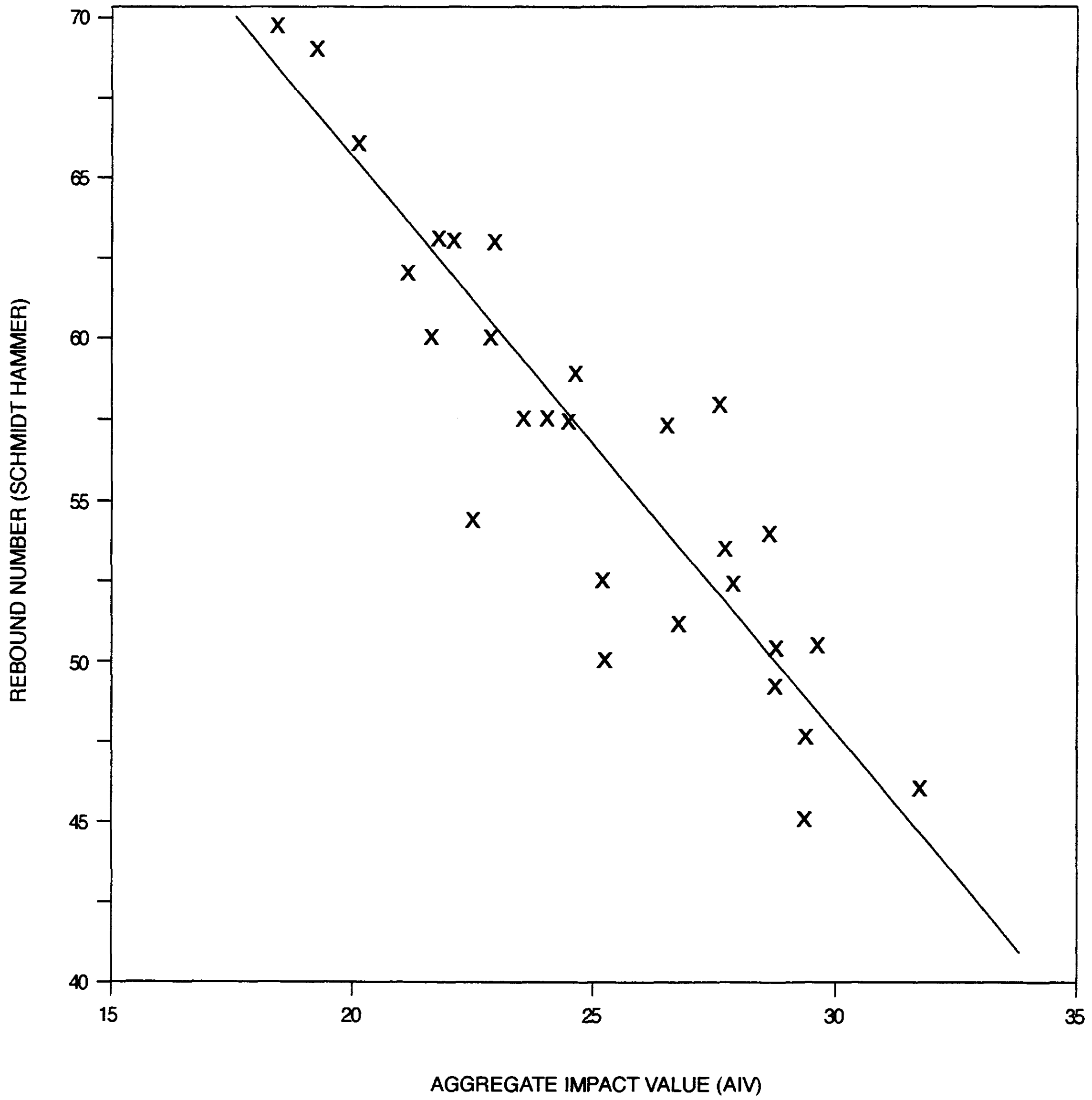


Figure 10 Relationship between Aggregate Impact Values and Schmidt hammer values from selected limestones and dolomites in the UK and Thailand

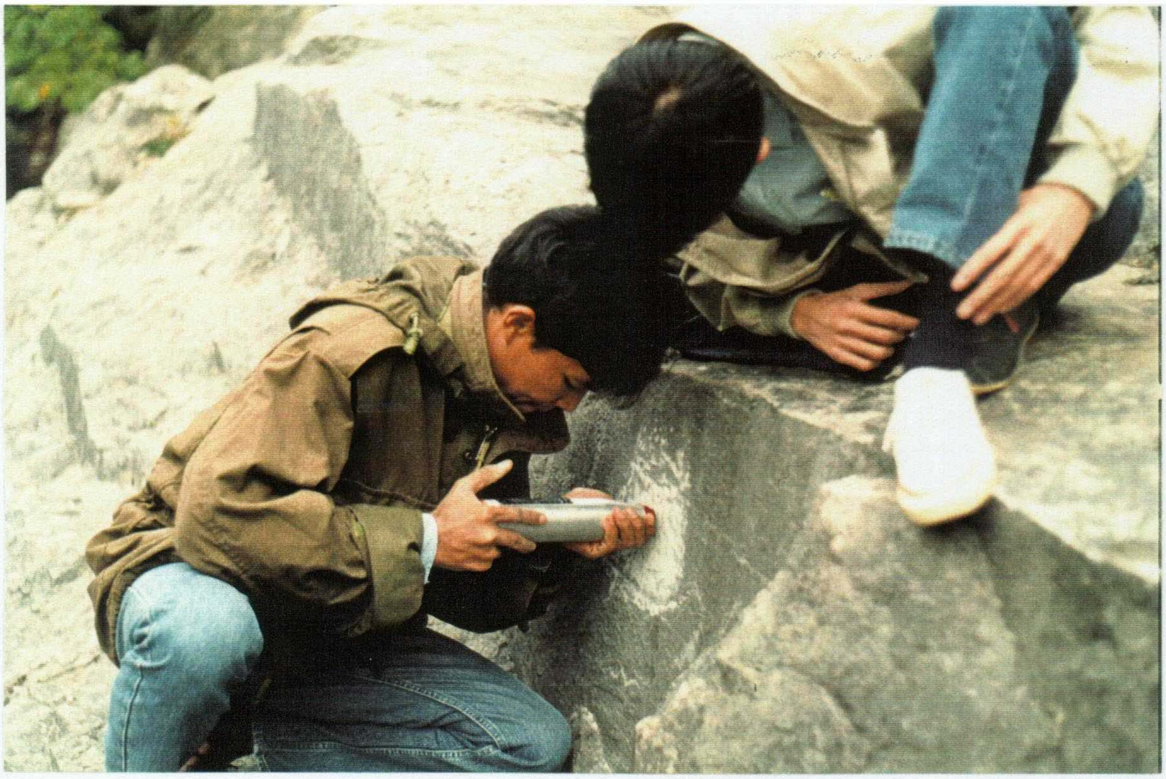


Plate 1. Field testing rock strength using the Schmidt hammer

Plate 2. Laboratory determination of the aggregate impact value

Table 10. Field and laboratory strength test results from carbonate rocks of Carboniferous age in the UK

		Field Tests		Laboratory Test
Formation	Rock Type	Schmidt hammer Rebound No (R)	Point load strength index (Is)	AIV
Derbyshire Limestones:				
Eyam Limestones	Knoll reef facies	51	4.55	29
Monsal Dale Limestone	Packstone	54	5.25	22
“	“	53	-	27
“	Dark, calcite mudstone	63	5.51	22
“	“	60	5.39	21
Bee Low Limestones	Packstone	50	-	28
“	“	46	4.52	31
“	“	50	5.57	25
“	Dolomite	44	3.16	28
Woo Dale Limestones	Grainstone	52	4.24	25
“	Packstone	52	-	22
“	Grainstone	49	4.31	28
“	Packstone	51	-	26
“	Calcite mudstone	63	6.37	22
“	“	57	-	23
“	Dolomitic limestone	47	4.11	29
South Wales Limestones				
Main Limestone	Grainstone	54	-	20
“	Grainstone	63	-	21
“	“	60	-	22
“	Dolomitic limestone	58	4.62	27
“	“	55	5.42	22
“	Dolomite, fine grained	65	5.44	20
“	“	70	6.45	19
“	“	70	6.54	18
“	Dolomite, fine grained	61	6.00	21
“	Dolomite, coarse grained	60	-	31

3.4.2 Determination of Dolomite

In many carbonate sequences it is not always easy in the field to reliably determine the presence of dolomite and it is even more difficult to estimate the relative proportions of dolomite and limestone. In many cases dolomite cannot be easily distinguished by crystal or textural form, particularly if the rock is fine grained. Also, colour is not always a diagnostic feature. It is, however, important for cement resource prospecting for a field geologist to be able to reliably identify the presence of dolomite and to be able to easily establish the likely proportion of dolomite in the rock.

Table 11 shows certain features which are diagnostic of some dolomites and dolomitised limestones. These characteristics, however, are not always recognisable, although with knowledge of local outcrops an experienced field geologist can usually distinguish dolomite from limestone in a mixed carbonate sequence. Lithology is not always, however, a diagnostic feature and it is particularly difficult to accurately predict the relative proportion of dolomite in the rock solely from field observations.

Table 11. Field identification of dolomite

Surface texture	- sugary, crystalline appearance, porous, elephant-skin[1]
Fabric	- lack of identifiable fossils or sedimentary features
Reaction with acid	- lack of effervescence (see Table 12)
Colour	- brown, yellowish brown or mottled purplish pink
Hardness	- may be either softer or harder than associated limestones
Smell	- sometimes bituminous/earthy smell when broken
Topography	- often subdued, rounded

[1] 'Elephant-skin texture' is a typical feature of Permian dolomites in Thailand. These dolomites are mostly fine grained and are fractured with a network of fine calcite veinlets. Tropical weathering results in a surface texture of deeply weathered veinlets in a rock of strong, positive relief, creating the characteristic 'elephant-skin' texture.

There are a number of techniques available to assist the exploration geologist in the determination of dolomite in the field. Limestone chippings can be distinguished from dolomite fragments by use of an acid reaction test (Table 12), although the relative proportion of calcite and dolomite cannot be accurately estimated. This method is also temperature dependant and is only effective in cool, temperate climates (this is because dolomite will react more vigorously with increased temperatures).

Table 12. Determination of carbonate types with acid (after Burnett and Epps, 1979)

Rock type	**Reaction of rock chips with cold, dilute HCl**
Limestone	Violent effervescence
Dolomitic limestone	Brisk, quiet effervescence
Calcite dolomite	Mild emission of CO_2 bubbles
Dolomite	No effervescence, slow formation of CO_2 beads on rock surface

Carbonate staining

Staining of limestone to determine carbonate mineralogy is a well established petrographic technique (see also 4.2), but can also be used at the exploration stage. One of the most popular stains for carbonates uses a combined solution of potassium ferricyanide and alizarin red S in 0.5% HCL. This is a valuable dual staining method that allows differentiation between dolomite, ferroan dolomite, ferroan calcite and calcite (Table 13). However, this method is purely qualitative, it can not give an indication of the relative amount of dolomite mineral present in the carbonate. A further selective staining method useful for calcite-dolomite differentiation, involves immersion of rock chips in solutions of ferric chloride and ammonium sulphide. The degree of colouration has been used to give an indication of MgO content (Table 14). This method is useful for field determination of dolomite content although the subjective categorisation of colour and its inherent inaccuracies limits the usefulness of this technique.

Table 13. Determination of calcite and dolomite by staining techniques

Method	Staining solution	Result
Dickson (1966)	Potassium ferricyanide and alizarin red S	Calcite - pink Dolomite - colourless Ferroan dolomite - turquoise
Keller and Moore (1937)	Ferric chloride and ammonium sulphide	Calcite - black Dolomite - colourless

Table 14. Staining carbonate chippings for calcite-dolomite differentiation (after Keller and Moore, 1937)

Colour index	Degree of colouration	Estimated MgO content
1	Black	<2%
2	White specks on black background	2 to 5%
3	White patches on black background	5 to 8%
4	Black and white patches	8 to 10%
5	Black patches on white background	10 to 15%
6	Black specks on white background	15 to 20%
7	White	>20%

Density determination

The principal component of limestone, calcite, has a density of 2.71 g/cm^3 whereas the main component of dolomite, the mineral dolomite, has a density of 2.85 g/cm^3. Discrimination would be simple if all limestone consisted of 100% calcite and all dolomite 100% dolomite mineral. However this is not the case and a complete spectrum exists from limestone, through dolomitic limestone and calcitic dolomite, to dolomite. Therefore any density testing needs to be sensitive enough to respond to small differences in the specific gravity between carbonate samples. Other factors provide complications, mainly the presence of non-carbonate mineral impurities (such as quartz and/or pyrite) and porosity / fracturing. These may increase or decrease the density of the carbonate.

Two methods for density determination were investigated during the project:

Plate 3. Determination of limestone density in the field using the heavy liquid method

Plate 4. Field station for limestone density trials

a) Pycnometer method
The weight and volume of a small sample of powdered carbonate can be determined using a pycnometer bottle and from this the specific gravity can be determined. The field method considered is given in Appendix B.

This method gives a very accurate measurement of specific gravity, avoiding the influence of porosity / fracturing (as the sample is ground). However, this method requires the use of a pestle & mortar and a portable digital balance. This makes the test less 'field work' friendly.

b) Sodium polytungstate (heavy liquid) method
Sodium polytungstate ($3Na_2WO_4.9WO_3.H_2O$) is a non-toxic, recyclable, water soluble inorganic salt, that is stable in a pH range of 2 to 14. It is a safe alternative to the toxic organic liquids (such as bromoform and di-iodomethane) used for heavy media separations. When mixed with deionised, water sodium polytungstate forms a stable solution. The density of this solution depends upon the amount of powder dissolved in water, within the range 1 to 3.1 g/cm^3.

The field method for limestone : dolomite discrimination is given in Appendix B.

The sodium polytungstate density method is the preferred limestone : dolomite discrimination test. The pycnometer density method gives a very accurate measurement of specific gravity. However the amount of equipment required makes it impractical to perform in the field. The sodium polytungstate method can rapidly (6 - 7 minutes per sample during field trials) give an indication of the proportion of dolomite mineral (>65%, >30%, <30% or <10%) present in a carbonate rock sample (Table 15).

Table 15. Classification of dolomite content according to sample density

Density	**Dolomite mineral content**		**MgO content**
(g/cm^3)	**Classification**	**Wt %**	**Wt %**
> 2.8 - 2.85	High	> 65%	> 14.2%
2.75 - 2.8 to 2.8 - 2.85	Moderately high	> 30%	> 6.6%
2.7 - 2.75 to 2.75 - 2.8	Moderately low	< 30%	< 6.6%
< 2.7 - 2.75	Low	< 10%	< 2.2%

Field trials of the sodium polytungstate density method have been carried out in the UK in the Peak District of Derbyshire and also in South Wales, both areas of Lower Carboniferous limestone (lithologically very similar to the Permian limestone in Thailand). These trials were successful in discriminating between limestone and dolomite. Trials (field and laboratory) were also carried out on samples of the Ratburi Limestone (Permian) from Surat Thani, Thailand (Plates 3 and 4). The results were confirmed by determination of dolomite mineral and calcite content by thermogravimetric analysis (TGA) (Table 16).

This method is effective in confirming the identification of limestone and dolomite in the field, and also in providing an objective basis for screening samples for laboratory analysis. During a lengthy field programme this would save time, rapidly identifying areas of high purity limestone and enabling follow-up work to be carried out almost immediately (without the delay of despatching samples back to the laboratory and waiting for the results of the analyses).

Table 16 Summary of density trials carried out on Ratburi Limestone, Thailand

Sample		Density testing		Thermogravimetric analyses	
BST (BGS)	SR (DMR)	Field Dolomite content Wt %	Laboratory Dolomite content Wt %	Dolomite content Wt %	Calcite content Wt %
1	1	nd	>65	94 #	6 #
2	2	nd	<30	nd	nd
3	3	nd	>65	nd	nd
4	4	nd	>30	97 #	3 #
5	5	nd	>30	nd	nd
6	6	nd	<30	5 #	94 #
7	21	nd	<30	-	89
*8	22	nd	>30	28	57
9	23-1	nd	<30	-	85
10	23-3	nd	<30	8	92
11	23-4	nd	<30	-	98
12	23-5	nd	<30	-	94
13	23-6	nd	<30	-	98
14	23-7	nd	>65	89	12
15	23-8	nd	>65	90	9
16	23-9	nd	<30	2	100
17	23-10	nd	<30	2	99
18	23-11	nd	<30	2	99
19	23-12	nd	<30	2	96
20	23-13	nd	<30	-	101
21	23-14	nd	<30	-	100
22	No sample				
23	25	< 10	<30	-	79
24	29	< 10	<30	2	97
25	28	>30	>65	95	5
26	30-1	< 10	<30	-	100
27	30-2	< 10	<30	-	98
28	26	< 10	<30	-	98
29	31	>30	>65	91	10
30	27	< 10	<30	2	99
31	32	>30	>65	91	12
32	33	>65	>65	87	12
33	34	>30	>65	89	13
34	35	< 10	<30	2	98
35	36	< 10	<30	8	91
36	37	>65	>65	88	7
37	38	>30	>65	88	12
38	39	>30	>65	90	6
39	40	nd	<10	-	90
40	41	nd	<30	2	100

N.B. nd = not determined; * = non-conformity between lab-derived density & TGA;
= calcite & dolomite contents calculated from DMR AAS data

Table 16 continued

Sample		Density testing		Thermogravimetric analyses	
BST (BGS)	SR (DMR)	Field Dolomite content Wt %	Laboratory Wt %	Dolomite content Wt %	Calcite content Wt %
41	48	nd	<10	-	82
42	49	nd	<30	-	92
43	87	nd	<30	-	92
44	88-1	nd	>65	82	16
45	88-2	nd	>65	91	8
46	80-1	nd	<30	5	92
47	80-2	nd	<30	14	80
48	80-3	nd	<30	2	96
49	80-4	nd	<30	-	99
50	74	nd	<30	-	97
51	75-1	nd	<30	-	101
52	75-2	nd	<30	2 #	96 #
53	61	nd	<30	8	91
54	58 / 94	nd	<30	4	94
55	53-1	nd	>65	90	7
56	53-2	nd	>65	92	8
57	52	nd	<30	19	75
58	82	nd	<30	-	88
59	80-1	<30	<30	-	99
60	80-2	<10	<30	-	93
61	80-3	>30	<30	5	97
62	80-4	>30	<30	2	99
63	?	<30	<30	2	99
64	?	>30	<30	-	99
65	100-1	<10	>30	91	9
66	100-2	>65	>65	89	9
67	100-3	>65	>65	94	6
68	101-1	>30	<30	-	102
69	101-2	>30	<30	-	102
70	102-1	>30	>30	74	28
*†71	102-2	<10	<30	36	66
†72	103-1	>30	<30	-	81
†73	103-2	>30	<30	-	99
74	105-1	>65	>65	87	12
75	105-2	<30	<30	6	96
76	106-2	<30	<30	1	101
77	106-2	>65	>65	93	9
†78	107	>30	<30	-	102
79	109	>65	>65	89	10
80	110	>65	>30	86	5

N.B. nd = not determined, * = non-conformity between lab-derived density & TGA; † = non-conformity between field-derived density & TGA; # = calcite & dolomite contents calculated from DMR AAS data

Table 16 continued

Sample		**Density testing**		**Thermogravimetric analyses**	
BST (BGS)	**SR** (DMR)	**Field**	**Laboratory**	Dolomite content	Calcite content
		Dolomite content			
		Wt %	Wt %	Wt %	Wt %
81	**111-1**	<30	<30	-	100
82	**111-2**	<30	<30	nd	nd
†83	**112-1**	>30	<30	2	100
†84	**112-2**	>30	<30	-	102
85	**114**	>65	>65	77	25
†86	**116**	>30	<30	-	102
87	**117**	>65	>65	94	7
88	**118-1**	>65	>65	91	9
89	**118-2**	>65	>65	96	7
90	**120**	>65	>65	97	5
91	**122**	>65	>65	89	11
92	**123**	>65	>65	91	9
93	**124**	>65	>65	84	9
94	**125**	>65	>65	88	10

N.B. nd = not determined; † = non-conformity between field-derived density & TGA

Portable Infrared Mineral Analyser (PIMA)

The PIMA is a compact, handheld spectrometer that provides the field geologist with a new analytical tool for the identification of rocks, minerals and soils. The manufacturers claim that it is capable of providing rapid, "laboratory" class, cost-effective detection of minerals containing OH, H_2O, CO_3 and NH_4 groups such as phyllosilicates, hydroxylated silicates, hydrated sulphates and carbonates. It has been principally used by exploration and mining geologists in Australia, Africa and the USA to assess alteration systems and to target mineralisation.

The PIMA measures the reflected radiation from the surface of rocks and minerals in the short wavelength infrared (SWIR), from 1300-2500 nm. Such a range allows mineral identification due to unique spectral signatures.

When a rock sample is illuminated by the light source of the PIMA, certain wavelengths of light are absorbed by its component minerals as a result of sub-molecular vibrations. This vibration is the result of bending and stretching of molecular bonds in the minerals. The majority of the absorption features in the PIMA wavelength region are related to the bending and stretching of the bonds in hydroxyl (OH), water (H_2O), carbonate (CO_3) and ammonia (NH_4).

The molecular absorption features occur in characteristic wavelength bands e.g. carbonate minerals have a major feature between c.2300 and 2350 nm with minor features at 1870 nm, 1990 nm and 2155 nm. Within these bands, different carbonate minerals produce features with slightly different wavelengths e.g. the principal absorption feature for calcite is at c.2340 nm whereas that for dolomite is at c.2320 nm.

Theoretically, therefore, it should be possible to identify and distinguish different carbonate species. Similarly, by accurate measurement of the position of the main carbonate absorption feature, it should be possible to give an indication of the relative proportions of two carbonate minerals (e.g. calcite and dolomite) present in a limestone.

The PIMA's ability to produce non-destructive surficial measurements in a c.2 minute analytical time would therefore appear to offer an ideal analytical tool for the rapid mineralogical assessment of limestones. The PIMA's portability also allows direct field-measurement on outcrop and comparison with cores or powder samples in the laboratory.

The results of PIMA analysis of selected Thai limestone samples are shown in Table 17 together with results obtained from other analytical techniques. Figures 11 and 12 show cross-plots of % calcite and % dolomite determined by the PIMA compared to atomic absorption spectrometry (AAS), X-ray diffraction (XRD) and thermogravimetry (TG)-determined values.

Analysis of laboratory synthetic standards and the well-characterised Thai limestone samples has proved that the PIMA is capable of detecting and identifying different carbonate minerals. The good correlation between the position of the 2330 nm carbonate absorption feature and the % different carbonate species in calcite/dolomite mixtures indicates that the PIMA is also capable of giving an accurate indication of % calcite and % dolomite in limestones predominantly formed of these minerals.

Comparison of PIMA-derived % calcite and % dolomite concentrations for the Thai limestones with other typical limestone analytical techniques reveals a strong positive correlation in all cases (Figures 11 and 12).

The strongest correlations are produced for the thermogravimetric analyses (calcite, r^2 = 0.942 and dolomite, r^2 =0.964). Particularly good correlations are achieved for the samples containing relatively high levels of dolomite and little calcite. Where high levels of calcite were determined by TG with no apparent dolomite detected, lower calcite contents with some dolomite are typically predicted by the PIMA. This is due to the normalisation of the PIMA data to 100% carbonate.

r^2 values of 0.883 (calcite) and 0.961 (dolomite) for correlation between the PIMA and AAS analyses again suggest strong correlations between the two analytical techniques. As with the TG analyses, the best agreements tend to be for the samples containing high levels of dolomite. The PIMA overestimates dolomite where AAS detects only low levels to be present.

Correlation between PIMA and XRD analyses is also good (calcite, r^2 =0.846 and dolomite, r^2 =0.939). The PIMA produces more realistic (i.e. <100%) values than those produced by XRD for high dolomite concentrations. Mixtures of calcite and dolomite produce very similar results from both techniques e.g. 90:10 and 10:90 calcite:dolomite. Again, the normalisation of the PIMA data produces errors where only one species was detected by XRD.

In conclusion, the PIMA appears to provide an extremely useful tool for the mineralogical assessment of limestone resources. Its rapid, non-destructive determination of carbonate mineralogy and concentration and field-portability make it an ideal tool for resource-assessment. Its greatest value is probably to provide a first step reconnaissance during field-appraisal, after which samples can be more accurately selected for further analytical work.

Table 17. Summary of Thai limestone analytical data

Sample	Simplified lithology	PIMA			TGA		Acid insoluble residue		AAS		Wet chemistry			XRD	
		µ 2330 (nm)	Calcite (%)	Dolomite (%)	Calcite (%)	Dolomite (%)	(%)	Mineralogy	Calcite (%)	Dolomite (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	Calcite (%)	Dolomite (%)
BST 9	Packst./wackest.	2338.51	100.71	-0.71	85.3	0.0	12.76	Qtz	90.8	6.0	1.27	0.12	0.25	75.3	2.7
BST 10	Wackest.	2336.87	86.96	13.04	91.5	7.1	7.07	Qtz	50.2	16.9	30.48	1.44	0.83	90.0	13.3
BST 11	Wackest.	2337.58	92.49	7.51	97.6	0.0	3.70	Qtz, kaol, mica	92.3	2.0	4.56	0.24	0.13	96.9	ND
BST 12	Wackest.	2337.67	93.24	6.76	93.0	0.0	6.72	Qtz, ?kaol, ?mica	77.6	1.7	18.07	1.81	0.23	80.3	ND
BST 13	Wackest.	2337.62	92.82	7.18	97.8	0.0	3.89	Qtz	93.8	2.4	3.70	0.09	0.11	82.5	ND
BST 14	Dolomite	2320.53	15.53	84.47	12.6	90.5	0.96	Qtz, kaol, mica	26.4	69.6	1.18	0.09	0.24	18.9	118.5
BST 15	Dolomite	2319.91	10.39	89.61	9.1	90.5	3.67	Qtz						12.0	111.7
BST 16	Grainst.	2336.75	86.09	13.91	101.8	0.0	0.05	Mica	96.9	1.3	0.13		0.03	99.9	ND
BST 17	Grainst.	2336.58	84.87	15.13	100.3	0.0	0.04	Mica	97.0	0.9	0.19	0.01	0.04	78.5	ND
BST 18	Algal mudst.	2336.35	83.28	16.72	100.6	0.0	0.04	ND	96.7	0.9	0.07	0.01	0.02	96.6	ND
BST 19	Algal mudst.	2335.81	79.78	20.22	97.6	0.0	0.10	Mica	95.8	1.2	0.01	0.01	0.03	81.9	1.7
BST 20	Packst.	2336.23	82.48	17.52	101.0	0.0	0.06	?Kaol, ?mica, ?qtz	96.8	0.9	0.13	0.01	0.04	81.1	ND
BST 21	Algal packst.	2336.41	83.69	16.31	99.2	0.0	0.89	Qtz, mica, kaol, ?smec	97.9	0.8	0.01	0.01	0.03	93.4	ND
BST 23	Wackest.	2336.28	82.81	17.19	78.2	0.0	21.69	ND	76.0	2.1	18.93	0.42	0.45	53.0	ND
BST 24	Wackest./packst.	2336.03	81.17	18.83	98.9	0.0	0.89	Mica	0.0	0.0				68.4	ND
BST 25	Dolomite	2318.01	-8.66	108.66	6.4	92.6	2.51	ND	16.6	82.6	0.49	0.02	0.06	1.3	118.2
BST 26	Ca mudst.	2336.01	81.04	18.96	77.1	0.0	1.47	Qtz, kaol, mica	94.5	3.5	1.22	0.18	0.12	84.6	1.0
BST 27	Ca mudst.	2336.07	81.43	18.57	98.4	0.0	3.36	Qtz, kaol, mica	0.0	0.0				77.1	0.4
BST 28	Wackest.	2335.95	80.66	19.34	98.4	0.0	2.47	Qtz, kaol, mica	91.7	2.4	6.03	0.19	0.12		
BST 29	Dolomite	2319.25	4.36	95.64	9.8	90.5	0.49	Mica, kaol	9.5	89.6	0.14	0.11	0.11	8.8	98.7
BST 30	Wackest./Ca mudst.	2336.11	81.69	18.31	98.8	1.7	0.15	Kaol, ?mica	95.6	1.4	1.82	0.17	0.05	75.3	0.4
BST 31	Dolomite (grainst.)	2318.12	-7.41	107.41	10.9	91.6	2.49	ND	0.0	0.0				6.8	85.6
BST 32	Dolomite	2317.59	-13.62	113.62	11.7	86.9		?Kaol, ?mica	7.0	92.2	0.10	0.04	0.06		
BST 33	Dolomite	2319.94	10.65	89.35	12.5	89.0	11.18	Kaol, mica	0.0	0.0				11.6	85.0
BST 34	Packst.	2337.94	95.54	4.46	97.6	2.1	1.14	Qtz, kaol, mica	94.6	3.6	0.92	0.17	0.15	89.3	0.4
BST 35	Packst.	2337.08	88.53	11.47	91.3	7.3	1.85	Qtz, kaol	97.3	1.6	0.02	0.03	0.05	73.4	6.6
BST 36	Dolomite	2318.78	-0.30	100.30	7.3	88.8	1.88	?Qtz	5.4	94.0	0.08	0.03	0.08	1.8	133.6
BST 37	Dolomite	2318.70	-1.13	101.13	11.6	87.6	0.14	Kaol, mica	6.6	92.6	0.08	0.10	0.06	9.3	119.0
BST 38	Dolomite	2318.40	-4.31	104.31	4.9	90.9	1.73	Kaol, ?mica	0.0	0.0				1.4	109.9
BST 39	Ca mudst.	2338.63	101.86	-1.86	88.7	0.0	11.72	Qtz, kaol	0.0	0.0				61.3	ND
BST 40	Wackest.	2336.50	84.31	15.69	99.4	2.1	0.35	Kaol, mica	94.7	2.8	1.15	0.06	0.08	100.7	ND

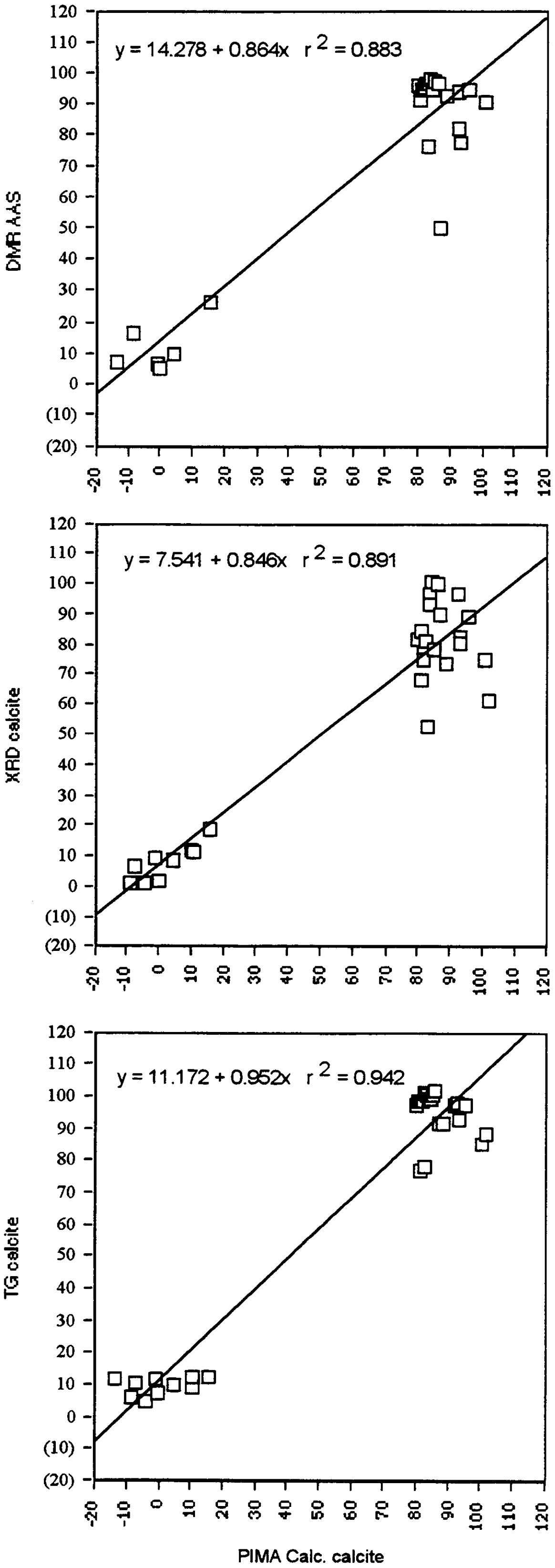


Figure 11. Cross plots to compare % calcite determined from the PIMA calibration curve with AAS, XRD and TG techniques.

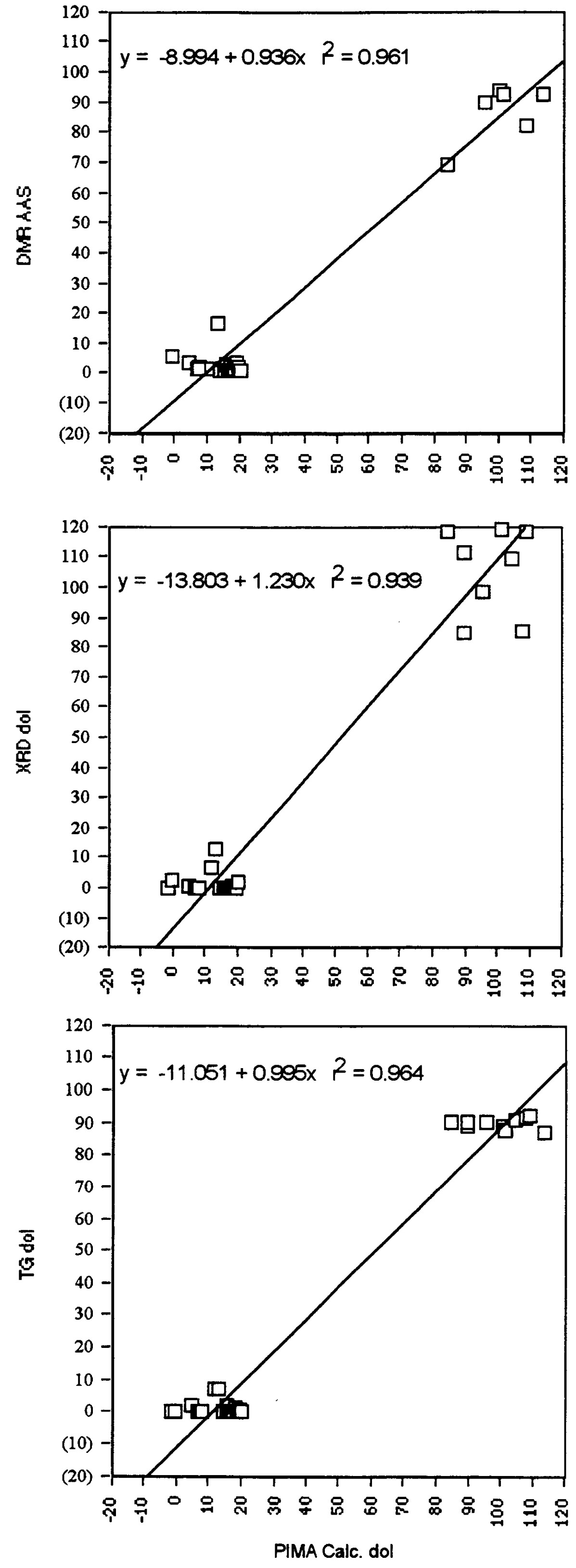


Figure 12. Cross plots to compare % dolomite determined from the PIMA calibration curve with AAS, XRD and TG techniques.

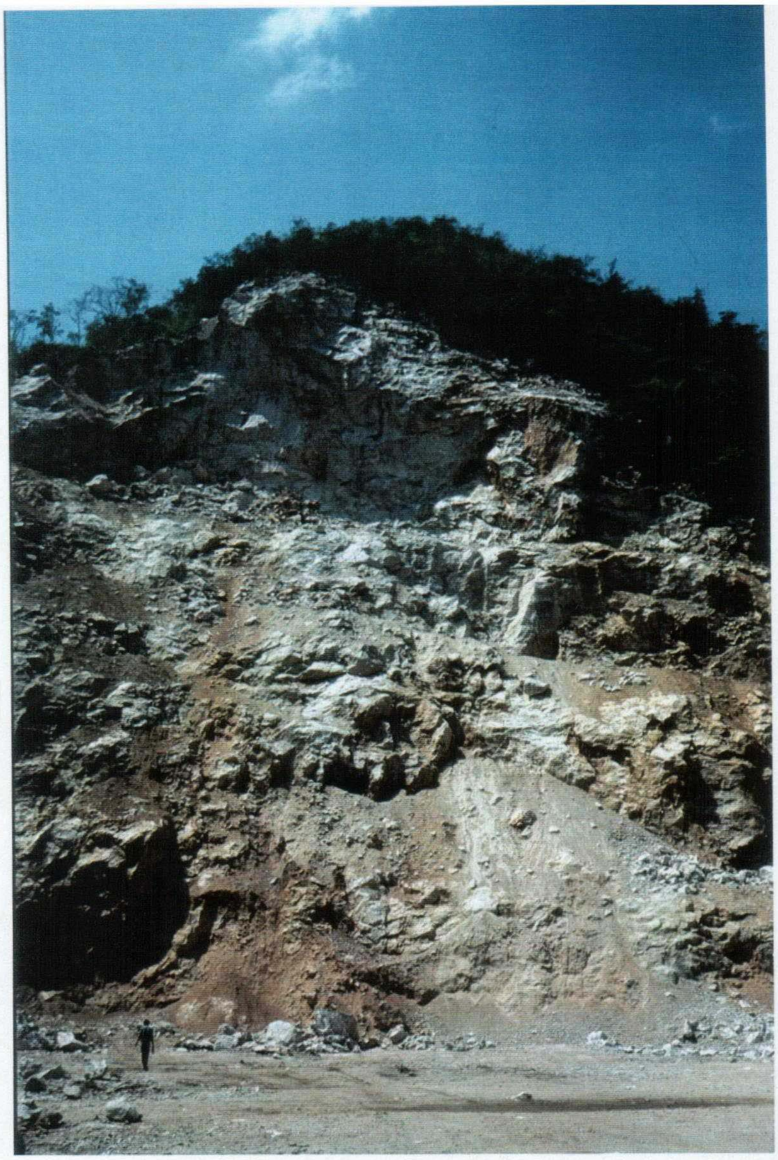


Plate 9. Massive dolomite quarried for lime and aggregates (Um Luk Formation), Surat Thani

Plate 10. Massive, relatively pure limestones (Um Luk Formation), Surat Thani

Plate 7. Typical steep-sided, tower karst, Surat Thani, Thailand

Plate 8. Thinly bedded, laminated limestones (Pha Nom Wang Formation), Surat Thani

Plate 5. Burning dolomite for production of 'lime', Surat Thani, Thailand

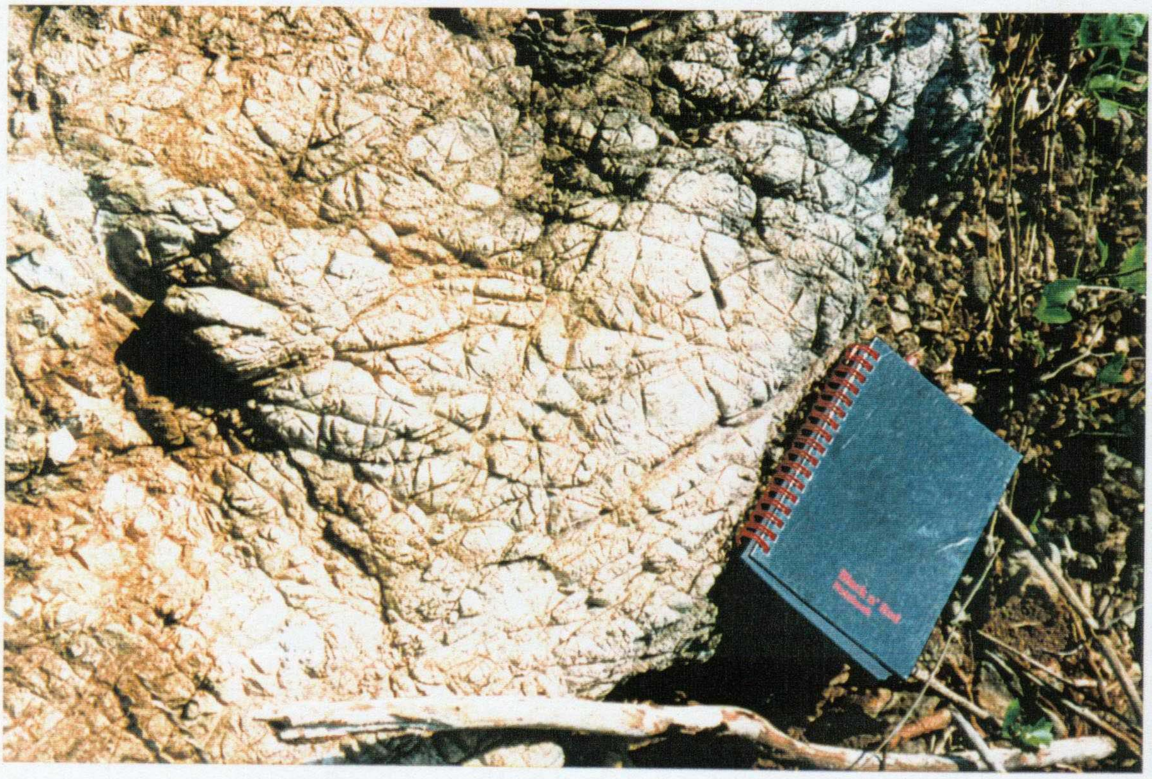


Plate 6. Dolomite 'elephant-skin' texture

4. LABORATORY PROCEDURES

In addition to field geological studies and basic field testing of rock properties, detailed laboratory studies are required to investigate the mineralogical, chemical and physical and mechanical properties of the rocks. This information can then be used for resource classification, to determine regional trends and to indicate the suitability of the rocks for particular end uses. Some of the laboratory investigative techniques are sophisticated and require expensively equipped laboratories; others are relatively simple and can be used in basic laboratories. Most of the techniques are conventional and many are usefully summarised in a manual for laboratory geologists (Harrison, 1992).

This report aims to identify laboratory methods suitable for rapid assessment of limestone resources. A 'rapid' method may be defined as one that is both simple and objective and combines high throughput with good quality results. Where more than one technique is available to assess particular properties, then the advantages and disadvantages of each technique have been determined and the relative performance of the methods has been assessed.

4.1 Petrographic Studies

The lithology, fabric, texture and mineralogy of many limestones are such that little detail is apparent in the field and consequently they require examination by optical microscopy using cut faces and thin sections. Typical observations are shown in Table 18. The information obtained, although essential for sedimentological studies, is also valuable for rock classification and for linking mineralogy, rock chemistry and physical property data to lithology.

Thin sections are a standard means of carbonate study but are relatively expensive to produce and their examination requires use of a relatively sophisticated polarising microscope. Much useful petrographic data can, however, simply be obtained by sawing slabs or cores and etching the cut surface in weak solutions of acids (usually dilute hydrochloric acid). Studying the surface under a simple binocular microscope in reflected light then readily allows interpretation of limestone lithologies and identification of dolomite or non-carbonate impurities. Hydrochloric acid dissolves calcite more rapidly than dolomite, with the result that any rhombs of dolomite stand out clearly. Quartz, chert, clay, bitumen, fluorite and pyrite are not dissolved and will also be differentiated.

Petrographic studies using cut and etched surfaces and binocular microscopy are recommended for rapid limestone resource surveys. Thin sections should be used selectively.

Table 18. Petrographical observations for limestone resource assessment

1. General lithology
2. Palaeontology - identification of grain types
3. Colour variations
4. Texture - grain size and shape
5. Diagenetic observations - type of cement, porosity etc
6. Sedimentary and organic structures
7. Carbonate mineralogy
8. Non-carbonate mineralogy

4.2 Carbonate Staining

The carbonate mineralogy of a limestone can be investigated using a chemical staining technique (Dickson, 1966; Friedman, 1971). This involves a reaction which produces a coloured precipitate on a mineral surface, making the mineral more easily recognised. It is used in resource surveys primarily to determine the presence of dolomite (see 3.4.2), although ferroan phases of calcite and dolomite may also be recognised and some techniques successfully determine feldspars, gypsum, anhydrite, aragonite and even particular clay minerals. The dual staining technique of Dickson (1966) using potassium ferricyanide and alizarin red S in 1.5% HCl is particularly valuable because in one operation it differentiates between calcite and dolomite and also between ferroan phases in both calcite and dolomite (Appendix C).

In rapid resource assessment surveys it is recommended that the staining of cut faces of lump samples is carried out only where dolomitisation is suggested by field studies. Thin sections should be stained routinely during preparation.

4.3. Analysis of Limestone and Dolomite

4.3.1. Wet Chemical methods

Atomic absorption spectrophotometry (AAS)

In modern chemical laboratories (including those at BGS) the use of AAS has been largely superseded by more advanced analytical techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES). However, AAS is still routinely used by many organisations in less-developed countries and remains a valuable method for the chemical analysis of limestone and dolomite.

Because AAS is widely regarded as outmoded, very little has been published on the method in the last 15 years. Barber (1974) described a methodology for the analysis of limestone and dolomite involving a two-stage chemical digestion and use of both X-ray fluorescence (XRF) spectrometry and AAS (Figure 13). Barber reported that Ca, Mg, Mn and Sr are generally only present in the acetic acid soluble fraction, i.e. within carbonate minerals. A Mn-dolomite and Sr-calcite chemical-mineral association was observed. Fe

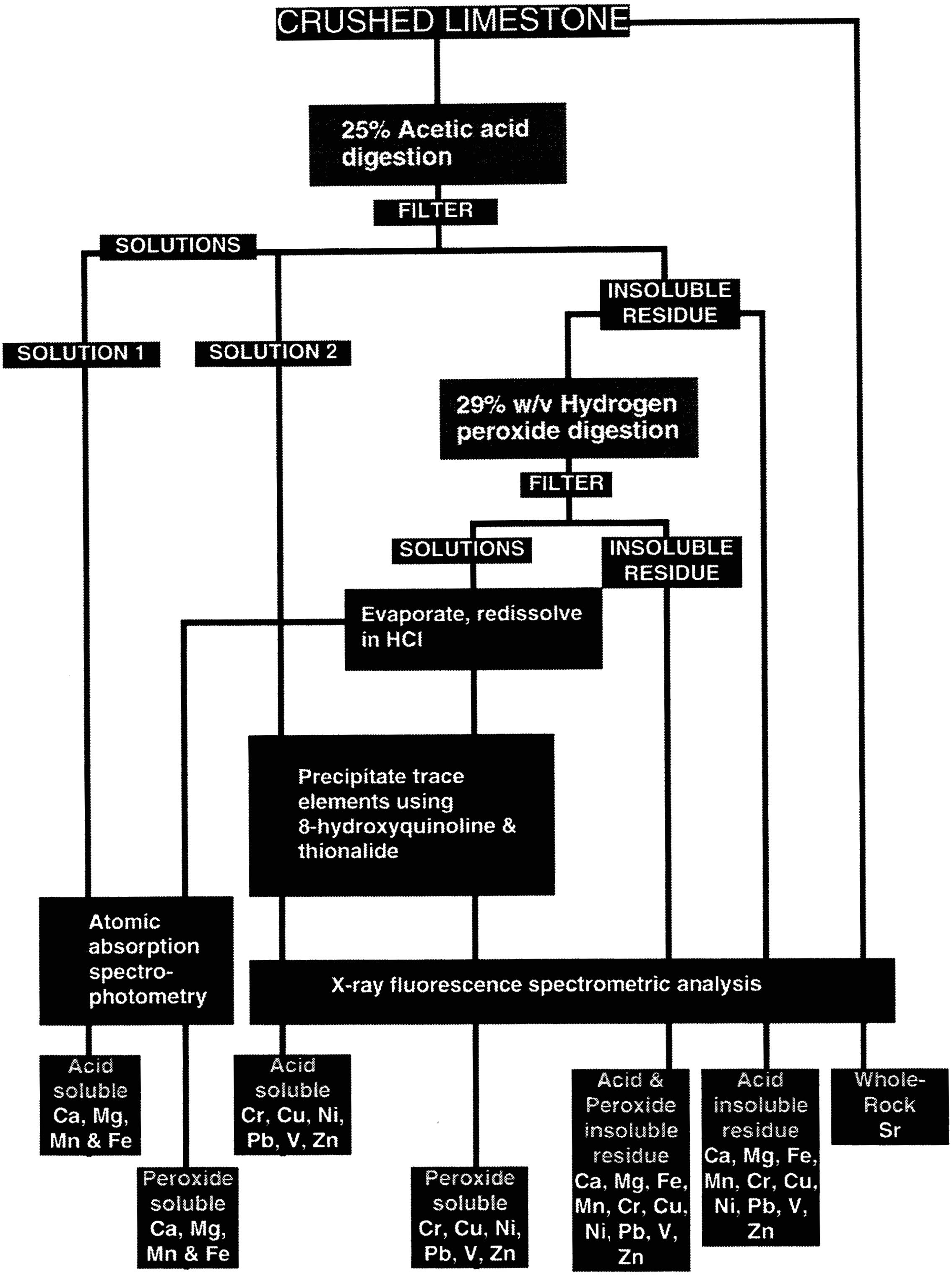


Figure 13. Chemical analysis of limestone and dolomite (after Barber, 1974).

was present in both acetic acid and peroxide soluble fractions. Cr, Cu, Ni, Pb, V and Zn, elements often associated with sulphides, were mostly present in both peroxide and acetic acid insoluble residues. It would be impractical to use this two-stage chemical digestion on large numbers of samples as the method is too time-counsuming. However, the approach is a useful means of establishing chemical-mineral associations of selected limestones and dolomites.

Whitehead (1976) suggested a number of refinements to AAS analysis of carbonate rocks. First, 0.1 g of sample was digested in 100 ml of 0.6% v/v acetic acid. Following digestion, Mg was analysed in 0.1% w/v KCl solution, and Ca was analysed in 0.5% w/v KCl solution. KCl acts as a "releasing agent" and prevents mutual interference between Ca and Mg. KCl is less expensive than the $LiCl_3$ releasing agent commonly used, with no loss of precision and accuracy.

Robinson (1980) reviewed methods for the digestion of carbonate fractions prior to analysis by AAS. Two methods of digestion were then tested. First, 1 g of sample was digested by standing in 500 ml of 0.3M acetic acid for one week. Secondly, 1 g of sample was digested in 50 ml of 1M HCl stirred intermittently over a period of 2 hours. Ca, Mg, Mn, Sr, Na, Fe were then determined by AAS. For purposes of comparison, whole-rock K_2O, Mn, Sr, Na and Fe were determined by XRF. Robinson concluded that digestion with HCl is rapid and is not accompanied by significant leaching of non-carbonate minerals. Mn, Na and Sr did not vary with the digestion method used. In contrast, Fe was dependent on the digestion procedure. The benefits of the HCl digestion were that trace elements (Mn, Sr, Na and Fe) could be measured directly on the small volume of solution obtained, and that Ca and Mg could be also determined on the same solution as the trace elements without adjustment of the dilution.

According to Siesser and Rogers (1971), the **advantages** of using AAS for routine carbonate analysis are:

- Method is accurate and precise
- Method is straightforward and rapid
- Ca and Mg can be determined from the same solution
- Method is sensitive (low Ca and Mg contents can be measured accurately)

Whereas the **disadvantages** of using AAS for routine carbonate analysis are:

- High capital cost of the instrument
- High degree of operator skill required
- Method is prone to systematic or experimental errors
- Solution preparation and instrument calibration are time consuming
- Throughput is about 2.5 samples per hour including preparation and calibration

Ethylene di-amine tetra-acetic acid (EDTA) titration

EDTA titration is capable of routine determination of Ca, Mg, Fe and Al in carbonate rocks. Because the method uses standard laboratory glassware and commonly available laboratory reagents, EDTA titration is well-suited to those laboratories in less-developed countries where more sophisticated analytical equipment is not available. The American

Society for Testing and Materials publish a rapid method for the determination of Ca and Mg content of limestone (ASTM C25-95, 1995). This methodology has been used to analyse a number of limestone and dolomite samples in the laboratories of the Zambian Geological Survey Department (Table 19, columns A and C). A very good correspondence (correlation coefficients of 0.99-1.00) was obtained between CaO and MgO contents measured using the EDTA method in Zambia and separate determinations of CaO and MgO measured by XRF at BGS laboratories in the United Kingdom (Table 19, columns B and D).

Table 19. Chemical analyses of carbonate rocks from Zambia. CaO and MgO determinations by the EDTA method of ASTM C25-95 (columns A and C) and by XRF analysis (columns B and D).

Sample and lithology/origin	(A) EDTA CaO (%)	(B) XRF CaO (%)	(C) EDTA MgO (%)	(D) XRF MgO (%)
1. Dolomite marble	31.30	30.24	25.39	21.83
2. Marble	53.88	55.14	0.68	0.22
3. Marble, dolomitic	51.57	51.84	3.20	3.47
4. Marble	53.32	55.59	1.48	0.38
5. Dolomite marble	30.52	30.93	23.67	21.87
6. Dolomite marble	30.42	30.98	23.61	21.85
7. Dolomite marble	32.28	33.06	23.67	20.08
8. Agricultural lime	54.75	55.47	0.61	0.46
9. Agricultural lime	54.21	54.48	0.36	0.41
10. Agricultural lime	55.02	55.21	0.37	0.50
11. Marble	53.78	53.72	0.30	0.73
12. Limestone	55.27	54.36	0.31	0.30
13. Dolomite	29.77	35.99	22.98	21.90
Correlation coefficient	0.99		1.00	

The British Standards Institution also publish an EDTA titration method for determining the Ca and Mg content of dolomite and limestone used as extenders for paint (BS1795, 1976) which is very similar to that described in ASTM 25-95. Bisque (1961) describes an EDTA titration procedure for determining Fe and Al in carbonate rocks, in addition to measurement of Ca and Mg (Figure 14).

According to Siesser and Rogers (1971), the **advantages** of using EDTA titration for routine carbonate analysis are:

- Low initial outlay
- Use of standard laboratory equipment and reagents
- Low running costs
- Accuracy = 1%
- Precision = 2.1%

Whereas, the **disadvantages** of using EDTA titration are:

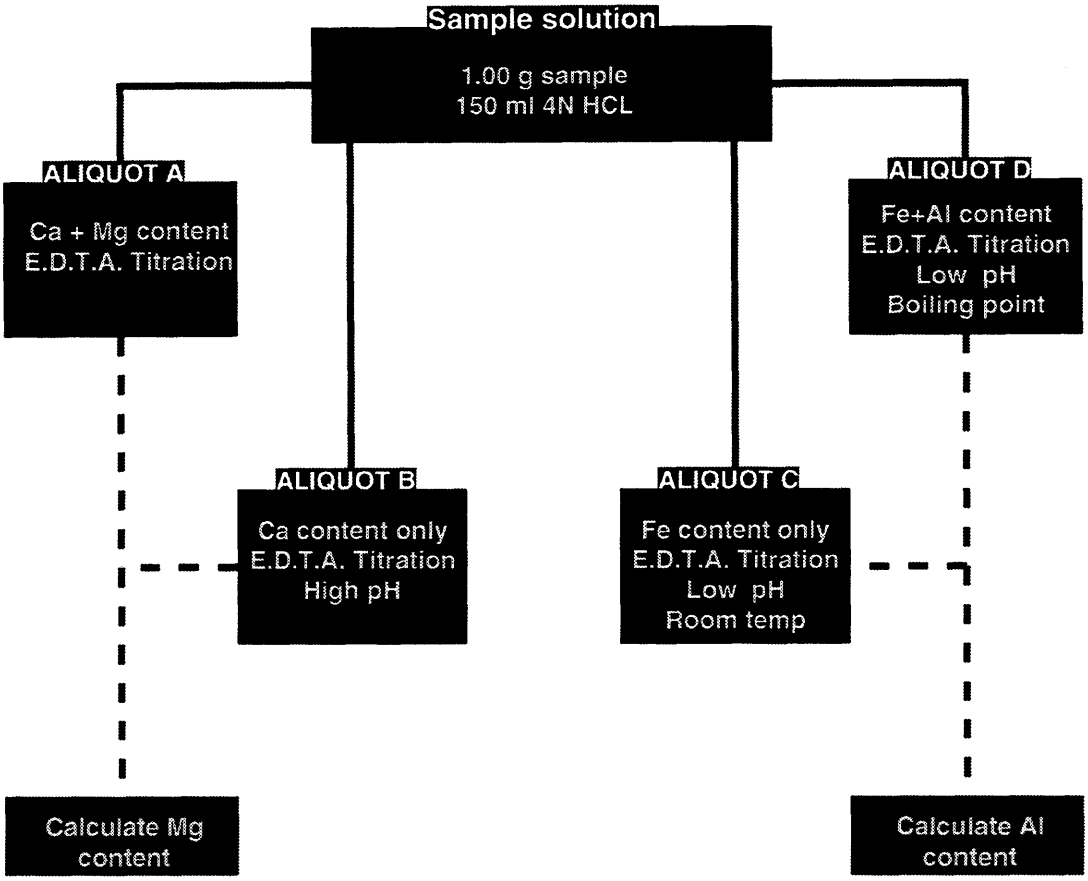


Figure 14. EDTA analytical procedure for carbonate rocks (after Bisque, 1961).

- Good level of chemical expertise is required
- Many time-consuming stages of preparation
- Low throughput of 1.5 samples per hour
- Unpleasant ammonia and toxic cyanide reagents used

Empirical standard curve method

Loeppert and others (1984) describe the "empirical standard curve" method for measuring carbonate content. In this procedure, a known quantity of acetic acid is partially consumed by reaction with the carbonate fraction of a sample and the final pH following complete dissolution is recorded. Calcium carbonate content is determined empirically from a standard calibration curve of pH versus weight $CaCO_3$, described by the following equation:

$$pH = K + n \log [\text{ weight } CaCO_3 / (T - \text{weight } CaCO_3)]$$

where

K = a constant
n = a constant
T = total carbonate required to completely neutralize the acetic acid

Goh and others. (1993) state that the Loeppert and others method is suitable for rapid and routine analysis of the carbonate content of large numbers of samples. However, because the method is intended for measurement of calcium carbonate content, the procedure is unsuitable for samples containing dolomite.

Calcium carbonate equivalent (CCE)

The ASTM publish a test method to measure carbonate content, expressed as the calcium carbonate equivalent (CCE) (ASTM C25-95, 1995), i.e. $\%CaCO_3$. 100 ml of 1N HCl is added to a 500 ml flask containing 5 g of ground limestone and boiled for 5 minutes. The solution obtained is cooled to room temperature and the excess acid titrated against 0.5N NaOH using phenolphthalein as an indicator. CCE is calculated as follows:

$$\%CaCO_3 \text{ (CCE)} = [5.0045 (V1N1 - V2N2)] / W$$

where

$V1$ = Volume of HCl solution, ml
$N1$ = Normality of HCl solution, N
$V2$ = Volume of NaOH solution, ml
$N2$ = Normality of NaOH solution
W = Sample weight, g

Trials conducted in 1997 in the Zambian Geological Survey Department, Lusaka, in conjunction with BGS, found the CCE method to be very rapid and reasonably precise (coefficient of variation = 0.19).

Citrate buffer method

Raad (1978) described a method in which calcite and dolomite are dissolved in a citrate buffer solution. Ca and Mg content in solution are determined by AAS analysis. Initially, dolomite content is calculated directly from Mg in solution, and an equivalent amount of Ca is assigned to dolomite on a 1:1 Ca:Mg basis. The remaining Ca in solution is then attributed to calcite. Dolomite content is checked by subtraction of the calcite content obtained from a total carbonate value determined by another method on a separate sub-sample.

Because the citrate buffer method is basically an alternative method of preparation for AAS analysis, its advantages and disadvantages are essentially the same as those of AAS (see above). Recently, Goh and others (1993) identified the Raad method as a suitable chemical procedure for quantification of calcite and dolomite.

4.3.2. Physical Methods

Gasometry

A method to determine carbonate content by gasometry is described by Hulseman (1966) which utilises standard Gas Law theory. Although this method is over 30 years old, BGS has used this procedure within the last 10 years, and the method is still used in the extractive industry to monitor the carbonate content of quarry feed. In the Hulseman method, the volume of CO_2 generated by digestion of 0.2-1.0 g of sample in 5 ml of 2N HCl is measured. Hulseman checked the accuracy and precision of the procedure by eight duplicate analyses of analytical-grade $CaCO_3$ reagent containing <0.2 % impurities. A mean $CaCO_3$ value of 100.72% was obtained at 0.77% standard deviation. The main source of error was found to be moisture, incomplete digestion and temperature fluctuation. Percentage carbonate is calculated as follows:

$$\%CO_3 = [\ 0.0961\ v\ (P - M)\ ]\ /\ [\ W(\ T + t\ )\ ]$$

where

v	= volume of CO_2 (ml)
P	= barometric pressure (mm Hg)
M	= vapour pressure of cooling water (mm Hg)
W	= weight of sample (g)
T	= room temperature (°C)
t	= 273.16 (conversion factor to Kelvin)
0.0961	= conversion factor from "mm Hg" to c.g.s units

Using Chittick gasometeric apparatus, Dreimans (1962) obtained a separate estimation of calcite and dolomite content by exploiting the different rates of carbonate mineral dissolution in 6N HCl.

According to Siesser and Rogers (1971), the **advantages** of using gasometry for routine carbonate analysis are:

- Initial outlay is low
- Method is "reasonably" accurate and precise
- Operation requires very little skill
- Crushing is the only sample preparation necessary

and the **disadvantages** of using gasometry are:

- Parts of apparatus must be specially constructed
- Precision is poor at low carbonate levels, e.g. 10% precision at 2% carbonate content
- Only $\%CO_3$ or equivalent calcite value generally obtained
- Does not distinguish calcite from dolomite

Acid-insoluble residue

A rapid, simple acid-insoluble residue method for estimation of carbonate content has been used by BGS in assessments of limestone and dolomite resources in the United Kingdom. Cox and others (1977), using the method of Molnia (1974), obtained a good correlation between insoluble residue values and % non-carbonate fraction as calculated from the results of XRF analysis. The insoluble residue method is also widely-used in industry for the determination of carbonate content. In the Molnia method, 2 g of sample is digested in dilute HCl acid in a filter funnel. Excess acid is removed by vacuum filtration and the insoluble residue is retained on a 47 mm diameter nitro-cellulose filter of 0.45-4.00 μm pore size. Molnia estimated that the precision of the method was <1% and obtained a typical throughput of 15-20 samples per hour. A schematic of the insoluble residue apparatus used by BGS is shown in Figure 15. The mineralogical composition of insoluble residues can be determined by XRD analysis of the residue-bearing filter discs.

The chemical digestion of carbonate rocks and the extraction of clay minerals was reviewed by Ostrom (1961), including the use of hydrochloric, acetic, formic, oxalic and sulphuric acids. Ostrom used reaction or non-reaction with 5M acetic acid for distinguishing calcitic and dolomitic samples, respectively. For digestion of calcite, Ostrom (1961) suggested repeated additions of 1L of <0.3M acetic acid to 10g of sample ground to -60 mesh until the reaction ceases. In contrast, for digestion of dolomite, Ostrom suggested substitution of <0.11M hydrochloric acid for <0.3M acetic acid.

According to Siesser and Rogers (1971), the **advantages** of using insoluble residue for routine carbonate analysis are:

- Method is very simple
- Minimal costs involved
- Standard laboratory equipment used
- >5-6 samples per hour throughput
- Method is widely used

and the **disadvantages** of using insoluble residue are:

- Method only estimates carbonate content
- Precision is greater than that of AAS, EDTA or gasometry procedures
- Method less accurate than many other methods (overestimates carbonate content)

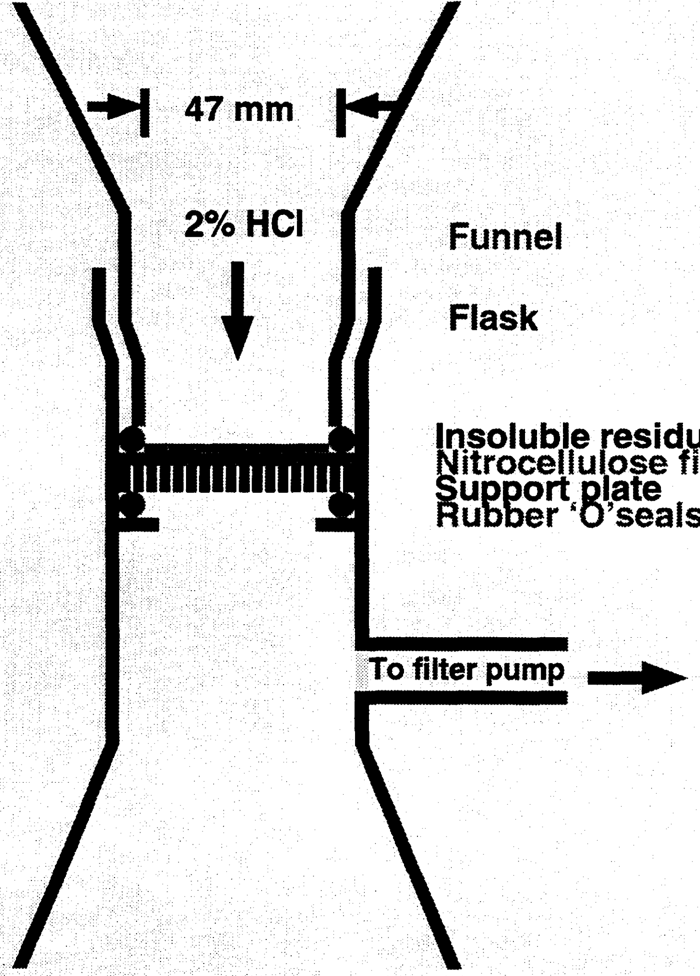


Figure 15. Insoluble residue apparatus used at BGS.

- Precision and accuracy deteriorate for <2 g samples
- Method does not distinguish between calcite and dolomite

Loss on ignition (LOI)

Galle & Runnels (1960) devised a rapid, simple, two-stage method for determining the loss on ignition (LOI) of carbonate rocks, based on the following calculation.

loss-on-ignition (%) $= [(C - B) / A]$

where

A= dried weight at 105°C
B= weight after heating at 550°C for 25 minutes
C= weight after heating at 1000°C for 1 hour

The intermediate heating stage (550°C) was added to correct for loss of volatiles from organic matter oxidation and clay mineral dehydroxylation between 105 and 550°C. A temperature of 550°C was chosen by Galle and Runnels as differential thermal analysis (DTA) indicated that this was the threshold above which dolomite decomposed. Waugh and Hill (1960) investigated the influence on pyrite content on LOI by the two-stage Galle and Runnels method. They proposed the following reaction between pyrite and calcite during heating:

$4FeS_2 + 8CaCO_3 + 15O_2 \text{-->} 2Fe_2O_3 + 8CaSO_4 + 8CO_2$

The evolution of CO_2 below 550°C as a result of this reaction introduces error into LOI values. Waugh and Hill suggested a correction for the presence of 0.2-2.0% pyrite content which involved a number of separate measurements of sulphate (%SO_4) and total sulphur (%S). However, this correction for pyrite is both time consuming and expensive and therefore undermines the rationale for using a supposedly simple and rapid method.

From the Galle and Runnels method, carbonate content can be estimated by expressing the LOI value obtained as a percentage of the theoretical decarbonation weight loss of pure calcite. Generally, the LOI method is only applicable to limestone samples. If both dolomite and calcite are present, carbonate content cannot be quantified from LOI as these two minerals exhibit a different decarbonation weight loss.

4.3.3. Mineralogical Methods

X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) methods for identification and measurement of carbonate minerals were reviewed by St Arnaud and others (1993). In the late 1950s and early 1960s, carbonate minerals were quantified on the basis of calibration curves constructed from XRD analysis of a dilution sequence of calcite (3.035Å peak) and dolomite (2.880Å peak) standards. Tennant and Berger (1957) described a method based on peak height measurement. Weber and Smith (1961) calculated a linear calibration equation from peak area measurement:

$$Y = 95.3X + 5.52$$

where

Y = dolomite content (weight %)
X = [peak area dolomite / (peak area dolomite + peak area calcite)]

This peak area measurement method was refined by Diebold and others. (1963) who used cadmium fluoride as an internal standard. From analysis of mixtures of mineral standards, calibration curves of quartz, dolomite and calcite contents were plotted against mineral peak area, the latter ordinate being expressed as a ratio to the peak area of the internal standard added. Gunatilaka and Till (1971) devised a "spiking" technique for quantification of calcite and quartz. Samples were analysed by XRD in the natural state and after a 50% addition of a "spike". In the example provided, the "spike" consisted of 30% calcite, 60% aragonite and 10% quartz. (However, for analysis of other types of sample, the composition of the "spike" can be adjusted to reflect their mineralogy.) Peak areas were measured for both natural and "spiked" sample and mineral contents then calculated using Brindley's equation (Brown, 1961). For carbonate minerals, coefficient of variation was between 1.4-8.7% with "no significant bias" in accuracy, except for samples where <10% calcite was present.

Roselle (1982) described an automated XRD method for quantifying the %$MgCO_3$ present in calcite based on step-scan peak area measurement which used the direct calculation of Hooton and Giorgetta, (1977).

In the last 10 years, XRD quantification routines have been developed using automated systems and modelling software. Martinez and Plana (1987) described a Lorentzian profile method for quantification of carbonates. This involves the modelling or "fitting" of a profile to an XRD pattern. This method overcomes many of the problems of conventional XRD quantification, such as deconvolution of overlapping peaks, variation in crystallinity, and differences in chemical composition between standards and sample. The Martinez and Plana approach combined Lorentzian profiling with a fluorite internal standard method. For carbonate phases present, d-spacings, crystallinity values and mineral contents were obtained. For a set of natural mineral mixtures, the variation between actual and calculated mineral content was <3.8%. Mansour and others. (1995) utilised Rietveld refinement for quantification of carbonates. This modelling method, based on a "whole-pattern fitting" approach, again overcomes some of the pitfalls of conventional methods. Aragonite, high-magnesian calcite, and low-magnesian calcite contents were measured. Modelling also enabled unit cell parameters and peak broadening to be defined. For a set of natural mineral mixtures, the maximum deviation between actual and calculated mineral content was ±5%.

In summary, the main **advantages** of quantification of carbonates by XRD are as follows:

- Identification of calcite (both high- and low-magnesian) and dolomite is possible
- Modern modelling methods are rapid and automated
- Short analysis time - only limited 2-theta scans usually required
- Accuracy of Rietveld and Lorentzian modelling <5%
- Method is non-destructive

Whereas, the main **disadvantages** of XRD are:

- For conventional XRD, precision and accuracy may be poor because of overlapping peaks and differences in crystallinity and mineral chemistry between standards and samples
- Crushing, grinding and micronization preparation necessary
- Detection limits of circa several percent mineral
- Generally, less accurate than chemical methods
- Expensive, sophisticated equipment required

Thermal analysis

Differential thermal analysis (DTA) measures the difference (△T value) between the temperature of a sample and that of a reference material in response to heating. DTA is therefore sensitive to the endothermic decomposition of carbonate minerals. During fieldwork, Jagolino (1966) used a portable DTA unit for estimation of %MgO in dolomitic limestones. A single endotherm at 850-1000°C was obtained for calcite, whereas two endotherms, at 750-850°C and 850-1000°C respectively, were obtained for dolomite. The height of the 750-850°C endotherm correlated with magnesia content and enabled estimation of %MgO to within +/- 2%. For the equipment used, the detection limit for MgO was approximately 5%.

Thermogravimetric analysis (TGA) measures the changes in the mass of a sample in response to heating. Dollimore and others. (1986) analysed limestones of the English Peak District by simultaneous DTA/TGA. The endotherm from DTA, together with TGA weight loss, was used to calculate carbonate content. Data from wet chemical analysis corroborated the % carbonate values obtained by thermal analysis. Dollimore and others concluded that simultaneous DTA/TGA was a good "fingerprint" method capable of distinguishing between different limestone formations.

Evolved gas analysis (EGA) measures gases evolved from a sample during heating. Milodowski and Morgan (1980) analysed a wide range of carbonate minerals by EGA. A non-dispersive infrared (NDIR) detector was used for analytical determination of CO_2. Generally, the method was capable of identifying and quantifying individual carbonate minerals. The method was more sensitive than conventional XRD, TGA or DTA with detection limits of circa 100 ppm carbonate. EGA with a porous cap placed over the sample crucible enabled calcite to be distinguished from dolomite.

In conclusion, many of the common methods of thermal analysis are suitable for estimation of calcite and dolomite content. However, a skilled and experienced operator is usually required to interpret the results obtained. Also, full interpretation of thermal analysis data is usually only possible if the mineralogical composition of the sample is known. Therefore, thermal analysis is essentially complementary to other methods such as XRD analysis and should not be used in isolation.

4.4 Determination of Brightness

Evaluation of mineral fillers will often involve the measurement of brightness. This can be carried out using a range of methods of varying technical sophistication, accuracy, simplicity and equipment costs, but for systematic resource investigation studies it is recommended that measurement of the spectral curve or brightness at 457 nm using a full-range spectrophotometer (such as the Datacolour Elrepho 3000) or an abridged spectrophotometer (such as the EEL spectrophotometer) are appropriate methods. A review of colour measurement, instrumentation and methods is given in Appendix C.

The brightness values of ten samples of carbonate from the Surat Thani area of southern Thailand were measured by DMR and BGS. The results are given in Table 20. The brightness of the samples (which have been ranked in order of decreasing brightness) has been measured using two different instruments. The DMR used a 577 reflection meter (a colorimeter) and the brightness was determined using a blue-wratten filter (with a peak transmittance of approximately 470 nm). The BGS used an EEL reflectance (abridged) spectrophotometer to determine the spectral curve from which the brightness at 457 nm was derived (see Appendix C)..

Table 20. Brightness of carbonates from Thailand

Sample	**DMR brightness** (577 colorimeter) 470 nm	**BGS brightness** (EEL abridged spectrophotometer) 457 nm	**Difference** between BGS & DMR values
788 (SR 57)	82.1	88.5	+6.4
787 (SR 56)	76.9	81.5	+4.6
797 (SR 75)	73.1	76.8	+3.7
792 (SR 64)	68.5	76.2	+7.7
798 (SR 77)	65.5	73.4	+7.9
778 (SR 47)	63.2	65.3	+2.1
776 (SR 42)	53.7	53.1	-0.6
779 (SR 48)	48.4	51.2	+2.8
784 (SR 53)	44.0	47.3	+3.3
764 (SR 25)	40.5	42.1	+4.7

The results indicate that both methods rank the carbonate samples in the same order of descending brightness. However the DMR values are consistently lower (on average 4.3% lower). This difference is due to the slight difference in the wavelength and bandwidths used, different calibration standards (ceramic tile, DMR; barium sulphate, BGS) and different background conditions (small covered sample, DMR; lightproof box, BGS).

The two different methods used for the measurement of these carbonate samples have given broadly similar brightness values. They are both simple methods, using relatively simple apparatus. Both of these methods are adequate for use as rapid evaluation tools for the study of carbonate resources. Whereas they do not give highly accurate brightness values they are useful for 'screening' out samples for further investigation and rejecting those samples with low brightness values. A full-range spectrophotometer (see Appendix C) should be used for further investigation of the potential of such samples for use as white mineral fillers.

4.5 Aggregate Testing

Limestones used as aggregates (in concrete or as roadstone) are required to be strong and durable and other properties such as specific gravity and water absorption are of importance. There are a number of laboratory tests to investigate the physical and mechanical properties of aggregate materials and to assess their potential 'in-service' performance (Harrison and Bloodworth, 1994). Methods commonly applicable to testing limestone raw material for aggregates are outlined in Table 21. Most of these procedures are British Standards or American Standards; similar standards apply in most other countries.

Table 21. Standard tests for evaluating limestone aggregates

Petrographic examination (BS 812, ASTM C295) - identification of potentially reactive minerals

Physical tests

1. Flakiness Index (BS 812) - measures degree of flaky particles.
2. Relative density (BS 812, ASTM C33, 136) - measures specific gravity.
3. Water absorption (BS 812, ASTM C127, 128) - measures porosity and capacity to absorb water.

Mechanical tests

1. Aggregate impact value, AIV (BS 812) - measures resistance to granulation under impact stresses.
2. Aggregate crushing value, ACV (BS 812) - measures resistance to crushing under a gradually applied load.
3. Ten per cent fines value, TPV (BS 812) - measures resistance to crushing by the application of a continuous load.
4. Los Angeles abrasion value, LAAV (ASTM C131) - measures resistance to attrition by impact and abrasion forces.
5. Aggregate abrasion value, AAV (BS 812) - measures surface wear following abrasion.

Testing is performed on the finished aggregate product and sample preparation facilities (laboratory crushing and sieving) are required to produce the necessary particle size fractions (mostly 10-14 mm chippings) for testing. Experience has shown (Adlam, 1984) that at least 25 kg of rock sample is required to produce sufficient chippings for a full range of index tests. Some tests, however, use relatively small test samples (eg AIV test) and tests such as determinations of relative density and water absorption are non-destructive.

For rapid reconnaissance appraisal of limestone resources and in situations where testing and sample preparation facilities are limited, it is recommended that laboratory testing procedures are restricted to the AIV test and to determinations of relative density and water absorption (detailed test procedures are given in Appendix C). The AIV test is a simple test procedure using relatively inexpensive apparatus involving small (<1 kg) test samples. The LAAV test is also a preferred method for evaluating aggregates (Harrison and Bloodworth, 1994) but it requires a large sample charge (5 kg of graded aggregate), increasing the burden of field collection and laboratory sample preparation. It may therefore replace the AIV test in certain testing programmes, but it is not normally an appropriate technique for rapid appraisals of limestone aggregate resources.

Investigations of the aggregate properties of the limestones and dolomites in the Surat Thani area, Thailand, is based on a limited amount of laboratory index testing (AIV and physical property testing) supplemented by data obtained by field strength testing (see 3.4.1). Sample processing was carried out at DMR in Bangkok and laboratory testing in the UK at BGS, Keyworth. A total of 30 determinations of aggregate impact value (and flakiness index) was obtained, supplemented by 10 determinations of relative density and water absorption. Results are given in Appendix A and are summarised in Table 22. These results show only small variations in physical and mechanical properties and are typical of results (Harrison, 1992; Smith and Collis, 1993) given by UK limestones used as roadstone or concreting aggregate materials. All of the Permian limestone formations produced consistently strong aggregates (AIVs <24), although the dolomites gave much more variable test results, indicating a range of strong and weak lithologies. Results indicate that the dark grey, fine grained wackestones and lime mudstones of the Phab Phar Formation are likely to produce the strongest aggregate materials (AIVs <22), although data are limited and further testwork is required to make a definitive assessment. Few data are available from the Ordovician limestones but the generally shaly and argillaceous character of these rocks suggests that they would tend to produce relatively weak, lower quality aggregates with high proportions of waste.

Table 22. Summary of aggregate property data from Surat Thani, Thailand

		Permian limestones	Permian dolomites
Aggregate Impact Value (AIV)	Range	20 - 28	18 - 33
	Mean	24	27
Schmidt hammer value (R)	Range	54 - 65	35 - 68
	Mean	57	59
Flakiness index (Is)	Range	25 - 42	16 - 34
	Mean	34	25
Relative density	Range	2.68 - 2.69	2.79 - 2.85
	Mean	2.69	2.82
Water absorption (%)	Range	0.3 - 0.4	0.3 - 0.6
	Mean	0.3	0.5

4.6. Lime Burning

Lime (CaO) is a basic industrial chemical essential for a diverse range of manufacturing processes.

Lime is produced on an industrial scale by the calcination of limestone. When heated above a certain temperature in a kiln, limestone decomposes releasing carbon dioxide, leaving calcium oxide, known as quicklime or lime, as a residue. The suitability of lime for industrial use ("quality") is primarily based upon physical properties, including reactivity, porosity, bulk density and surface area. Also, because chemical purity is an essential prerequisite, only relatively pure limestone is suitable for lime production. However, not all high purity limestone will produce lime of adequate physical quality. Therefore, in considering a limestone deposit for lime manufacture, it is essential to undertake lime burning trials to determine the quality of lime which may be obtained. Theoretical aspects of limestone calcination are briefly outlined in Appendix C.

4.6.1. Lime Burning Trials

Methodology

The BGS method for evaluating the burning characteristics of crushed limestone and dolomite was adapted from the approach of both Lyon (1980) and Scott and others (1983). Most industrial rotary kilns use crushed stone feed of between 10 and 22 mm in size. In other kiln types, such as shaft kilns, a narrower size range is used to obtain a porous bed of stone through which CO_2 from calcination can pass freely.

In the lime burning method used by BGS, portions of closely-sized rock, crushed to between 12.7 mm and 6.35 mm in size, were shock-calcined at 950, 1000, 1050, and 1100°C for 1.5 hours in a muffle furnace. Lime burning performance was then assessed from the decrepitation of the limestone and the loss on ignition (LOI), reactivity and surface area of the lime product obtained.

Physical and chemical tests

The American Society for Testing and Materials (ASTM) publish a comprehensive list of physical and chemical specifications for the industrial use of lime, and also five standard test methods for lime quality. Test methods for the physical testing of quicklime, hydrated lime and limestone are outlined in ASTM C110-95 (1995), including the slaking rate of hydrated lime. Chemical analysis procedures for limestone, quicklime and hydrated lime are contained in ASTM C25-95(1995), including a suitable loss on ignition (LOI) procedure.

In addition to the above ASTM methods, decrepitation and specific surface area are also measured routinely in BGS lime burning trials (Harrison, 1992). Decrepitation is determined immediately after shock-calcination of the stone. The lime product is removed from the furnace and screened on a 6.35 mm metal sieve. Undersize and oversize fractions are weighed, and decrepitation expressed as percentage weight undersize. Specific surface area of lime is calculated from the single-point BET method of nitrogen adsorption using a Micromeritics Flowsorb 2300 II surface area analyser.

Results of lime burning trials

Results of lime burning trials for two samples (BST22, BST69) from the project study area are listed in Table 23 below. Additional results given by a UK Carboniferous limestone used in the commercial production of lime are included for comparison purposes. LOI values are good indicators of whether calcination has resulted in complete decomposition of limestone. For both BST22 and 69, LOI values indicate that lime produced by calcination at 950° and 1000° is under-burnt.

From the data in Scott and others and Lyon, commercial quality soft-burnt lime has a reactivity of 45-60°C and a surface area of at least 3-4 m^2/g. On the basis of these two criteria, calcination of BST22 and 69 at 1050°C produced good quality soft-burnt lime. When calcined at 1100°C, the decrease in surface area suggests that the lime produced is slightly dead-burnt. Therefore, 1050°C is likely to be the optimum calcination temperature for both BST22 and 69. No clear relationship is evident between decrepitation and calcination temperature. However, at all calcination temperatures, the decrepitation of BST22 and 69 is appreciably higher than that of the UK Carboniferous limestone (Sample C). The main conclusions of the lime burning trials have been summarized in Table 24.

Table 23. Results of lime burning trials for limestone samples (BST22, BST69) from Surat Thani, Thailand. **For purposes of comparison, results are also included for a UK Carboniferous limestone (Sample C) used for commercial lime production.**

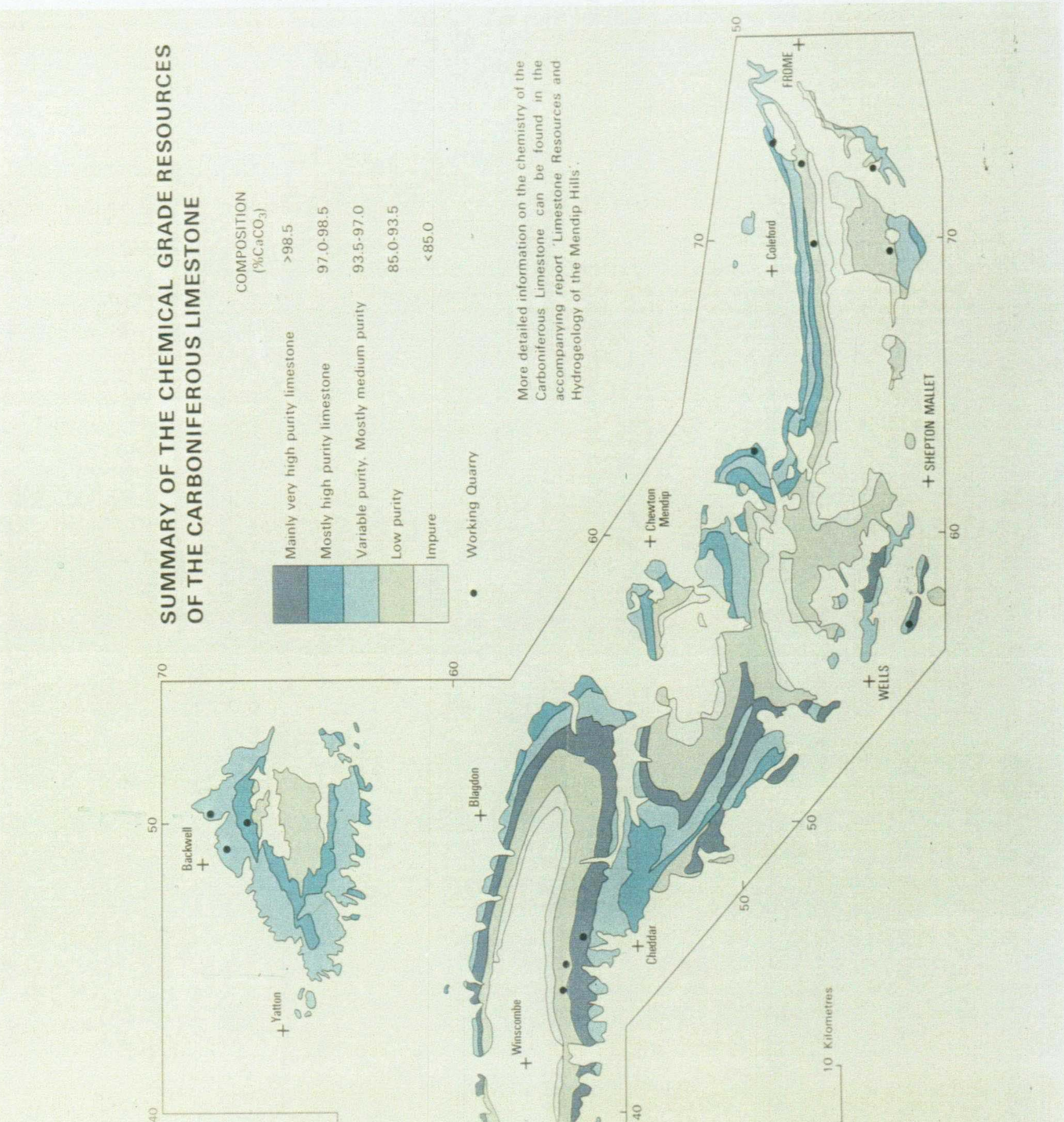
Sample	Calcination Temperature (°C)	Limestone Decrepitation (Weight %)	Lime LOI (Weight %)	Lime Reactivity (°C)	Surface Area (m2/g)
BST 22	950	2.7	17.1	27.4	3.3
BST 22	1000	8.2	2.5	55.9	5.2
BST 22	1050	4.1	0.7	64.1	4.3
BST 22	1100	8.0	0.0	42.9	3.0
BST 69	950	5.5	16.7	19.3	4.2
BST 69	1000	11.9	2.2	49.7	5.5
BST 69	1050	10.2	0.2	59.9	4.9
BST 69	1100	9.3	0.4	61.2	4.2
Sample C	950	2.4	12.7	30.5	6.1
Sample C	1000	3.1	1.1	56.1	N/A
Sample C	1050	2.0	0.2	60.6	N/A
Sample C	1100	4.3	0.0	47.2	9.2

N/A - results not available.

Table 24. Summary of types of lime formed at different calcination temperatures.

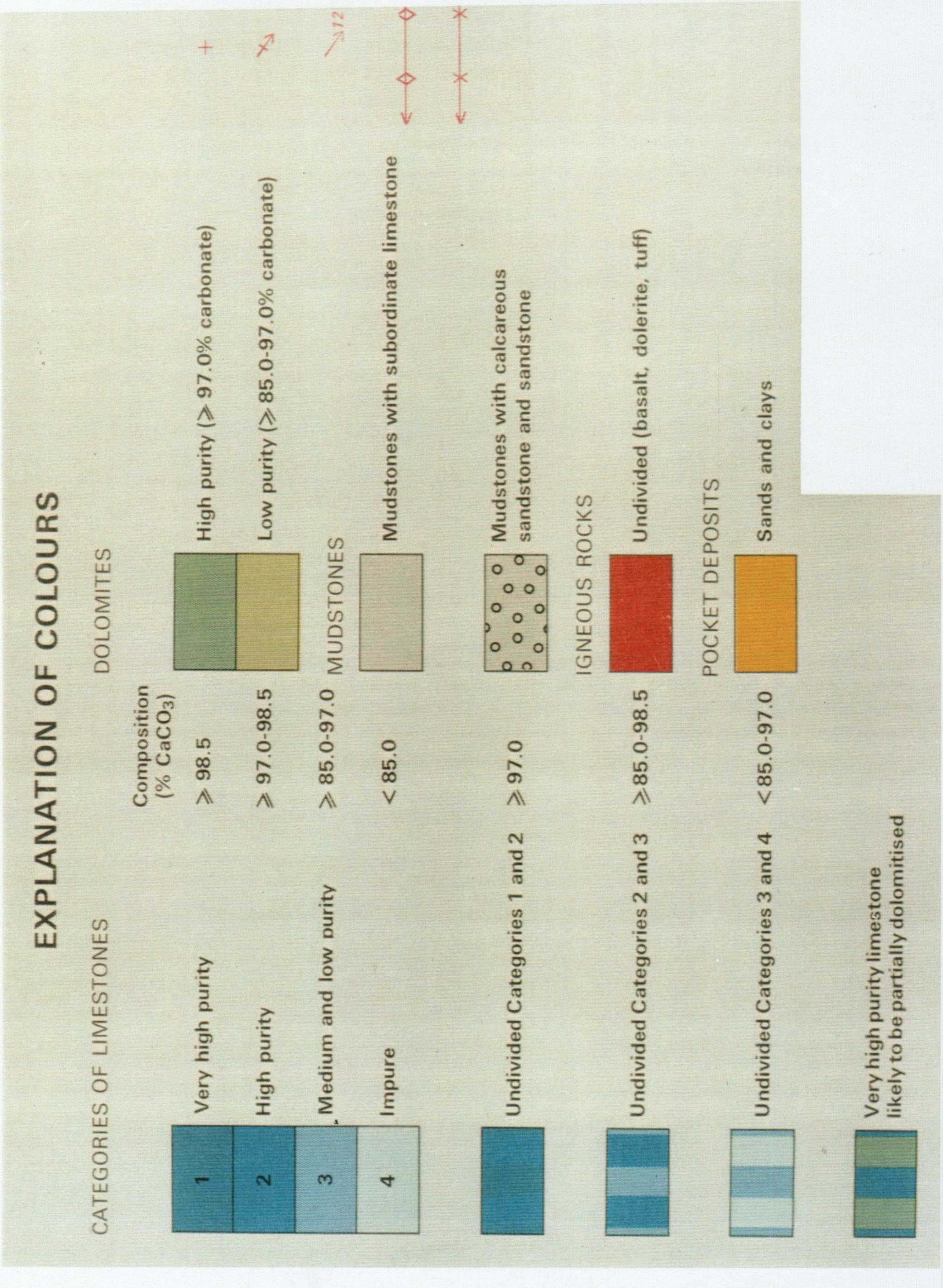
Sample	(A) Calcination Temperature (°C)	(B) Type of lime
BST 22	950	Under-burnt (high lime LOI)
BST 22	1000	Slightly under-burnt/soft-burnt (low lime LOI)
BST 22	1050	Soft-burnt (high reactivity and surface area)
BST 22	1100	Soft-burnt/slightly dead-burnt (surface area and reactivity falls)
BST 69	950	Under-burnt (high lime LOI)
BST 69	1000	Slightly under-burnt/soft-burnt (low lime LOI)
BST 69	1050	Soft-burnt (high reactivity and surface area)
BST 69	1100	Soft-burnt/?slightly dead-burnt (surface area falls)

The simple laboratory lime burning trials described in this report provide preliminary information on the suitability of a limestone for lime production. The standard theory of limestone calcination is the shrinking core model (see Appendix C). This model predicts that the diffusion and release of CO_2 from the interior of rock particles during calcination is a critical control on limestone decomposition. The wide variation in crystal size and porosity exhibited by different types of limestone have a profound influence on calcination properties due to the influence of these rock properties on decrepitation, heat transfer and CO_2 diffusion. Limestone burning rate and the time necessary for total limestone decomposition can be calculated from the results of isothermal kinetic experiments using thermogravimetric analysis (TGA). Also, because TGA experiments can be interpreted in terms of the shrinking core model, the data provided are of direct relevance to specialists in the lime industry such as chemical engineers.



More detailed information on the chemistry of the Carboniferous Limestone can be found in the accompanying report 'Limestone Resources and Hydrogeology of the Mendip Hills'.

Figure 16. Limestone resource (chemical grade) map of the Mendip Hills, UK.



EXPLANATION OF COLOURS

CATEGORIES OF LIMESTONES		Composition (% $CaCO_3$)
1	Very high purity	≥ 98.5
2	High purity	≥ 97.0-98.5
3	Medium and low purity	≥ 85.0-97.0
4	Impure	< 85.0
	Undivided Categories 1 and 2	≥ 97.0
	Undivided Categories 2 and 3	≥85.0-98.5
	Undivided Categories 3 and 4	<85.0-97.0
	Very high purity limestone likely to be partially dolomitised	

DOLOMITES

High purity (≥ 97.0% carbonate)

Low purity (≥ 85.0-97.0% carbonate)

MUDSTONES

Mudstones with subordinate limestone

Mudstones with calcareous sandstone and sandstone

IGNEOUS ROCKS

Undivided (basalt, dolerite, tuff)

POCKET DEPOSITS

Sands and clays

Figure 17. Classification scheme for reconnaissance assessment of limestone resources used on BGS maps.

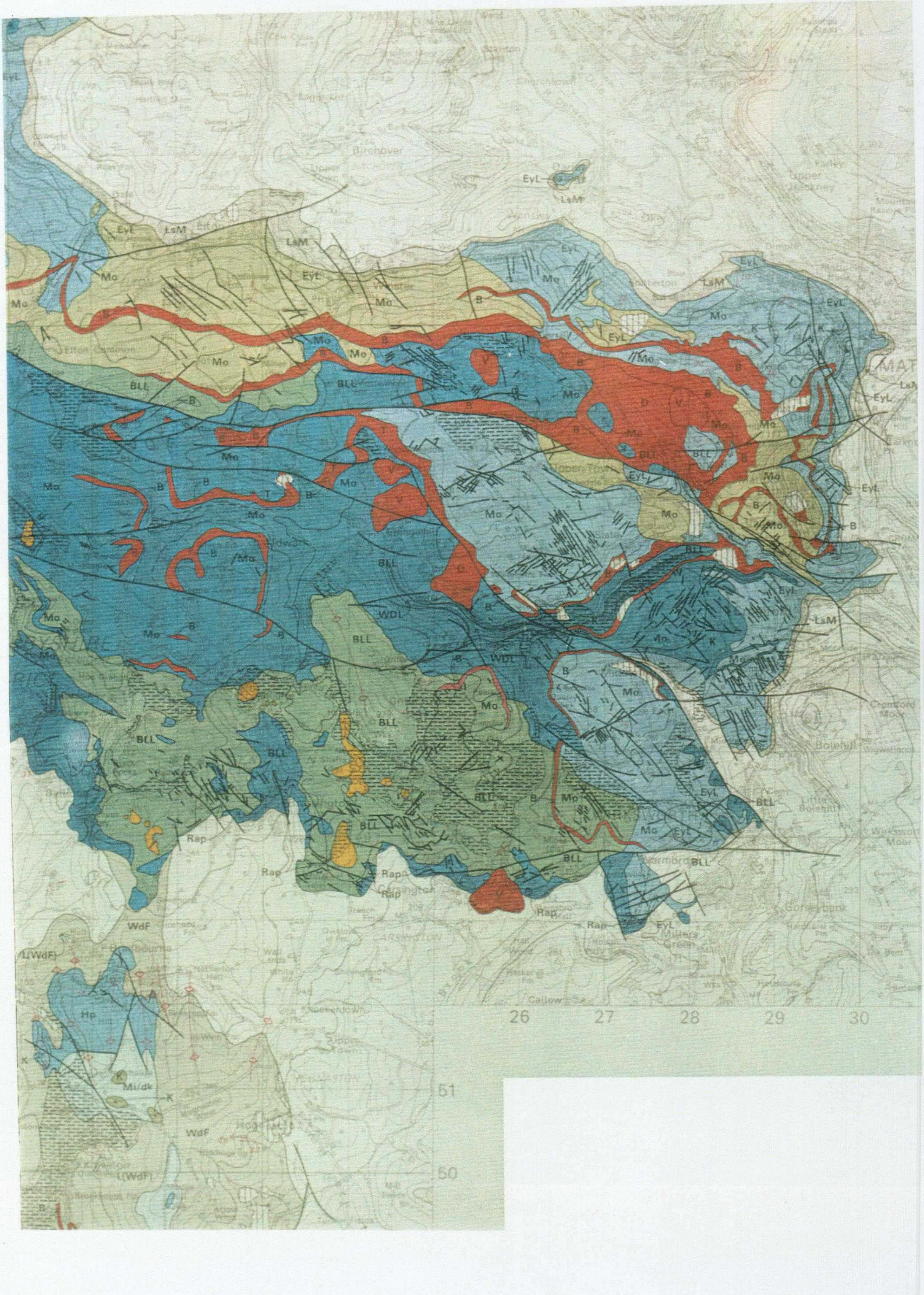


Figure 18. BGS limestone resources map (1:50 000) scale of southeastern parts of the Peak District, UK.

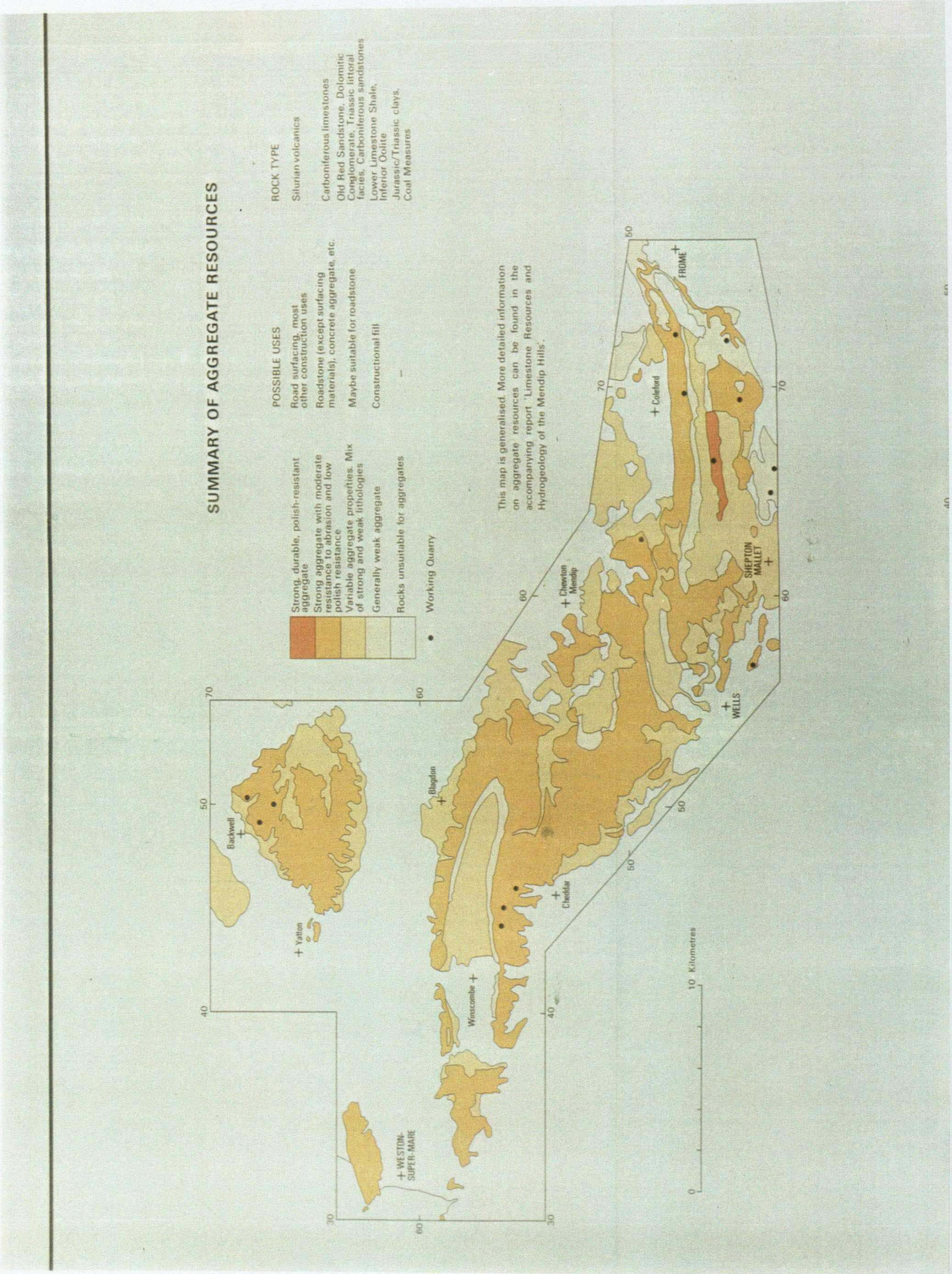


Figure 19. Limestone resource (aggregate grade) map of the Mendip Hills, UK.

5. RESOURCE MAPPING

To be able to assess limestone resources, it is essential to have a reliable geological base. Resource mapping must, therefore, be based on accurate topographic and geological maps which demonstrate the three-dimensional geological model of the deposits being studied (see 3.1). A resource map should aim to clearly illustrate the known quality of a deposit, highlighting rock properties and their variation. The degree of detail shown, however, will vary according to the purpose of the resource investigation. Investigation of limestone resources can be divided essentially into a three-tier regime.

1. Regional (reconnaissance) resource assessment - a government-funded strategic resource assessment programme to provide an overview for mineral planning prior to detailed investigation.

2. Area resource assessment - a government- or company-funded assessment tailored to a specific area, depending on existing or developing markets, administrative strategy and extraction technology.

3. Detailed resource/reserve assessment - a company-funded appraisal identifying and quantifying resources/reserves and all constraints (physical, environmental, legal, administrative, economic etc) on development.

5.1 Regional Resource Mapping

The aim of a resource map prepared for a regional resource inventory is to establish limestone resources at a strategic level by illustrating the general variation in resource quality. Such maps may also show topographic information, underlying geology and sample points. Additional information which may also be shown on the map include administrative and legislative boundaries, extraction licences and transportation routes. The recommended scale of these maps is 1:50 000, although 1:75 000, 1:100 000 or even 1:200 000 may be appropriate for reconnaissance surveys covering large areas.

Limestone resources can be defined in terms of their chemical, physical and aggregate properties. Because carbonate content is of fundamental importance when considering most industrial uses, it is recommended that limestone resource maps should illustrate its distribution. BGS has developed a simple classification of limestone resources based on calcium carbonate content (Table 5) and this system can be used to illustrate (Figure 16) various grades of limestone purity. On BGS limestone assessment maps, limestone resource information has been shown in shades of blue for limestone and green for dolomite (Figures 17 and 18). The grade shown reflects information on purity determined from rock samples together with other relevant observations (e.g. the geological consistency of the deposit).

Limestones may also be classified on the basis of their aggregate properties (aggregate strength, durability, porosity etc). BGS has been involved in several regional studies of limestone aggregate resources, both in the UK and internationally and has developed classification schemes based on aggregate test results (Table 25). The distribution of the varying resource groups can then be demonstrated on resource maps. Shades of yellow and orange have been used on BGS maps (Figure 19) to demonstrate the general aggregate properties of the rocks at, or near, surface. Uncoloured areas are underlain by mudstones, shales, marls etc.

Table 25. Classification of coralline limestone aggregates in the Kingdom of Tonga (from Harrison, 1993)

Group	Possible Uses	Description	Typical index test values	Quarry sources
1	Road surfacing aggregate. Also suitable for most construction purposes.	Relatively strong and durable. Least porous aggregate.	AIV and LAAV <32. Rel. Den. >2.3, Water Abs. <4.4%	Ahononou, Farm, Tefisi (upper), Pangaimotu
2	Base and sub-base (roadstone). Most concreting aggregate.	Moderate strength and durability. Porous aggregate.	AIV and LAAV <40. Rel. Den. >2.1, Water Abs. <8.0%	Holonga, Mat'ihoi, Pili, Longoteme, Tapuhia, Cockers
3	Generally only suitable for road sub-base or constructional fill.	Weak with low durability. Highly porous, low density.	AIV and LAAV >40. Rel. Den. <2.1. Water Abs. >8.0%	Vaipua Landing, Tefisi (lower), Fualu, Mataki'eua, South Malapo

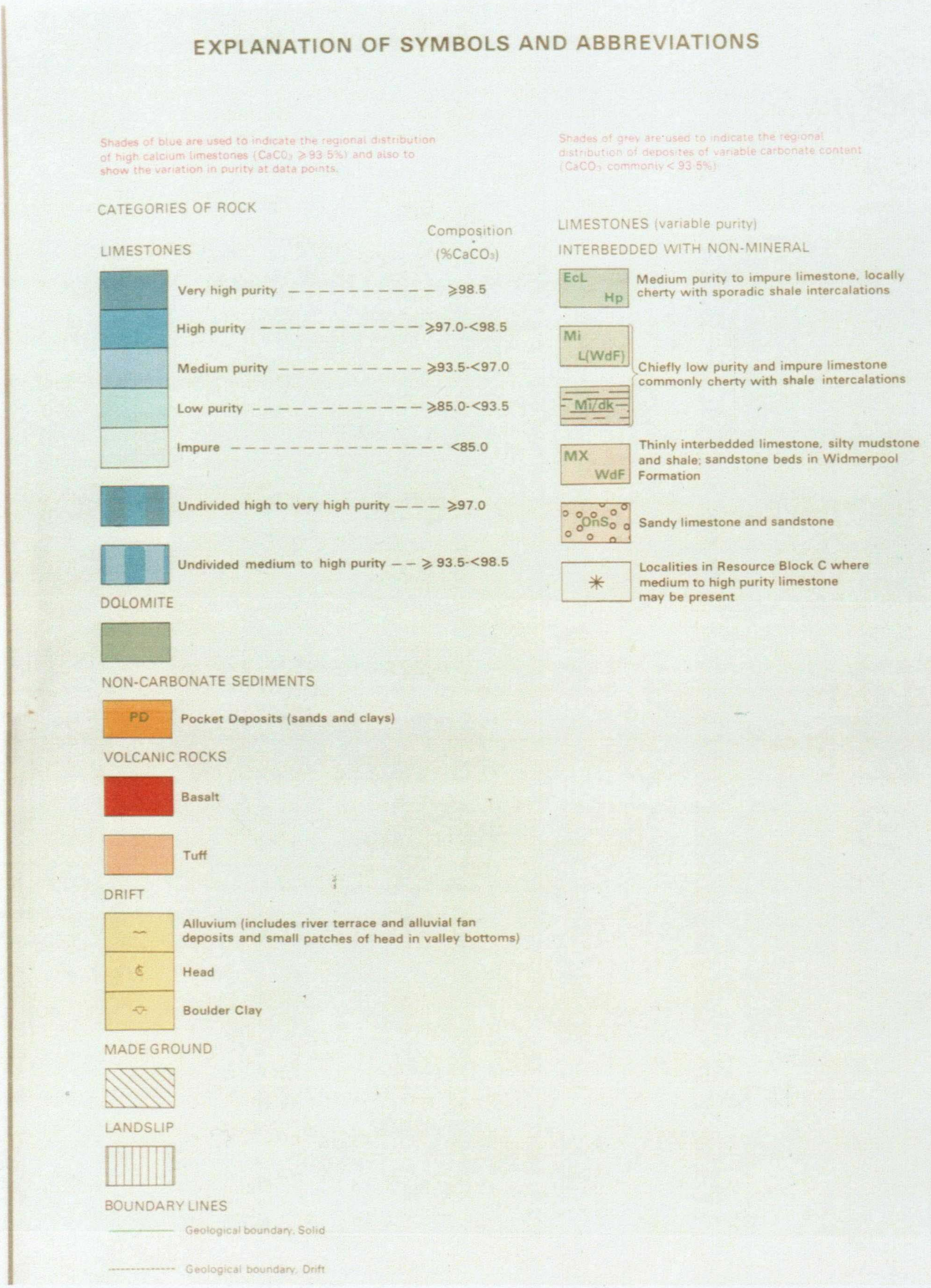
5.2 Area Resource Mapping

In order to provide more reliable information for land planning and development of limestone deposits it may be necessary to construct more detailed resource maps, based on characterisation at the 'indicated' level of resource appraisal (McKelvey, 1972). Such maps would usually be drawn at the 1:25 000 scale.

This type of resource assessment will be based on a considerable amount of sample test data and the maps will show mineral resource information in some detail (Figures 20, 21, and 22) including:

- horizontal sections, illustrating resource distribution at depth
- zones of intermixed resource quality (within uppermost 10 m)
- boundaries of superficial deposits (>3 m thick)
- tablets at sample sites showing purity and lithological variations at depth
- structural data (fold axes, faults, dips/strikes)
- mineral veins or zones of mineralisation
- resource block boundaries (the area is subdivided into blocks for descriptive purposes)

The map is an integral part of the limestone assessment report in which the aims, limitations and results of the investigation are presented with a summary of the assessment data. It contains an account of the regional and local lithostratigraphy, geological structure, chemical, physical and mechanical properties of the limestones, and a quantitative assessment of the resources found in each resource block.



EXPLANATION OF SYMBOLS AND ABBREVIATIONS

Shades of blue are used to indicate the regional distribution of high calcium limestones ($CaCO_3 \geqslant 93{\cdot}5\%$) and also to show the variation in purity at data points.

Shades of grey are used to indicate the regional distribution of deposites of variable carbonate content ($CaCO_3$ commonly $< 93{\cdot}5\%$)

CATEGORIES OF ROCK

LIMESTONES

		Composition ($\%CaCO_3$)
	Very high purity	$\geqslant 98.5$
	High purity	$\geqslant 97.0 - < 98.5$
	Medium purity	$\geqslant 93.5 - < 97.0$
	Low purity	$\geqslant 85.0 - < 93.5$
	Impure	< 85.0
	Undivided high to very high purity	$\geqslant 97.0$
	Undivided medium to high purity	$\geqslant 93.5 - < 98.5$

DOLOMITE

NON-CARBONATE SEDIMENTS

PD	Pocket Deposits (sands and clays)

VOLCANIC ROCKS

Basalt

Tuff

DRIFT

~	Alluvium (includes river terrace and alluvial fan deposits and small patches of head in valley bottoms)
	Head
	Boulder Clay

MADE GROUND

▨

LANDSLIP

▥

BOUNDARY LINES

Geological boundary, Solid

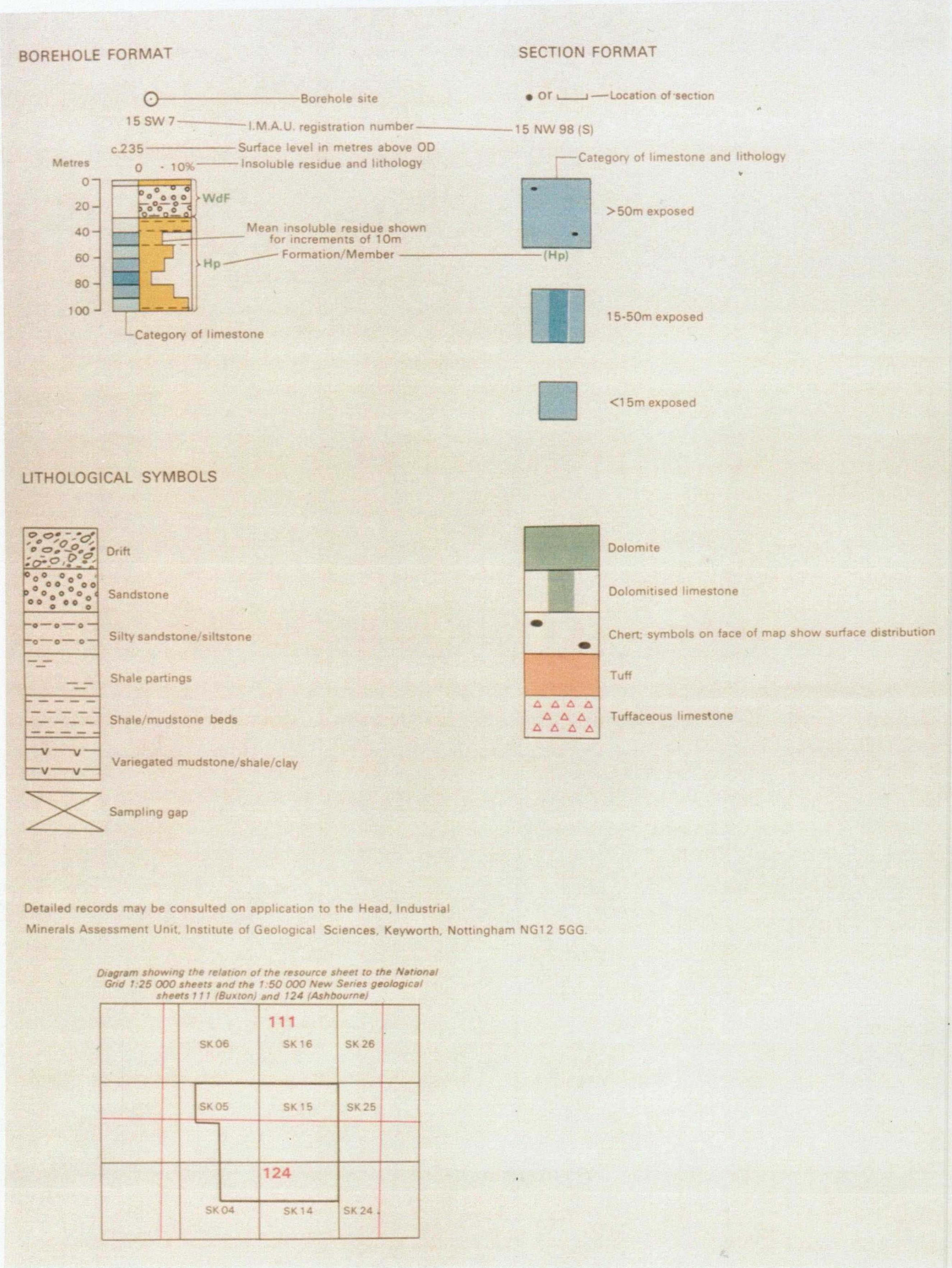
Geological boundary, Drift

LIMESTONES (variable purity)

INTERBEDDED WITH NON-MINERAL

EcL Hp	Medium purity to impure limestone, locally cherty with sporadic shale intercalations
Mi L(WdF) Mi/dk	Chiefly low purity and impure limestone commonly cherty with shale intercalations
MX WdF	Thinly interbedded limestone, silty mudstone and shale; sandstone beds in Widmerpool Formation
OnS	Sandy limestone and sandstone
✳	Localities in Resource Block C where medium to high purity limestone may be present

Figure 20. Classification scheme for detailed assessment of limestone resources used on BGS maps.



Detailed records may be consulted on application to the Head, Industrial Minerals Assessment Unit, Institute of Geological Sciences, Keyworth, Nottingham NG12 5GG.

Diagram showing the relation of the resource sheet to the National Grid 1:25 000 sheets and the 1:50 000 New Series geological sheets 111 (Buxton) and 124 (Ashbourne)

Figure 21. Borehole and sample data format shown on BGS limestone assessment maps.

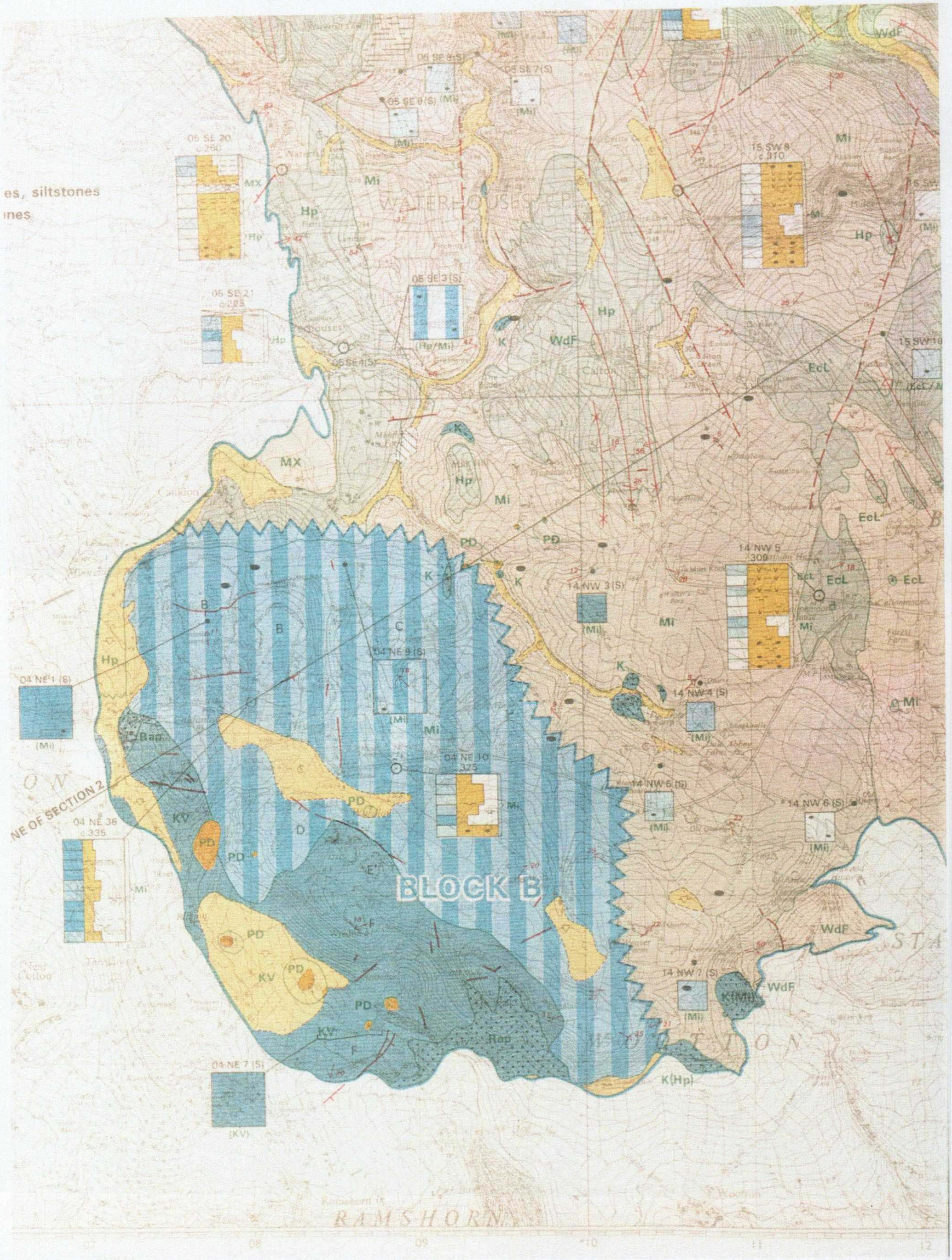


Figure 22. Part of BGS detailed limestone assessment resource map, 1:25 000 scale, Ashbourne, Derbyshire, UK.

5.3 Detailed Resource/Reserve Assessment

In the United Kingdom, and in many other countries, resource maps are frequently used by the extractive industry as supporting documentation for mineral planning applications and, in this case, the emphasis will be a detailed assessment of resources (or reserves), coupled with illustrations of the mineral working and restoration plans. Detailed site specific studies of this type may involve detailed geological mapping and extensive mineral resource exploration and characterisation studies, followed by precise reserve estimations. Additional information provided may include quarrying parameters, environmental parameters and economical parameters (both of the deposit and the social environment).

Limestone resources are usually classified on the basis of their industrial properties, such as limestone purity (Jefferson, 1983), and detailed resource maps are constructed to show the three-dimensional distribution of the various grades of limestone, in relation to topography, lithofacies and structure. Map scales typically range between 1:10 000 and 1:5000, although more detailed scales may be preferred.

5.4 Limestone Resource Mapping in Thailand

The assessment of limestone resources in the project's trial study area in Surat Thani Province, Thailand is based on the field survey which, as well as mapping lithostratigraphy, also assessed the geological factors (proportion of chert, interbedded shales, distribution of dolomite, geological structure, rock strength) which may affect resource quality. These data, together with the information from the laboratory programme (petrographic analysis, carbonate determination, chemical analysis, aggregate tests, brightness tests and lime burning trials) have been used to assess at reconnaissance scale the quality of the limestones and dolomites. All resource data (Appendix A) are archived in a project database at the Industrial Rock Resources section at the Department of Mineral Resources, Bangkok.

Table 26. Summary of limestone resources in the project's study area

Rock unit	**Lithofacies**	**Thickness**	**Resource category**
Um Luk Formation	Massive, pale grey limestones	>200 m	High purity (>97% carbonate)
Phab Pha Formation	Bedded limestones, dark grey, some chert and shale partings	200 m	Medium purity (93.5-97.0% carbonate
Thung Nang Ling and Phra Nom Wang Formations. Also Chong Lot Formation (Ordovician)	Mainly thickly bedded limestones, mid grey, chert nodules and/or argillaceous horizons	>300 m (Chong Lot). 80 m (Thung Nang Ling and Phra Nom Wang)	Low purity (<93.5% carbonate)
Permian clastic	Sandstone/mudstone with thin limestone beds	>50 m	Non-mineral
Various (Permian)	Fine and coarse grained dolomite	Variable	Dolomite (mostly >18% MgO)

Although the geological mapping and the property testing have been undertaken only at the reconnaissance level, sufficient data have been collected to allow resource categorisation (Table 26) based on carbonate content (purity). Estimation of the purity of the limestones and dolomites is based on laboratory data and on field observations of the lithofacies in quarries and natural exposures. Field determinations of rock density helped to identify and quantify dolomite in the limestone sequence.

The various resource categories are shown by colours on the project's 1:50 000 scale resource map. Uncoloured areas are underlain by alluvium which is mostly very thick (>10 m). The map demonstrates the average chemical quality of the rocks at surface. Additional data on the map face include structural information, location of quarries and sampling sites. Smaller peripheral maps have been used to show the aggregate potential of the limestones and demonstrate other information relating to land use planning. Text boxes on the map are also used to summarise geology and resources.

6. METHODOLOGY FOR RAPID ASSESSMENT OF LIMESTONE RESOURCES

The recommended field and laboratory procedures for rapidly investigating limestone resources are summarised below. Figure 20 shows a suggested flow chart for rapid regional (reconnaissance) assessment of limestone resources.

Recommended Rapid Field Procedures

1. **Rapid geological mapping** (1:50 000 scale) to identify and map carbonate units (formations) and geological structure. Estimation of geological factors affecting resource potential (e.g. proportion of chert, clay layers etc).

2. **Surface lump sampling** to provide adequate stratigraphic coverage and geographical spread at reconnaissance level of appraisal. Small (1 kg) samples of unweathered rock are adequate for most laboratory tests but larger (25 kg) samples are required for aggregate testing and lime burning trials.

3. **Rock strength testing** using the Schmidt hammer to estimate aggregate properties.

4. **Determination of dolomite** by density discrimination using the sodium polytungstate (heavy liquid) method. Alternatively the PIMA portable spectrometer may be used to determine dolomite in the field.

Recommended Rapid Laboratory Procedures

1. **Petrographic studies** of cut and acid etched rock surfaces using binocular microscopy.

2. **Carbonate staining** using the dual staining technique where dolomitisation is suggested by field studies.

3. **Systematic determination of carbonate content** by acid insoluble residue techniques. Alternatively, loss on ignition techniques may be used.

4. **Chemical analysis** of selected samples (around 1 in 10 samples) by instrumental techniques (XRF, AAS etc) or by wet chemical methods (EDTA etc).

5. **Estimation of brightness** of carbonate powders using a reflectance spectrophotometer.

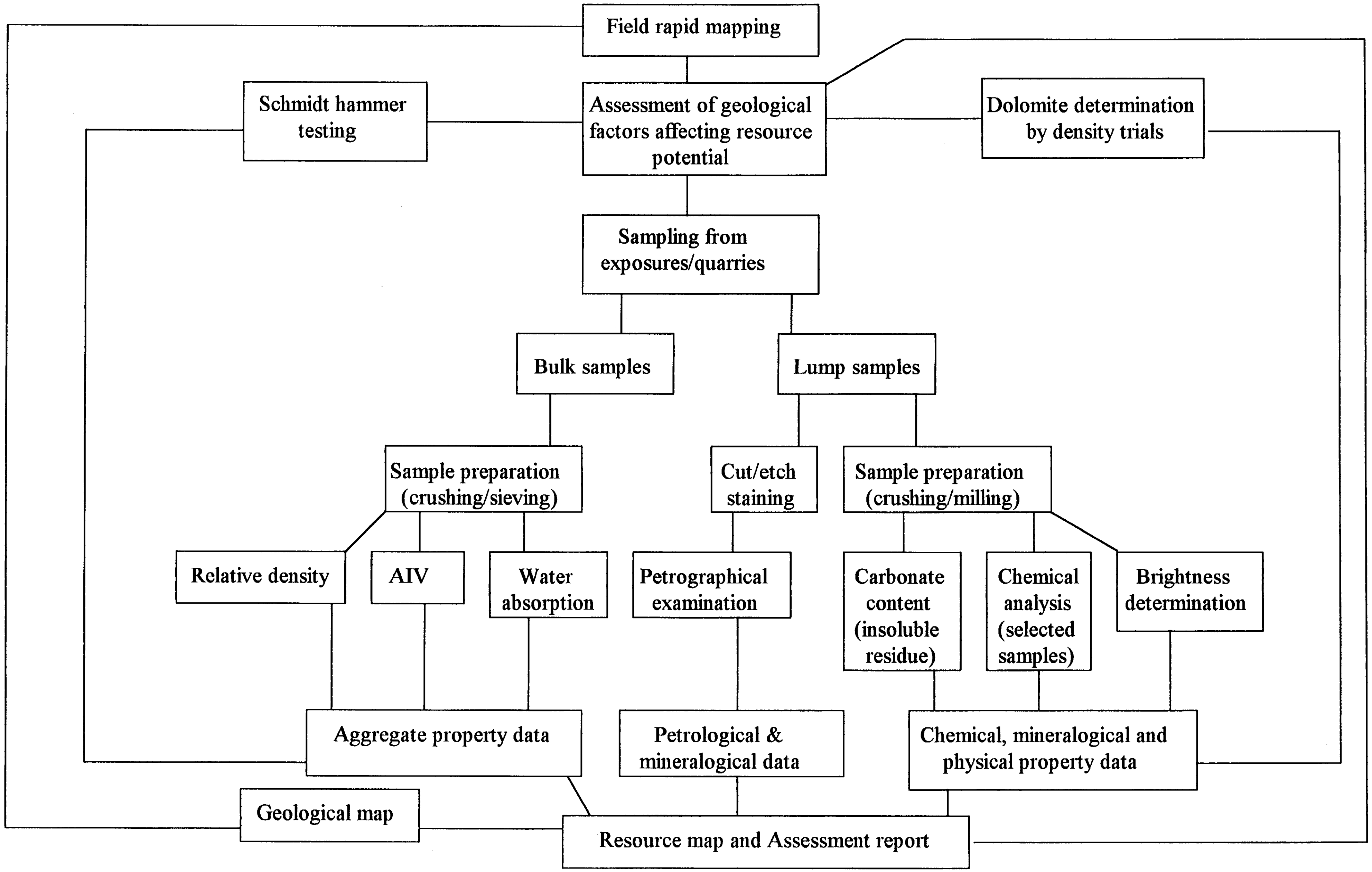
6. **Aggregate property testing** based on the AIV test (aggregate strength) and on determinations of relative density and water absorption (porosity).

Recommended Resource Mapping Procedures

1. Categorisation of resources using a classification based on carbonate content and dolomite content. The map therefore demonstrates the average chemical quality of the rocks at surface.

2. Categorisation of resources using a classification based on aggregate properties. This demonstrates the aggregate potential of the limestones.
3. 1:50 000 map scale.
4. Peripheral maps may be used to demonstrate other information relevant to limestone extraction and land use planning such as the distribution of industrial or agricultural areas, infrastructure etc. Text boxes on the map may be used to summarise geology and resources.
5. Ideally, all map data should be stored in digital format to maximise future use of the information.

Figure 20. Flowsheet for rapid reconnaissance investigation of limestone resources



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APPENDIX A. Surat Thani Project Data File

Sample Numbers																	
DMR	BGS	Formation name	Grid	TopoName	Rock Name	$CaCO_3$	$MgCO_3$	CaO_3	MgO	SiO_2	Al_2O_3	Fe_2O_3	Loss	Schmidt Hammer	AIV	Flaki-ness	Btness 470nm
SR1	BST1	Phap Pha	745116	Kuan din Daeng	dolost												
SR2		Um Luk	726109	Khao Ha	dolost	56.7	42.8	31.77	20.46	0.34	0.02	0.05					
SR3		Um Luk	724126	Khao Ton Chan													
SR4		Um Luk	740140		dolost	55.6	44.2	31.13	21.11	nil	0.01	0.05					
SR6		Um Luk	735166	Khao Nui		96.9	2.4	54.31	1.17	nil	0.01	0.03					
SR7		Um Luk	730163	Khao Chong Khok		97.9	1.1	54.87	0.52	1.05	0.06	0.07					
SR8		Um Luk	699123	Dolomite Quarry	dolost	55.7	44.0	31.21	21.01	0.40	0.03	0.05					
SR9		Clastic	605048	Khao Thung Nang Ling													
SR10		Phap Pha	668048	Khao Phra Nom Wang													
SR17		Um Luk	693006			94.0	5.2	52.69	2.50	nil	0.06	0.06					
SR21	BST7	Chong Lot	813114	Khao Chong Lot	Wkst												
SR22	BST8	Chong Lot	818091	Khao Chong Lot	l-mdst	73.1	10.8	40.96	5.15	9.57	5.29	1.02	37.91				31.9
SR23-1	BST9	Phra Nom Wang	673048	Khao Phra Nom Wang	wkst	94.1	2.8	52.72	1.32	1.27	0.12	0.25	42.80				50.9
SR23-3	BST10	Phra Nom Wang	673048	Khao Phra Nom Wang	wkst	59.3	8.3	33.25	3.96	30.48	1.44	0.83	29.91				58.7
SR23-4	BST11	Phra Nom Wang	673048	Khao Phra Nom Wang	wkst	93.4	0.9	52.34	0.43	4.56	0.24	0.13	41.54				53.4
SR23-5	BST12	Phra Nom Wang	673048	Khao Phra Nom Wang	wkst	78.5	0.8	43.99	0.37	18.07	1.81	0.23	34.81				54.2
SR23-6	BST13	Phra Nom Wang	672047	Khao Phra Nom Wang	wkst	95.1	1.1	53.28	0.52	3.70	0.09	0.11	42.22				52.4
SR23-7	BST14	Phra Nom Wang	672047	Khao Phra Nom Wang	dolost	64.2	31.8	35.98	15.22	1.18	0.09	0.24	44.86				60.9
SR23-8	BST15	Phra Nom Wang	672047	Khao Phra Nom Wang	dolost												
SR23-9	BST16	Phra Nom Wang	672047	Khao Phra Nom Wang	gnst	97.6	0.6	54.70	0.28	0.13	-	0.03	43.15				81.6
SR23-10	BST17	Phra Nom Wang	672047	Khao Phra Nom Wang	gnst	98.4	0.4	55.13	0.19	-	0.01	0.04	43.03				81.4
SR23-11	BST18	Phra Nom Wang	672047	Khao Phra Nom Wang	bdst	97.2	0.4	54.47	0.19	0.07	0.01	0.02	42.95				83.7
SR23-12	BST19	Um Luk	672047	Khao Phra Nom Wang	bdst	97.3	0.5	54.54	0.26	0.01	0.01	0.03	42.70				82.4
SR23-13	BST20	Um Luk	672047	Khao Phra Nom Wang	pkst	98.3	0.4	55.06	0.19	0.13	0.01	0.04	42.94				78.7

Sample Numbers																	
DMR	BGS	Formation name	Grid	TopoName	Rock Name	$CaCO_3$	$MgCO_3$	CaO_3	MgO	SiO_2	Al_2O_3	Fe_2O_3	Loss	Schmidt Hammer	AIV	Flakiness	Btness 470nm
SR23-14	BST21	Um Luk	672047	Khao Phra Nom Wang	pkst	98.3	0.4	55.07	0.17	0.01	0.01	0.03	43.15				82.
SR23-9-1	BST22	Phra Nom Wang	672047	Khao Phra Nom Wang													
SR25	BST23	Phap Pha	612076	Khao Thung Nang Ling	wkst	77.2	1.0	43.25	0.46	18.93	0.42	0.45	34.86	62	21	42	40.
SR26	BST28	Phra Nom Wang	613120	Khao Yom Doi	wkst	93.0	1.1	52.09	0.53	6.03	0.19	0.12	41.21	57	26	42	46.
SR27	BST30	Um Luk	658192	Wat Khao Tham	wkst	96.3	0.6	53.97	0.31	1.82	0.17	0.05	42.78	54	27	32	64.
SR28	BST25	Um Luk	583087	Khao Na Yai Un	dolost	61.4	37.8	34.40	18.05	0.49	0.02	0.06	46.34	60	29	25	66.
SR29	BST24	Thung Nang Ling	607067	Khao Thung Nang Ling	pkst												
SR30	BST26	Phra Nom Wang	598107	Khao Mai Dang	l-mdst	96.4	1.6	54.03	0.77	1.22	0.18	0.12	43.26	54			49.
SR31	BST29	Thung Nang Ling	647130	Khao Thong Lang	dolost	58.1	41.0	32.57	19.58	0.14	0.11	0.11	46.68	63			40.
SR32	BST31	Um Luk	563212	Khao Phra Nim	dolost									65			
SR33	BST32	Um Luk	604157	Khao Ngam	dolost	57.1	42.2	31.98	20.16	0.10	0.04	0.06	46.89	0	33	24	6
SR34	BST33	Um Luk	602152	Khao Ngam	dolost												
SR35	BST34	Um Luk	603164	Khao Noi	pkst	96.6	1.7	54.11	0.79	0.92	0.17	0.15	43.36	57	23	37	47.
SR36	BST35	Um Luk	606165	Khao Ngam	pkst	98.1	0.8	54.99	0.36	0.02	0.03	0.05	43.55	59	24	25	6
SR37	BST36	Um Luk	606115	Khao Mon	dolost	56.5	43.0	31.63	20.55	0.08	0.03	0.08	46.90	69			69.
SR38	BST37	Um Luk	647107	Khao Mon	dolost	56.9	42.4	31.86	20.25	0.08	0.10	0.06	47.21	66	23	16	68.
SR39	BST38	Um Luk	646106	Khao Mon	dolost												
SR40	BST39	Um Luk	599184	Khao Lik	mdst										28	27	
SR41	BST40	Um Luk	600184	Khao Lik	wkst	96.2	1.3	53.92	0.61	1.15	0.06	0.08	43.37	57			55.
SR42		Um Luk	565216	Khao Phra Nim		63.7	35.7	35.67	17.06	0.05	0.03	0.05	46.65	62			53.
SR43		Um Luk	640215	Khao Phra Nim		56.0	42.7	31.35	20.39	0.26	0.01	0.06	46.89	65			64.
SR45		Phra Nom Wang	565220	Khao Khoi										60			
SR46		Um Luk	601188	Khai Lik										58			
SR47		Um Luk	594196	Khao Thewada Bon		98.2	1.0	55.04	0.49	0.17	0.08	0.06	43.56	0			63.
SR48	BST41	Phap Pha	640155	Khao To		85.8	4.3	48.07	2.07	5.72	1.41	0.64	40.84	54	23		48.
SR49	BST42	Phap Pha	640157	Khao To		61.4	36.4	34.42	17.40	1.09	0.68	0.34	46.11	59			3
SR50		Thung Nang Ling	640144			56.7	42.7	31.75	20.39	0.07	0.06	0.09	47.15	62			59.

Sample Numbers																	
DMR	BGS	Formation name	Grid	TopoName	Rock Name	$CaCO_3$	$MgCO_3$	CaO_3	MgO	SiO_2	Al_2O_3	Fe_2O_3	Loss	Schmidt Hammer	AIV	Flaki-ness	Btness 470nm
SR51		Phap Pha	643133	Khao Liu		54.8	44.3	30.68	21.17	0.31	0.19	0.11	46.93	63	28		3
SR52	BST57	Phap Pha	639135	Khao Liu		82.3	9.3	46.10	4.45	6.47	0.80	0.34	40.93	56	24	34	25.
SR53	-	Um Luk	640133	Khao Liu		54.8	44.3	30.71	21.16	0.33	0.08	0.09	47.04	65			44.
SR53-1	BST55	Phap Pha	640133	Khao Liu		55.5	43.5	31.07	20.81	0.58	0.13	0.19	46.93	0			
SR53-2	BST56	Phap Pha	640133	Khao Liu		54.7	44.2	30.65	21.15	0.34	0.28	0.11	47.00	0			
SR54	-	Um Luk	650099	Khao Chong Niang		98.6	1.1	55.22	0.52	0.06	0.02	0.05	43.87	57			55.
SR55		Um Luk	640086	Khao Chong Niang		98.5	0.8	55.21	0.36	0.04	0.02	0.03	43.76	60			56.
SR56		Um Luk	634091	Khao Chong Niang		98.8	0.4	55.37	0.21	0.02	0.02	0.02	43.72	58			76.
SR57	-	Um Luk	640071	Khao Suan Tra		98.8	0.2	55.34	0.11	0.04	0.02	0.02	43.62	58			82.
SR58	BST54	Um Luk	644059	Khao Suan Tra										60			
SR60		Phap Pha	640065	Khao Suan Tra		90.7	0.7	50.81	0.35	7.95	0.21	0.11	40.22	0	22	36	3
SR61	BST53	Phap Pha	636069	Khao Suan Tra		98.5	0.7	55.19	0.33	0.28	0.07	0.05	43.49	59			62.
SR62	-	Um Luk	578045	Wat Khao Nang Phao		98.1	0.8	54.98	0.37	0.35	0.05	0.02	43.43	58			64.
SR63	-	Um Luk	632049	Khao Fa Pha										59			
SR64	-	Um Luk	632048	Khao Fa Pha		54.7	44.9	30.67	21.45	0.13	0.03	0.07	47.39	64	18	31	68.
SR65	-	Um Luk	633044	Khao Fa Pha		0.0	0.0							63			
SR66	-	Um Luk	581111	Khao Nom Long		54.8	44.6	30.68	21.34	0.09	0.02	0.08	47.20	64			48.
SR67	-	Um Luk	585089	Khao Na Yai Un										60			
SR68	-	Um Luk	574087	Khao Na Yai Un										60			
SR69	-	Um Luk	585054	Khao Na Yai Un										53			
SR70	-	Um Luk	608157	Khao Ngam										63			
SR71	-	Um Luk	606157	Khao Ngam		98.1	1.4	54.98	0.65	0.07	0.04	0.06	43.88	59			63.
SR72	-	Phra Nom Wang	599178	Khao Lik		96.1	1.7	53.85	0.83	1.19	0.26	0.19	43.23	56			3
SR73	-	Um Luk	607162	Khao Ngam		57.9	41.5	32.45	19.83	0.06	0.03	0.04	47.19	63	31	23	68.
SR74	BST50	Phap Pha	608083	Khao Phap Pha										58			
SR75	BST51/52	Phap Pha	610083	Khao Phap Pha		97.5	1.0	54.65	0.48	0.90	0.20	0.16	43.25	59	23	22	
SR76	-	Um Luk	647111	Khao Mon		56.3	43.3	31.56	20.71	0.00	0.01	0.04	47.69	61			73.
SR77	-	Um Luk	645096	Khao Chong Niang		56.2	42.3	31.50	20.22	0.16	0.06	0.07	47.23	68			65.
SR78	-	Phap Pha	607058	Khao Thung Nang Ling		0.0	0.0							56			
SR79	-	Phap Pha	612063	Khao Thung Nang Ling		97.0	2.2	54.36	1.07	0.41	0.21	0.08	43.60	55			56.
SR80-1	BST59/46	Thung Nang Ling	608067	Khao Thung Nang Ling	gnst									57	21	37	

Sample Numbers		Formation name	Grid	TopoName	Rock Name	$CaCO_3$	$MgCO_3$	CaO_3	MgO	SiO_2	Al_2O_3	Fe_2O_3	Loss	Schmidt Hammer	AIV	Flaki-ness	Btness 470nm
DMR	BGS																
SR80-2	BST60/47	Thung Nang Ling	608067	Khao Thung Nang Ling	pkst												
SR80-3	BST61/48	Thung Nang Ling	608067	Khao Thung Nang Ling	pkst	97.3	1.2	54.50	0.56	0.55	0.27	0.13	43.34	0			67.
SR80-4	BST62/49	Thung Nang Ling	608067	Khao Thung Nang Ling	pkst									0			
SR81	-	Thung Nang Ling	608067	Khao Thung Nang Ling										54			
SR82	BST58	Phra Nom Wang	612117	Khao Yom Doi		94.3	0.9	52.83	0.41	3.54	0.14	0.29	41.92	0	26	40	
SR84	-	Um Luk	641085	Khao Chong Niang										53			
SR85	-	Phra Nom Wang	642088	Khao Chong Niang		98.7	0.8	55.30	0.40	0.16	0.01	0.02	43.45	62	27	36	56.
SR86	-	Um Luk	645090	Khao Chong Niang		98.4	0.8	55.12	0.40	0.31	0.12	0.05	43.41	54			59.
SR87	BST43	Phap Pha	639155	Khao To													
SR88	BST44/45	Phap Pha	639154	Khao To		55.4	44.0	31.02	21.01	0.53	0.09	0.13	47.01	0	21	29	
SR89			607067	Khao Thung Nang Ling													
SR90																	
SR91																	
SR92		Phap Pha	607082	Khao Phap Pha		96.0	1.5	53.80	0.74	1.54	0.14	0.17	42.94	0			
SR93		Phra Nom Wang	636069	Khao Suan Tra													
SR94	BST54	Um Luk	644058														
SR95																	
SR96			612116														
SR97		Phra Nom Wang	587106	Khao Mai Dang		95.4	1.4	53.48	0.69	2.14	0.14	0.19	42.75	0			
SR98		Phra Nom Wang	628991	Khao Nom Tro		96.3	0.8	53.94	0.38	1.96	0.11	0.14	42.79	0	26	32	
SR99		Um Luk	625010	Khao Nom Tra		67.6	32.6	37.87	15.60	0.07	0.05	0.02	46.49	0			
SR100	BST65	Phap Pha	673044	S-Khao Phra Nom Wang	dolost	56.3	42.3	31.54	20.22	0.73	0.43	0.19		51			
SR100	BST66	Phap Pha	673044	S-Khao Phra Nom Wang	dolost	0.0	0.0							0			
SR100-1	BST67		673044	S-Khao Phra Nom Wang	dolost	56.6	42.3	31.73	20.20	0.67	0.38	0.31		0	32	24	
SR101-2	BST68		692045	Khao Na Ta Chuai	pkst	0.0	0.0							65			
SR101-1	BST69		692045	Khao Na Ta Chuai	gnst	99.4	0.2	55.68	0.10	<0.01	0.10	0.10		0			

Sample Numbers																	
DMR	BGS	Formation name	Grid	TopoName	Rock Name	$CaCO_3$	$MgCO_3$	CaO_3	MgO	SiO_2	Al_2O_3	Fe_2O_3	Loss	Schmidt Hammer	AIV	Flaki-ness	Btness 470nm
SR102-1	BST70	Um Luk	677018	Khao Um Luk	dolost	0.0	0.0							51			
SR102-2	BST71	Um Luk	677018	Khao Um Luk	dolost	79.4	20.0	44.47	9.54	0.23	0.24	0.17		0			
SR103	BST72	Phra Nom Wang	705069	Khao Phrik	wkst	89.3	0.4	50.02	0.19	10.29	0.10	0.17		57	27	33	
SR103	BST73	Phra Nom Wang	705069	Khao Phrik	mdst	0.0	0.0							0			
SR105	BST74	Phra Nom Wang	703048	E-Khao Na Ta Chuai	dolost	55.8	43.7	31.27	20.89	<0.01	0.08	0.15		62	22	24	
SR105-1	BST75	Phra Nom Wang	703048	E-Khao Na Ta Chuai	mdst	0.0	0.0							0			
SR106	BST76	Um Luk	706116	Khao Kap Chan	mdst	98.2	1.3	55.01	0.63	<0.01	0.12	0.10		57	24	36	
SR106-1		Um Luk	706116														
SR106-2	BST77	Um Luk	706116		dolost												
SR107	BST78	Um Luk	683120	Khao Nui	pkst	99.6	0.0	55.82	ß0.01	<0.01	0.11	0.10		56			
SR108		Um Luk	717041														
SR109	BST79	Um Luk	730023	Khao Yuan Mo	dolost												
SR110	BST80	Um Luk	731016		dolost												
SR111	BST81/82	Phap Pha	743009	Khao Sam Na	mdst	96.3	0.6	53.98	0.30	1.58	0.49	0.23		56	24	34	
SR112	BST83	Um Luk	596015	Khao Um Luk	wkst	95.1	4.4	53.28	2.12	<0.01	0.10	0.11		57	26	33	
SR112	BST84	Um Luk			wkst												
SR113		Um Luk	702990														
SR114	BST85	Um Luk	701993	Khao Chong Niang	dolost	72.3	27.3	40.51	13.03	<0.01	0.09	0.16		54	26	24	
SR116	BST86	Um Luk	711140	Khao Lak	mdst	97.5	1.7	54.65	0.80	0.05	0.43	0.13		56	24	28	
SR117	BST87	Um Luk	725153	Khao Thong Nong	dolost									36			
SR118-1	BST88	Um Luk	745124		dolost												
SR118-2	BST89	Um Luk	745124		dolost												
SR119		Um Luk	744132														
SR120	BST90	Um Luk	740139		dolost												
SR121		Um Luk	741145														
SR122	BST91	Um Luk	748163	Khao Thaeng	dolost									62			
SR123	BST92	Um Luk	728145		dolost									0			
SR124	BST93	Um Luk	762054	Khao Phan Ruak	dolost									35			

Sample Numbers		Formation name	Grid	TopoName	Rock Name	$CaCO_3$	$MgCO_3$	CaO_3	MgO	SiO_2	Al_2O_3	Fe_2O_3	Loss	Schmidt Hammer	AIV	Flaki-ness	Btness 470nm
DMR	BGS																
SR125	BST94	Thung Nang Ling	764076	Khao Sua Tai	dolost									61			
SR132		Chong Lot	810093	Khao Tham Sap		95.7	0.6	53.60	0.30	1.70	0.35	0.32	43.00				
SR155		Phra Nom Wang	639000	Khao Wai		55.4	44.8	31.05	21.41	0.12	0.04	0.10	47.08				
SR160		Phra Nom Wang	682994	Khao Nui		63.3	35.1	35.46	16.80	0.52	0.31	0.25	46.17				
SR161		Phap Pha	823045	Khao Wong		97.6	1.6	54.70	0.78	0.16	0.33	0.70	43.70				
SR162		Thung Nang Ling	804059	Khao Thaeng		57.8	41.7	32.40	19.91	0.12	0.08	0.33	47.00				
SR164		Chong Lot	788969	Khlong Khram		95.2	1.5	53.36	0.71	2.13	0.13	0.14	42.50				
SR165		Phap Pha	773053	Khao Maen		96.6	2.8	54.10	1.36	1.25	0.10	0.07	42.96				
SR166		Phra Nom Wang	751035	Khao Nui		54.4	44.7	30.50	21.36	0.22	0.02	0.06	47.49				
SR168		Um Luk	752045	Khao Phan Ruak		55.2	43.2	30.92	20.63	0.26	0.03	0.04	47.00				
SR170		Um Luk	741059	Khao Nong Rong		56.7	41.3	31.79	19.74	0.71	0.02	0.15	46.90				
SR171		Um Luk	743065	Khaom Sai Wi		56.6	41.9	31.72	20.03	0.28	0.59	0.15	46.64				
SR172		Thung Nang Ling	658957	Khao Khrok Bua		96.1	1.7	53.87	0.81	0.98	0.86	0.07	42.98				
SR173		Phap Pha	662967	Khao Krok Bua		56.5	42.0	31.64	20.06	0.31	0.02	0.05	46.99				
SR174		Phap Pha	696974	Unname		97.7	1.3	54.72	0.64	1.13	0.16	0.13	43.01				
SR175		Thung Nang Ling	715915	Khao Hin Pun		98.5	1.2	55.18	0.55	0.00	0.04	0.07	43.77				
SR176		Phra Nom Wang	664975	Khao Khrok Bua		86.5	12.4	48.49	5.95	0.10	0.03	0.06	44.46				
SR177		Thung Nang Ling	635970	Khao Atsachan		98.3	1.2	55.05	0.57	0.74	0.05	0.06	43.28				
SR178		Clastic	674949	Unname		0.0	0.0										
SR179		Thung Nang Ling	675956	Unname		96.5	0.9	54.05	0.41	1.05	0.03	0.05	42.96				
SR180		Phap Pha	677963	Unname		97.9	1.1	54.87	0.51	0.48	0.06	0.09	43.58				
SR181		Phra Nom Wang	675966	Unname		82.2	16.5	46.04	7.91	0.04	0.01	0.03	44.79				
SR182		Phra Nom Wang	669968	Khao Khrok Bua		56.8	42.3	31.81	20.20	0.07	0.03	0.06	46.97				

Sample Numbers DMR	 BGS	Formation name	Grid	TopoName	Rock Name	$CaCO_3$	$MgCO_3$	CaO_3	MgO	SiO_2	Al_2O_3	Fe_2O_3	Loss	Schmidt Hammer	AIV	Flaki-ness	Btness 470nm
SR183		Um Luk	692997	Khao Chong Niang		95.0	3.7	53.25	1.79	0.65	0.01	0.03	43.45				
SR184		Phra Nom Wang	683999	Khao Rim Ban		99.2	0.5	55.58	0.23	0.08	0.01	0.02	43.85				
SR185		Phap Pha	699966	Unname		98.2	1.0	55.01	0.50	0.62	0.05	0.10	43.82				
SR186		Phap Pha	714984	Khao Chong Khok		98.1	0.7	54.95	0.32	0.91	0.14	0.10	43.59				
SR187		Um Luk	706984	Khao Mi Lang		56.7	42.8	31.75	20.48	0.16	0.01	0.08	47.36				
SR188		Phra Nom Wang	626003	Khao Nom Tra		90.6	8.3	50.77	3.97	1.26	0.06	0.08	44.06				
SR189		Um Luk	599968	Khao Nom Phala		56.8	42.6	31.83	20.36	0.10	0.03	0.05	47.29				
SR191		Um Luk	596971	Khao Nom Phala		55.6	44.0	31.18	21.02	0.02	0.02	0.05	47.46				
SR193		Um Luk	567055	Khao Nom Phala		97.7	1.2	54.73	0.59	1.38	0.16	0.14	43.15				
SR222		Phra Nom Wang	636069	Khao Suan Tra		98.8	0.2	55.33	0.10	0.07	0.01	0.06	43.75				
SR223		Um Luk	638070	Khao Suan Tra		97.7	2.1	54.74	0.99	0.10	0.01	0.04	43.98				

APPENDIX B. FIELD TECHNIQUES

B.1 Determination of dolomite using pycnometer density method

i) Sample preparation. Grind approximately 20g of carbonate, using a small pestle & mortar, to <125 µm. If wet allow to air dry.
ii) Weigh a pycnometer bottle, plus stopper, to nearest 0.01g (using a portable digital balance). Note reading as A.
iii) Add 10g of sample to bottle, replace stopper and weigh to nearest 0.01g. Note reading as B.
iv) Add distilled water to bottle to cover sample until bottle is three quarters full. Agitate bottle by gentle shaking to release any trapped air from the sample. Top up with water until level just below brim. Replace stopper, until both the bottle and fine capillary opening in stopper are full of water. Dry the outside of the bottle and weigh to nearest 0.01g. Note reading as C.
v) Rinse out bottle and repeat iv) without sample. Note reading as D.
vi) The specific gravity of the sample is calculated as follows:

$$\text{Specific gravity (SG)} = \frac{B - A}{(B + D) - (A + C)}$$

vii) Repeat the SG determination and average (if results are within +/- 0.1 g/cm^3).

B.2 Determination of dolomite using sodium polytungstate density method

Source of sodium polytungstate
The only source at present is a company called Sometu (Falkenreid 4, D-14195, Berlin, Germany). The cost per kilogram is approximately 350 Deutsch Marks (£160) as of November 1995.
Source of density beads
The density beads for this work were purchased from the following company: Van Eck & Lurie (Pty) Ltd, P.O. Box 25937, East Rand, 1462, Republic of South Africa.
Preparation of sodium polytungstate solutions
i) Prepare a sodium polytungstate (SPT) solution of a density of approximately 2.9 g/cm^3. Place a 500 ml beaker on a magnetic stirrer (with hotplate). Add 160 ml of deionised water and simultaneously heat (approx. 50°C) and stir the water. Add 840 g of SPT to the water in small increments (approximately 50 g at a time). The SPT will have dissolved fully when the solution becomes clear.
ii) Step i) will have resulted in a solution of approx. 375 ml. Split this into three equal portions and place each into a beaker.
iii) To the first beaker add two density beads one 2.8 g/cm^3 and the other 2.85 g/cm^3. Add a small amount of deionised water (approx. 2 ml) and stir thoroughly. Continue until the 2.85 g/cm^3 density bead has sunk to the bottom of the beaker but the 2.8 g/cm^3 remains afloat. Pour this solution into an airtight plastic bottle and label 'SPT 2.8 - 2.85 g/cm^3'.
(iv) Repeat step iii) with two density beads one 2.75 g/cm^3 and the other 2.8 g/cm^3. Label the bottle 'SPT 2.75 - 2.8 g/cm^3'.
vi) Place SPT solutions, with beakers, stirring rods, plastic forceps and sample bags, into a durable plastic container.

Field trials

i) Sampling. Collect representative rock chips (~1 cm cubes), at least 5 per sample. Examine each chip in order to ensure that no non-carbonate materials and porosity / fracturing are present. Number each chip with a permanent marker pen. Collect several samples from each distinct carbonate lithology. Place chips in numbered bags. Collect 10 samples before carrying out density trials (50 sample chips).

ii) Establish a small flat area to use as a temporary field laboratory (e.g. back of Land Rover).

iii) Immerse all rock chips in 10% HCl acid for 2 - 3 seconds and then rinse in deionised water. This will remove any dust and/or dissolved calcium. Calcium combines with sodium polytungstate to form insoluble calcium polytungstate, which then precipitates and lowers the density of the solution. Dry each chip carefully (avoid removing number) and place into correspondingly numbered compartment in aluminium sample tray.

iv) Pour sodium polytungstate solution (2.8 to 2.85 g/cm^3) into plastic beaker. Check density range with beads. (if the solution is too dense add a small amount of deionised water & stir , if it is too light-weight allow some water to evaporate until it reaches the correct density range). Using tongs place the first sample chip into the solution. Gently agitate the solution to dislodge any air bubbles that may be adhering to the surface of the sample (as these may make the sample float). Record whether it sinks, floats or is suspended. If the sample sinks it has a density greater than 2.8 to 2.85 g/cm^3 and is excluded from further testing. If the sample floats it has a density lower than 2.8 to 2.85 g/cm^3 and is included in further testing.

v) Rinse the sample in deionised water, dry carefully and place back into aluminium tray. **NB** The sodium polytungstate can be recovered by evaporation of the rinse water.

vi) Repeat steps iv) and v) using a sodium polytungstate solution of 2.75 to 2.8 g/cm^3. Samples that sink have a density greater than 2.75 to 2.8 g/cm^3 but less than 2.8 to 2.85 g/cm^3 and should be excluded from further testing. Samples that float have a density less than 2.75 to 2.8 g/cm^3 and should be tested further.

vii) Repeat steps iv) and v) using sodium polytungstate solutions of 2.7 to 2.75 g/cm^3. Samples that sink have a density greater than 2.7 to 2.75 g/cm^3 but less than 2.75 to 2.8 g/cm^3. Samples that float have a density less than 2.7 to 2.75 g/cm^3.

viii) Results. The dolomite mineral content of the samples can be quantified using Table 15.

B.3 Measurement of rock strength using the Schmidt hammer

1. For testing rocks, a type N or L Schmidt hammer is used.

2. To avoid surface effects the test surface should be free of cracks and flaws and the test site should not be near rock edges.

3. Prepare (smooth) the rock surface using the carborundum block provided with the hammer.

4. Test the rock surface with the axis of the hammer horizontal. Record the rebound value.

5. Record ten rebound values from the prepared area, moving the hammer to a new spot for each test.

6. Reject the lowest five values and average the upper five. The average value is the rebound number (R).

Note: Each field reading only takes about 10 seconds, so the testing is a very rapid process. Surface preparation, particularly on hard rocks may, however, be a time consuming process.

APPENDIX C. LABORATORY TECHNIQUES

C.1 Limestone staining procedure
Potassium ferricyanide and Alizarin Red S in 1.5% HCI

1. Immerse sample in etching solution (dilute HCl at room temperature for approximately 15 seconds.
   NB: The success of the staining depends on the quality of the etch; cold solutions give poor results; weak etching gives a patchy stain; and over-etching produces a very dense stain.

2. Immerse sample in combined staining solution. This consists of 3:2 mixture of dye (0.2 g Alizarin Red S dissolved in 100 ml 1.5% HCl) and ferricyanide (2 g of potassium ferricyanide dissolved in 100 ml 1.5% HCl) for 30 - 35 seconds.
   NB: Solutions must be freshly made for each staining session.

3. Wash stained sample gently in distilled water and dry in a stream of warm air.

Staining is usefully employed on rock outcrop, sawn block or core samples, acetate peels (the peel takes up the colour of the stained surface) and thin sections. The success of staining depends on staining times, solution strength, age of reagents and temperature.

C.2 Relative density and water absorption

1. Wash the test portion (1 kg sample of 10-14 mm size chippings) to remove all traces of undersize material.

2. Immerse the sample in water (in a gas jar) for 24 hours at 15^0 to 25^0C and weigh (mass B).

3. Empty the gas jar, refill with water and weigh (mass C).

4. Place the sample on a dry cloth and allow to surface dry until visible water films are removed. This is the saturated and surface dried condition (SSD). Weigh the aggregate (mass A).

5. Place the SSD aggregate in an oven at 100^0 to 110^0 for 24 hours. Cool and weigh (mass D).

6. Relative density (oven dried) =

$$\frac{D}{A - (B - C)}$$

Relative density (saturated and surface dried) =

$$\frac{A}{A - (B - C)}$$

Apparent relative density =

$$\frac{D}{D - (B - C)}$$

7. Water absorption (%) = $\frac{(A - D)}{D} \times 100$

C.3 Los Angeles Abrasion Value (LAAV)

Test procedure for 10-14 mm sized aggregate

1. Wash the aggregate and dry in an oven at 110^0C.
2. Weigh the test sample (5000 g) - mass M_1 - and place in LAAV test machine.
3. Place the 11 balls weighing 4800 (+20 - 150 g) in the machine.
4. Replace the cover and rotate for 150 revolutions.
5. Remove the crushed material from the cylinder and wet sieve using a 1.6 mm sieve.
6. Dry the aggregate retained on the sieve in an oven at 110^0C.
7. Weigh this oversize material (M_2).
8. The LAAV = $\frac{M_1 - M_2}{M_1} \times 100$
9. The result is quoted to the nearest whole number.

C.4 Aggregate Impact Value (AIV)

An impact testing machine, as specified in BS 812, is required for this test and should be fixed to a concrete block or floor at least 450 mm thick. The test is carried out on 10-14 mm sized aggregate in a surface dry condition.

1. Place sample portion (mass A) in the 102 mm diameter x 50 mm deep hardened steel cup.

2. Fix cup firmly to base of impact testing machine.

3. Subject the sample to 15 blows from the hammer, which has a 100 mm diameter cylindrical head and a total mass of 13.5-14.1 kg, falling through 381±6.5 mm.

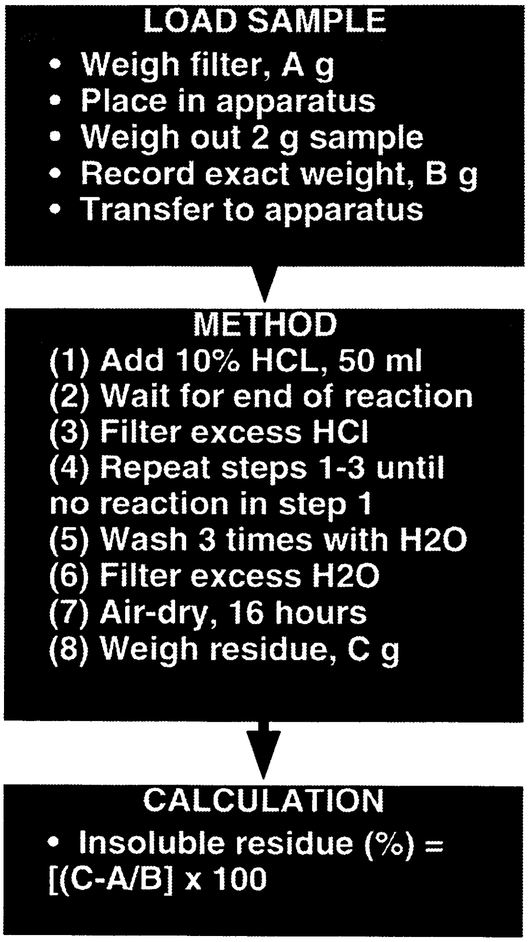
4. Remove the crushed aggregate from the cup and determine the mass of material (mass B) passing through a 2.36 mm sieve.

5. $\text{AIV} = \frac{B}{A} \times 100$

6. The test result is the mean of two determinations and is reported to the nearest whole number. A lower numerical value indicates a more resistant rock.

C.5 Determination of the acid insoluble residue of carbonate rocks, after Molnia (1974).

Method used by the British Geological Survey (BGS), UK.



LOAD SAMPLE

- Weigh filter, A g
- Place in apparatus
- Weigh out 2 g sample
- Record exact weight, B g
- Transfer to apparatus

METHOD

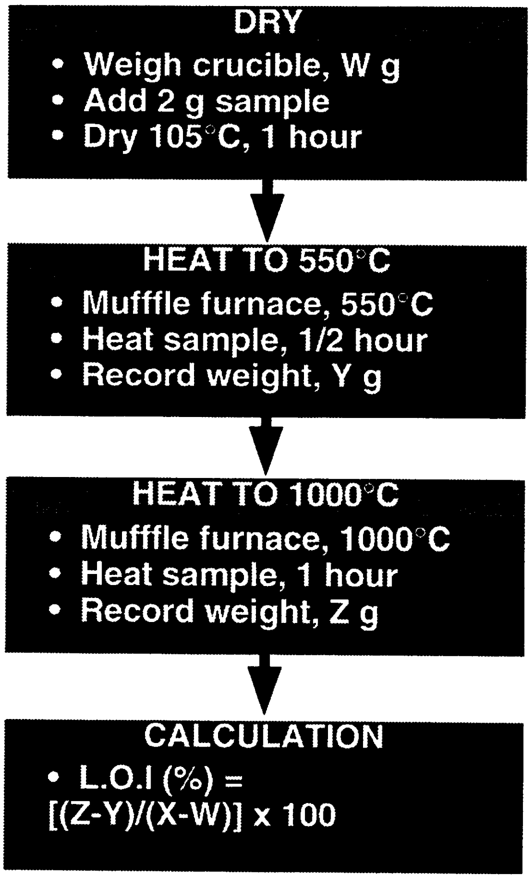
(1) Add 10% HCL, 50 ml
(2) Wait for end of reaction
(3) Filter excess HCl
(4) Repeat steps 1-3 until no reaction in step 1
(5) Wash 3 times with H2O
(6) Filter excess H2O
(7) Air-dry, 16 hours
(8) Weigh residue, C g

CALCULATION

- Insoluble residue (%) = [(C-A/B] x 100

C.6 Determination of the loss-on-ignition (LOI) of carbonate rocks, after Galle & Runnels (1960).

Method used by the British Geological Survey (BGS), UK.



DRY

- Weigh crucible, W g
- Add 2 g sample
- Dry 105°C, 1 hour

HEAT TO 550°C

- Mufffle furnace, 550°C
- Heat sample, 1/2 hour
- Record weight, Y g

HEAT TO 1000°C

- Mufffle furnace, 1000°C
- Heat sample, 1 hour
- Record weight, Z g

CALCULATION

- L.O.I (%) = [(Z-Y)/(X-W)] x 100

C.7 Determination of the calcite and dolomite content of carbonate rocks by thermogravimetric analysis (TGA).

Method used by the British Geological Survey (BGS), UK.

PREPARATION

- Load 9-10 mg of sample
- Select 10 mV range
- Variab weight to 100%
- Tare 50% of weight
- Select 5 mV range

ANALYSIS

- Run conditions:

20°C/min. heating rate
Room temp - 1100°C
50% Full scale deflection
CO2 atmosphere
2 mm/min. chart speed

MEASUREMENT

- MgCO3 weight loss, A
- CaCO3 weight loss, B

CALCULATION

- % Dolomite =
[(2Ax88.018)/184.408]x100
- % Calcite =
[(B-A)x44.009/100.088]x100

C.8 Internal standard method for determination of the calcite and dolomite content of carbonate rocks by X-ray diffraction (XRD) analysis.

Method used by the British Geological Survey (BGS), UK.

PREPARATION

- Weigh out 2g of sample
- Add 1g fluorite standard
- Micronize, 10 minutes
- Dry 105°C
- Back-load XRD mount

ANALYSIS

- Run conditions:

Analysis prog 30
31-38° two theta
0.02° step size
3 secound count time

MEASUREMENT

- Peak area (DPROC):

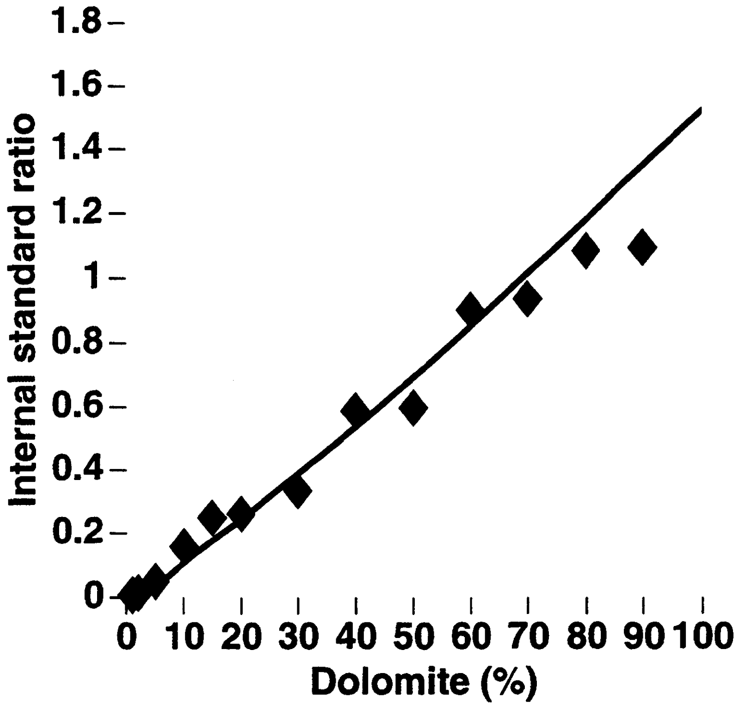
Fluorite 3.155Å, X
Calcite 3.035Å, Y
Dolomite 2.880Å, Z

CALCULATION

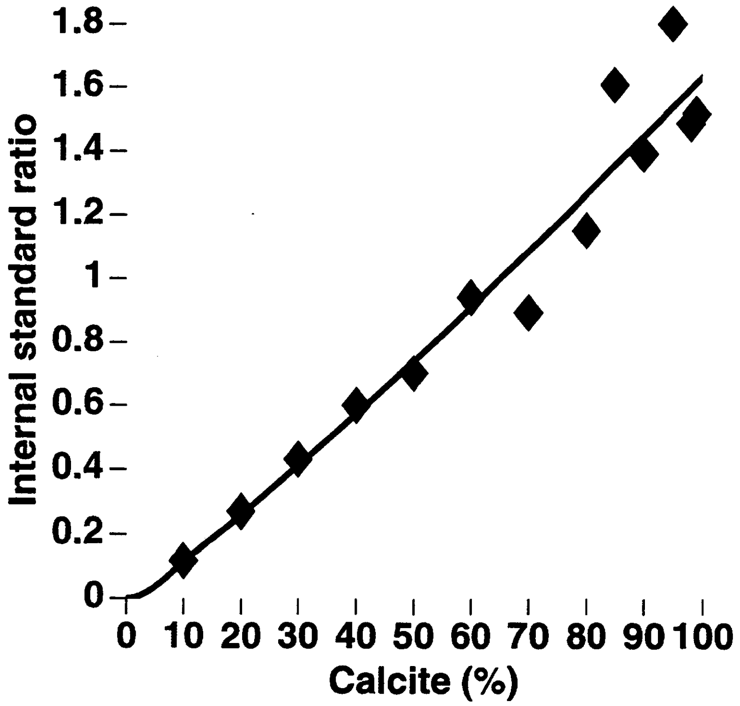
- Calculate calcite ratio = Y/X -> place in calibration equation
- Calculate dolomite ratio = Z/X -> place in calibration equation

C.9 X-ray diffraction (XRD) calibration curves for calcite and dolomite.

Method of British Geological Survey (BGS), UK.



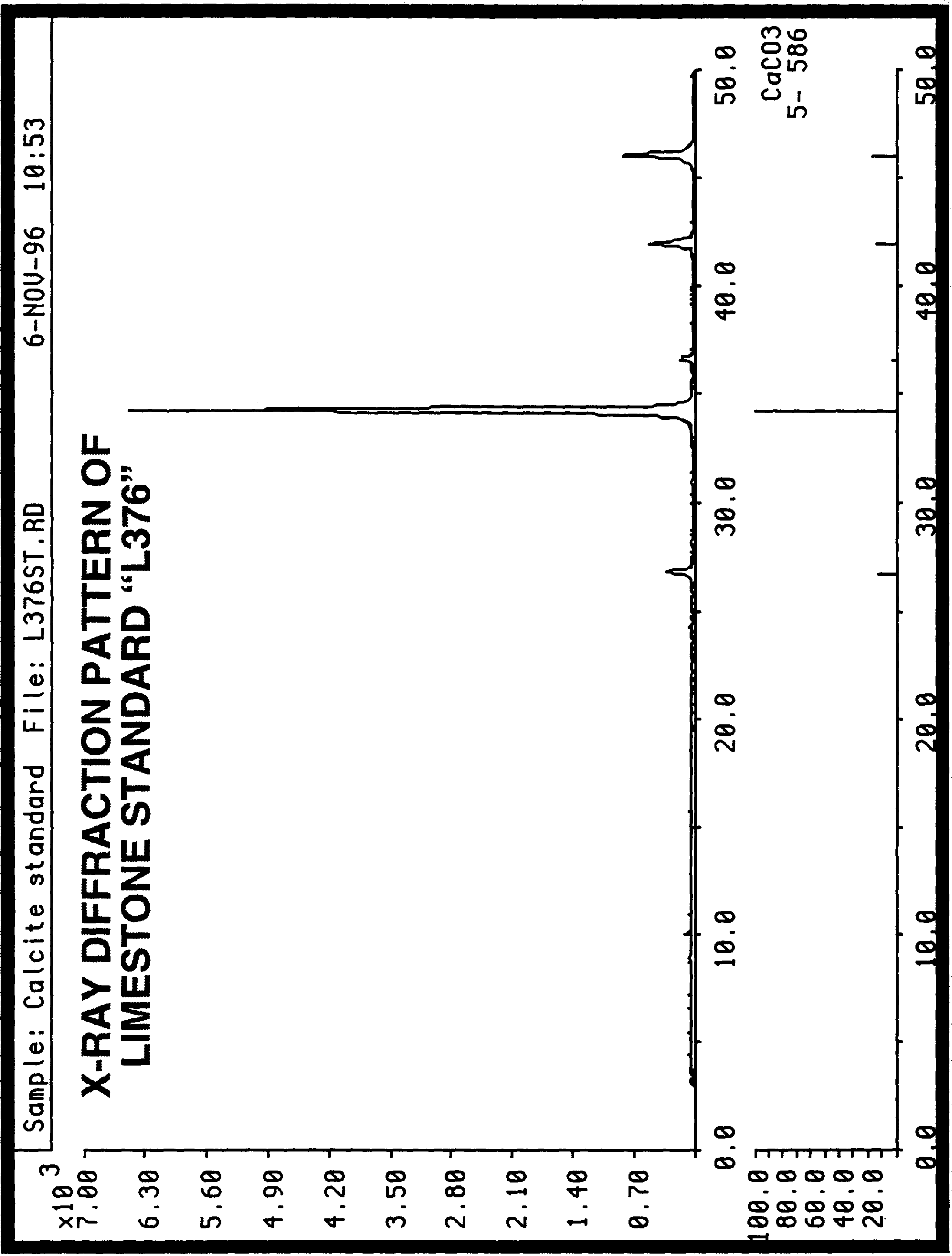
%Dolomite = 69.26459 x
(internal standard ratio^0.8824154)
R^2 = 0.9872300



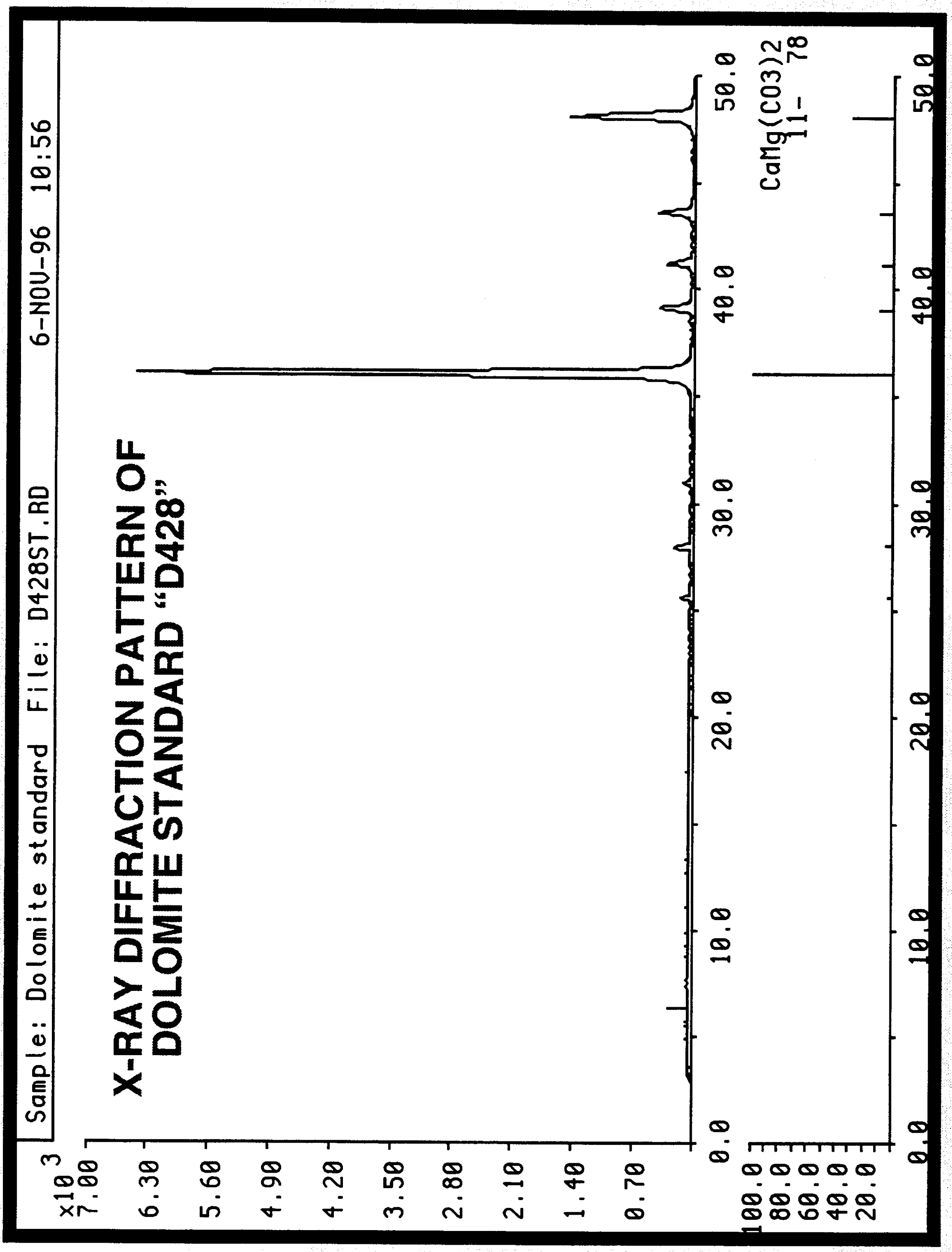
%Calcite = 65.2337 x
(internal standard ratio^0.8757794)
R^2 = 0.9847055

C.10 BGS limestone and dolomite standards

Standard	Limestone	Dolomite
BGS Lab No	376	428
Source	Bee Low Limestone	Durness Limestone
Locality	Derbyshire, England	Ullapool, Scotland
Remarks	Typically >55% CaO	?Minor vein calcite
XRD analysis	Calcite only	Dolomite, trace quartz
Particle-size:	87.5% <63 µm	96.0% <63 µm
Na2O (%)	<0.1	0.1
MgO (%)	0.3	21.9
Al2O3 (%)	<0.05	0.42
SiO2 (%)	0.36	2.59
P2O5 (%)	0.27	<0.05
K2O (%)	<0.05	0.38
CaO (%)	54.36	35.99
TiO2 (%)	<0.050	<0.050
MnO (%)	0.015	0.02
Fe2O3t (%)	0.02	0.34
V (ppm)	7	5
Cr (ppm)	Not detected	Not detected
Co (ppm)	2	3
Ba (ppm)	13	26
Sc (ppm)	Not detected	6
F (ppm)	<500	<500



X-RAY DIFFRACTION PATTERN OF LIMESTONE STANDARD "L376"



X-RAY DIFFRACTION PATTERN OF DOLOMITE STANDARD “D428”

C.11 Determination of the Ca and Mg content of carbonate rocks by atomic absorption analysis (AAS).

Method used by Department of Mineral Resources (DMR), Thailand.

MOISTURE CONTENT

- Weigh out 0.5g
- 105°C 1 hour
- Weigh
- Calculate % moisture

LOSS-ON-IGNITION (L.O.I.)

- Muffle furnace
- 1050-1100°C, 0.5 hour
- Weigh
- Calculate % L.O.I

ACID DIGESTION

- Weigh out 0.1g
- Add 10 ml, 25% HCl
- 50°C hotplate, 0.5 hour
- Add 10 ml conc. HCl
- Dilute to 250 ml
- Leave overnight

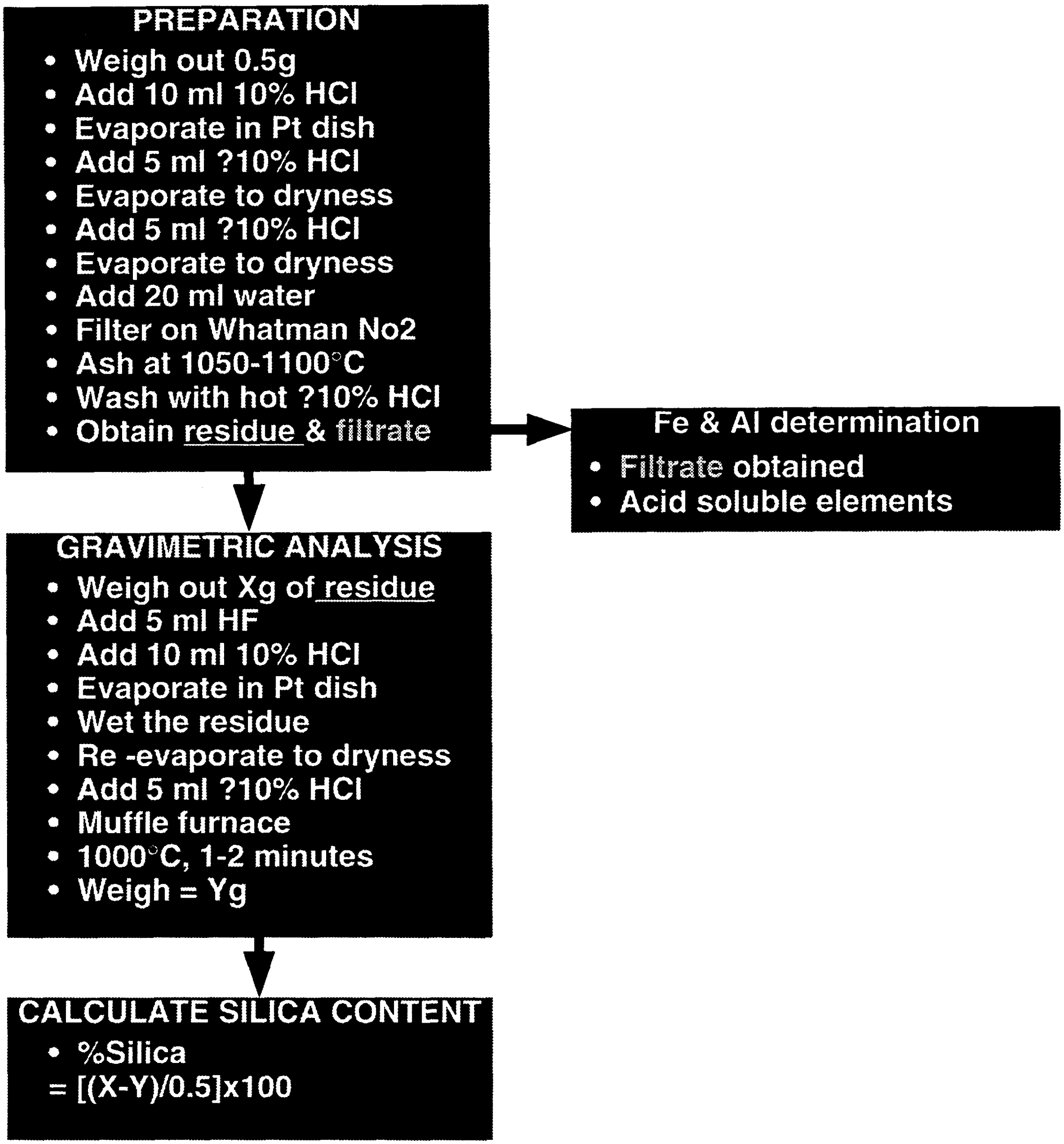
ANALYSIS

- Aliquot taken
- Diluted by factor of 10
- 30-40 sample batch
- Ca, Mg determined
- 3 days machine time
- 4 reference solutions:

(1) High Ca concentration
(2) Low Ca concentration
(3) High Mg concentration
(4) Low Mg concentration

C.12 Determination of the silica content of carbonate rocks by gravimetric analysis.

Method used by the Department of Mineral Resources (DMR), Thailand.



PREPARATION

- Weigh out 0.5g
- Add 10 ml 10% HCl
- Evaporate in Pt dish
- Add 5 ml ?10% HCl
- Evaporate to dryness
- Add 5 ml ?10% HCl
- Evaporate to dryness
- Add 20 ml water
- Filter on Whatman No2
- Ash at 1050-1100°C
- Wash with hot ?10% HCl
- Obtain residue & filtrate

Fe & Al determination

- Filtrate obtained
- Acid soluble elements

GRAVIMETRIC ANALYSIS

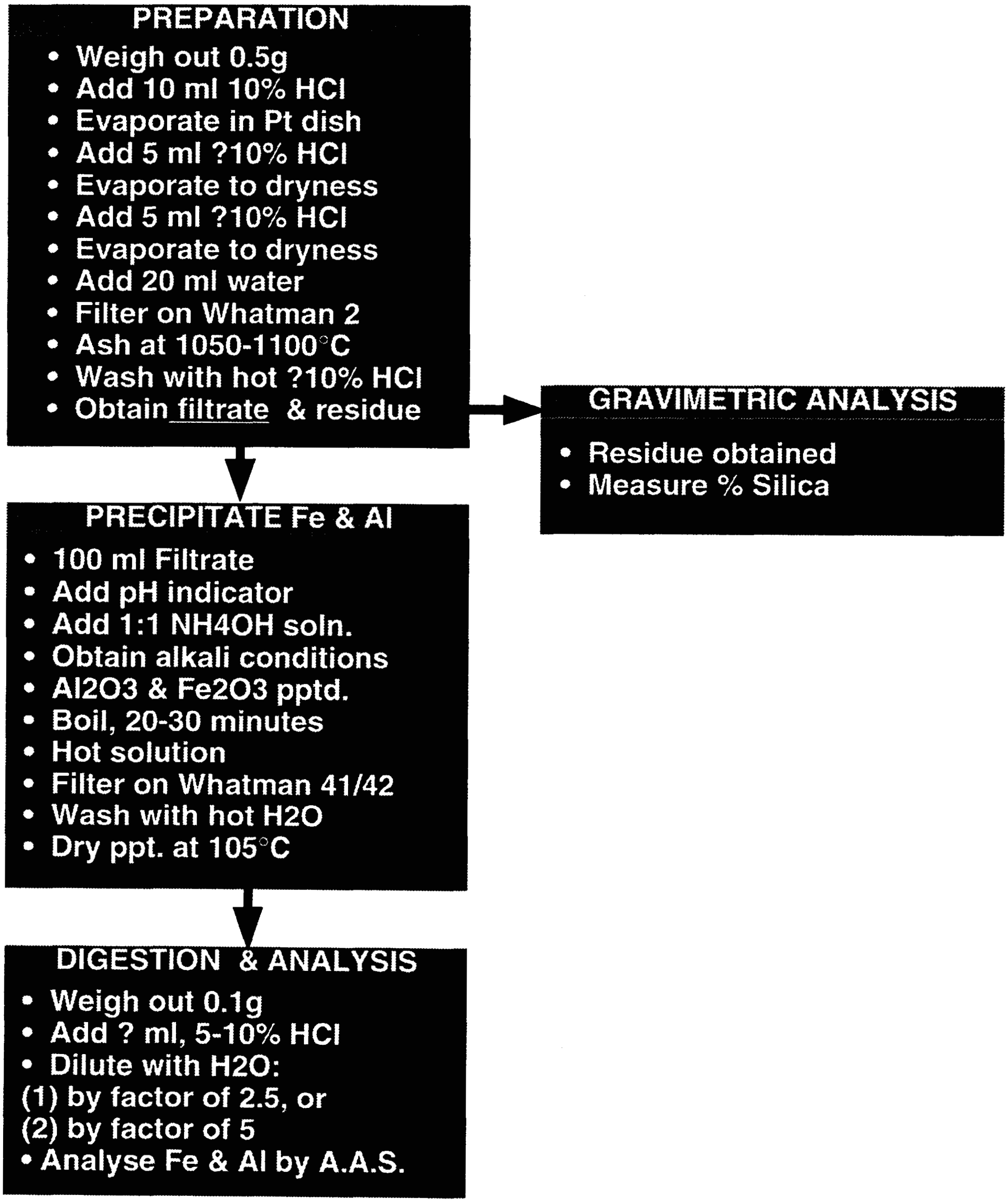
- Weigh out Xg of residue
- Add 5 ml HF
- Add 10 ml 10% HCl
- Evaporate in Pt dish
- Wet the residue
- Re -evaporate to dryness
- Add 5 ml ?10% HCl
- Muffle furnace
- 1000°C, 1-2 minutes
- Weigh = Yg

CALCULATE SILICA CONTENT

- %Silica
  = [(X-Y)/0.5]x100

C.13 Determination of the Fe and Al content of carbonate rocks by atomic absorption analysis (AAS).

Method used by the Department of Mineral Resources (DMR), Bangkok.



PREPARATION

- Weigh out 0.5g
- Add 10 ml 10% HCl
- Evaporate in Pt dish
- Add 5 ml ?10% HCl
- Evaporate to dryness
- Add 5 ml ?10% HCl
- Evaporate to dryness
- Add 20 ml water
- Filter on Whatman 2
- Ash at 1050-1100°C
- Wash with hot ?10% HCl
- Obtain filtrate & residue

GRAVIMETRIC ANALYSIS

- Residue obtained
- Measure % Silica

PRECIPITATE Fe & Al

- 100 ml Filtrate
- Add pH indicator
- Add 1:1 NH_4OH soln.
- Obtain alkali conditions
- Al_2O_3 & Fe_2O_3 pptd.
- Boil, 20-30 minutes
- Hot solution
- Filter on Whatman 41/42
- Wash with hot H_2O
- Dry ppt. at 105°C

DIGESTION & ANALYSIS

- Weigh out 0.1g
- Add ? ml, 5-10% HCl
- Dilute with H_2O:

(1) by factor of 2.5, or
(2) by factor of 5

- Analyse Fe & Al by A.A.S.

C.14 Colour (and brightness) measurement

Perception of colour is subjective and can lead to problems when attempting to define the colour of an object. The perceived colour of an object can be influenced by the light conditions under which it is observed, the sensitivity of the observers eyes, the size of the object concerned, whether it is placed in front of a bright or a dark background ("contrast effect") and the direction from which the object is observed. A colour can be classified according to its:

Hue (colour)	Hue is the term used for the classification of colour. The spectrum can be subdivided into a series of hues as follows:

Hue		Violet		Blue		Green		Yellow		Orange		Red	
Wavelength (nm)	400	-	424	-	491	-	575	-	585	-	647	-	700

Brightness (lightness)	Brightness is the light intensity of a colour. This is an indication of whether a colour is light or dark.
Saturation (purity or vividness).	Saturation is the colour density measured against white light (zero). The colour produced by the spectrum is the pure colour. Increasing the proportion of white light mixed with any hue decreases saturation e.g. red is a pure colour and pink is unsaturated red.

The brightness (otherwise referred to as 'whiteness') is a critical property of mineral products used as fillers (paint, plastic, rubber, paper, etc). The measurement of brightness is generally carried out by determining the percentage reflectance from a sample (typically a pressed-pellet or loose-mounted powder) compared to a calibration standard (commonly barium sulphate). There are several methods for determining colour, utilising a range of instrumentation (Table 27).

Table 27. Brightness measurement

Instruments	Methods
Visual	Comparison charts
Reflectance spectrophotometer	Spectral curve
Colorimeter	Colorimetric values, including CIE tristimulus (XYZ), CIELAB, etc..

Instrumentation

i) Visual : The human eye.

Advantages	Ability to rapidly discriminate subtle variations in colour, hue and lightness. Simple.
Disadvantages	Subjective, no two people have the same perception of colour. Light conditions & fatigue influence the perception of colour.

ii) Reflectance spectrophotometer

A reflectance spectrophotometer consists of a light source (directed at 45° to the surface of a sample) and a photocell detector (generally positioned normal, 90°, to the sample surface to minimise the effects of specular reflection, or gloss). The intensity of light reflected from the surface is recorded for a range of wavelengths across the visible spectrum (approximately 380 to 780 nm). Percentage reflectance values are calculated as the ratio of the reflectance from the sample to the reflectance from a calibration standard (sometimes referred to as the 'perfectly reflecting diffuser'). The standards used in most laboratories, for example calibrated ceramic tiles or barium sulphate, can be related back to the standards issued by ISO-approved laboratories.

Two types of reflectance spectrophotometer are used, the full-range spectrophotometer and the abridged spectrophotometer.

The **full-range spectrophotometer** uses a source of unfiltered white light. The light reflected from the sample is passed through an optical prism (or diffraction grating) where it is split into light of different wavelengths (a process known as spectral dispersion) and the intensity of the light is measured across the spectrum, typically in 10 nm increments (known as 'bandwidths').

Widely used examples include : "Chromagraph" (Durst, Italy); "Luci 100" (Dr. Lange, Germany); "Spectrophotometer CM series" (Minolta, USA); "Microflash series" & "Elrepho 3000 series" (both Datacolour International, Switzerland).

The **abridged spectrophotometer** uses a light source which is filtered prior to exposure to the sample surface. In the EEL spectrophotometer (as used by BGS, UK and many other laboratories) a 'filter wheel' is used. This contains 9 different filters as shown in Table 28.

Table 28. Abridged spectrophotometer filter wheel wavelengths

Filter no.	Wavelength	Filter no.	Wavelength
601	426 nm	606	580 nm
602	470 nm	607	600 nm
603	490 nm	608	660 nm
604	520 nm	609	684 nm
605	550 nm		

Each filter produces light of a relatively broad bandwidth (the wavelengths quoted are the peak transmittance) which may vary from 35 - 85 nm depending upon the filter used. Additional filters can be used to determine primary colour reflectance.

Table 29. Summary characteristics of full-range and abridged spectrophotometers

Instrument	Advantages	Disadvantages
Full-range	Rapid measurement (from < 1 second to 3 seconds) Narrow bandwidths which produce accurate spectral curves (therefore used mainly in research). Can measure metamerism (difference in colour due to light source variation)	Expensive Not readily portable
Abridged	Relatively inexpensive. Portable.	Relatively slow measurement (up to 30 minutes). Broad bandwidths which produce less accurate spectral curve (mainly used to give broad indication of brightness)

iii) Colorimeter

A colorimeter is similar in many respects to a reflectance spectrophotometer but only a limited range of wavelengths are measured. Typical examples include the "Chroma Meter" colorimeter series (Minolta) and the "577 Reflection Meter" (Photovolt, USA- as used by DMR, Thailand). Each contains three photocells, designed to measure the light reflected at the wavelength of a primary colour, 440 nm (blue), 550 nm (green) and 590 nm (red). The bandwidths of the 577 colorimeter are broad, 540 - 660 for red, 450 - 620 for green and 410 - 490 for blue. This is claimed to allow greater sensitivity of measurement.

Advantages	Rapidity of measurement (less than 1 second to 3 seconds) Most colorimeters are small and portable, enabling their use for the measurement of colour difference for quality control in production and inspection.
Disadvantages	Restricted to measurement of colorimetric values.

Methods of measurement

i) Comparison charts (mainly for visual determination)

The Munsell Renotation system uses a colour chart to give any given colour a letter / number combination (H V/C) in terms of hue (H), value (V) and chroma (C).

Advantages	Simple to operate.
Disadvantages	Requires experienced operator. Notation does not allow ready comparison between samples of different colours.

ii) Spectral Curve

The percentage reflectance values determined using a reflectance spectrophotometer are plotted against their respective wavelengths to produce a spectral curve. The ISO brightness (percentage reflection at 457 nm) and yellowness (difference between the percentage brightness at 570 nm and 457 nm) can be determined from the spectral data. Munsell renotation can also be generated.

Advantages	Useful to display all spectral data (only method which demonstrates the response at the high wavelength - red - end of the spectrum). Brightness, yellowness and colorimetric values can be derived from the spectral curve.
Disadvantages	The spectral curve itself is not as convenient as a numerical recording of the specification of a colour. Can require lengthy preparation.

iii) Colorimetric values

Tri-colour reflectance involves the determination of the percentage reflectance values at the primary colour wavelengths (using both spectrophotometer and colorimeter). Tri-colour absorption involves the calculation of the reflection density from the tri-colour reflectance values. This is a measure of light absorption and enables the relative concentrations of the primary colours to be calculated.

The most commonly used colorimetric system is the CIE (Commission International De L'eclairage) tristimulus (XYZ) method. The tricolour reflectance values (X, red; Y, green; & Z, blue) are determined and converted to their coefficients (x, y & z) as follows:

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Z}{X+Y+Z}$$

The sum of the coefficients is 1. Therefore to define any colour it is only necessary to refer to two of the coefficients namely x & y. The x and y values can then be plotted on a chromaticity chart.

Other colorimetric systems are variations of the CIE method. The CIE L*a*b (otherwise known as CIELAB) method is currently widely used to measure the colour of objects. The chromaticity co-ordinates (a and b) and lightness (L) are plotted together. The CIE L*C*h method plots lightness (L), chroma (C) and hue (h). The Hunter lab colour space method is similar to CIELAB.

Advantages	Measures light reflected from the object using three sensors filtered to have the same sensitivity as the human eye. It is a simple test as only 3 measurements are made (which can easily be used for reference purposes). It readily allows the comparison of 2 different colours.
Disadvantages	Not as sensitive to small colour differences as the spectral curve. Equal distances on the chromaticity chart do not correspond to perceived colour differences.

C.15 Theoretical aspects of limestone calcination

The calcination reaction

Keener & Khang (1992) proposed a sequence of six steps for the decomposition of $CaCO_3$ during heating:

Summary of the calcination reaction

(1) Heat transfer from the surroundings to the surface of the $CaCO_3$ particle.
(2) Heat transfer from the particle surface to the reaction interface.
(3) Endothermic decomposition of $CaCO_3$ at the reaction interface.
(4) Formation of CaO and evolution of CO_2.
(5) Internal mass transport of CO_2 to the particle surface through pores in CaO.
(6) External mass transport of CO_2 from the particle surface to the surroundings.

For the calcination of large limestone particles and/or kiln temperatures above 900°C, heat transferral (steps 1 and 2) is the predominant rate controlling mechanism. In contrast, at lower temperatures (720-900°C), both heat transferral and mass transport of CO_2 to the particle surface (step 5) are thought to control the rapidity of calcination. However, Keener & Khang indicate that several physical and chemical processes at the reaction interface (including cracking of the solid $CaCO_3$ phase) also control the rate of limestone decomposition.

Rock properties

The production of good quality lime is dependent on the properties of the limestone raw material as well as the conditions of calcination. Early work by Hedin (1962) indicated that dense, coarsely-crystalline limestones are relatively slow-burning due to the slow outward diffusion of CO_2 and poor heat transfer. Conversely, more porous and finely-crystalline types of limestone were found to be quick-burning as CO_2 was able to diffuse rapidly outwards via natural pores and fractures. Decrepitation is a measure of the susceptibility of limestone to disintegration during calcination. Within an industrial shaft kiln, a porous bed of closely-sized limestone allows CO_2 generated by calcination to pass freely and vent to atmosphere. Decrepitation of stone within this porous bed is undesirable as it results in blockages which inhibit or prevent removal of CO_2 and consequently reduce kiln performance. Percentage decrepitation during calcination is thought to correlate with the crystal size of limestone, i.e. coarsely-crystalline types of stone are more prone to disintegration during calcination than finely-crystalline types.

Physical properties of lime

It is generally recognised that three types of lime can form from limestone as a result of progressive calcination:

(1) **Under-burnt** lime contains both unburnt $CaCO_3$ and CaO. Under-burnt lime forms if calcination temperature is too low or calcination time is insufficient for complete decomposition.
(2) **Soft-burnt** lime is relatively soft and friable and consists of an open porous structure of small CaO crystallites. Soft-burnt lime only forms under optimum conditions of calcination

temperature and calcination time. The physical properties or "quality" of soft-burnt lime (i.e. high reactivity, porosity, surface area and low bulk density) are commercially desirable.
(3) **Dead-burnt** lime is hard and dense and consists of close-packed agglomerates of large CaO crystallites formed as a result of sintering reactions. Dead-burnt lime forms if calcination temperature and/or calcination time is excessive.

From previous calcination experiments (510-910°C) on calcite and limestone, Keener & Khang (1992) provided some typical values for the physical properties of lime:

Physical property	Range of values
Porosity	40-59 %
Pore size	0.01-10 microns
Surface area	5-100 m2/g

Keener and Khang (1992) made the following observations on the relationship between the physical properties of lime and calcination conditions: (1) Small stone size and lower calcination temperature produce lime of higher porosity; (2) Surface area of lime is generally optimised by calcination of small sized stones in environments of high CO_2 partial pressure; (3) Mean pore diameter of lime correlates both with limestone rock type and calcination conditions. Typically, larger size pores form at high calcination temperature and high CO2 partial pressure.

Shrinking core model of calcination

The standard theory of limestone calcination is the **shrinking core model**, a version of which is shown schematically in Figure 21 (after Keener & Khang, 1992). In the shrinking core model an unreacted spherical core of limestone is separated from an outer concentric layer of lime by a reaction boundary. Pores in this concentric layer of lime grow inwards from the surface towards the reaction boundary. CO_2 is formed at the bottom of such pores and diffuses outwards towards the surface of the sphere. The shrinking core model predicts that the transport and release of CO_2 from the reaction interface are key controls on limestone decomposition.

A **simultaneous calcination and sintering model**, an adaptation of the shrinking core model, was proposed by Fuertes and others (1993). In this model the spherical particle is envisaged to consist of a number of multiple concentric layers (Figure 22). As calcination proceeds inwards to the core of the limestone particle, the outer concentric layers of lime sinter - such that both sintering and calcination are occurring simultaneously, but at different zones within the sphere. Sintering is a solid state reaction involving the growth of lime crystals. Sintering is generally undesirable as it is detrimental to the quality of the lime obtained. The model of Fuertes and others predicts that calcination at high temperature, and CO_2 diffusing outwards from the reaction interface, both promote sintering of CaO in the outer concentric layers of the particle.

Calcination kinetics

Zhong and Bjerle (1993) carried out some practical experiments to investigate the kinetics of limestone calcination (i.e. the rate of decomposition) using thermogravimetric analysis (TGA).

Again, CO_2 partial pressure was shown to be a critical control on limestone decomposition. According to Zhong and Bjerle, limestone decomposition is a reversible reaction:

$CaCO_3$ (s) < ----> CaO (s) + CO_2 (g)

and also
$K = -r_a \, pCO_2 / r_b$

where
$-r_a$ = decomposition rate, i.e. the above reaction going from left to right
r_b = composition rate, i.e. the above reaction going from right to left
pCO_2 = partial pressure of CO_2
K = constant

The above equation clearly indicates that increasing the partial pressure of CO_2 (pCO_2) results in a decrease in the rate of decomposition ($-r_a$).

Ray and Chowdhury (1986) also carried out kinetic studies on limestone and dolomite, of -90+45 microns particle-size, by isothermal TGA. For a constant furnace temperature, "degree of decomposition" versus "time" were plotted graphically. At high temperature (>860 centigrade), decomposition curves obtained for limestone and dolomite obeyed the following relationship:

At isothermal temperature

$Kt = 1 - (1 - a) 1/3$

where
a = degree of decomposition
t = time
K = reaction rate constant = slope of graph of "a" versus "t"

Subsequently, Lee and others (1993) carried out large scale isothermal TGA experiments on a single limestone sample at different particle sizes (7, 5, and 2 mm, respectively). The decomposition curves obtained by Lee and others also obeyed the above equation of Ray and Chowdhury (1986). Lee and others calculated the reaction rate constant ("K") of decomposition curves for a number of different calcination temperatures. They also suggested that the time required for complete decomposition of limestone could be estimated from the following equation:

At isothermal temperature

$tc = pCaO \, MCaO \, r / k \, MCaCO_3$

where
tc = time required for complete decomposition of limestone to lime
pCaO = density of CaO particle
MCaO = molecular weight of CaO
r = radius of limestone particle

k = reaction rate coefficient
$MCaCO_3$ = molecular weight of $CaCO_3$

Lee and others indicated that theoretical values of the time required for complete decomposition, "tc" as derived from above equation, correspond closely with experimental measurements of "tc" from isothermal TGA experiments.

C.16 Measurement of Carbonate Content: Experimental Trials

Trials using several laboratory methods for determination of carbonate content were carried out in order to identify suitable procedures for rapid limestone resource assessment.

Before carrying out the experimental trials it was necessary to establish a set of criteria which a "rapid" method for measuring carbonate content should ideally fulfil. This is not necessarily a straightforward and simple matter. For example, adoption of a very quick method of limestone analysis would not be desirable if the results obtained were imprecise and inaccurate. Six suggested criteria for a "rapid" laboratory method are listed in Table 30 below. The main requirements are for a simple, rapid, objective procedure that provides good quality data that are valuable for resource assessment purposes.

Table 30. Criteria for a "rapid" laboratory method of analysis for limestone and dolomite.

Criteria	Comment
(1) Throughput	High sample throughput is paramount
(2) Quality	Precise and accurate results are required
(3) Value	Data is of practical value to resource assessment
(4) Ease-of-use	Simple, inexpensive methods are favoured
(5) Objectivity	Procedure should not be operator-sensitive
(6) Advantages/Disadvantages	Strengths and weaknesses of method are known

After reviewing the chemical, physical and mineralogical methods for analysis of limestone and dolomite (see 4.3.1-4.3.3), and taking into account the laboratory facilities available at the Department of Mineral Resources (DMR), Thailand, and the British Geological Survey (BGS), United Kingdom, the following five methods were selected for the experimental trials:

(1) Atomic absorption spectrophotometry (AAS)
(2) Loss on ignition (LOI)
(3) Acid insoluble residue
(4) Thermogravimetric analysis
(5) X-ray diffraction (XRD) analysis

A step-by-step flowsheet is provided for each of these five methods in Appendix C.
23 samples of limestone and dolomite, collected from the project's study area, Surat Thani, Thailand, were selected for analysis. Results obtained, including estimates of calcite and dolomite content, are given in Table 31, and are summarized in Table 32.

A statistical hypothesis test, the "T-test" was used to examine whether the carbonate contents obtained from each of the four methods in Table 32 are equivalent. Because an identical batch of 23 samples was analysed, any disparity in mean carbonate content is directly attributable to the intrinsic performance of each method.

Prior to carrying out a "T-test," it was necessary to apply another statistical hypothesis test known as the "F-test" (Table 33). This is because the "T-test" is only valid if the variances of the populations under comparison are equivalent, i.e. if "F-test" values are <2.01 for 23 results at a 5% level of significance. All data fulfilled this criterion and the "T-test" was therefore applied. In the "T-test," the mean carbonate contents obtained from each method (designated A, B, C and D) are tested against each other, resulting in six possible permutations:

(1) Method A versus Method B
(2) Method A versus Method C
(3) Method A versus Method D
(4) Method B versus Method C
(5) Method B versus Method C
(6) Method C versus Method D

For all six of these permutations, the "T-test" values are <1.684 for 23 results at a 5% level of significance (Table 33). This indicates that the mean carbonate contents obtained from each of the four methods are equivalent. Therefore, from an objective statistical analysis of results for 23 samples of limestone and dolomite, there are no measurable differences in the ability of the four methods to estimate carbonate content.

The relative performance of each method was also assessed in terms of sensitivity, precision, accuracy and throughput, as summarized in Table 34. Precision and accuracy were determined from five duplicate analyses of a 50%:50% mixture of calcite and dolomite (Table 35). A description of the calcite and dolomite standards used and their XRD patterns are given in Appendix C. Results indicate that:

(1) **Physical methods** (LOI, insoluble residue) are simple, rapid and precise but are relatively inaccurate and not able to differentiate calcite from dolomite.
(2) **Mineralogical methods** (XRD, TGA) are capable of identifying and quantifying calcite and dolomite but are slow and often imprecise and inaccurate.
(3) The **wet chemical method** tested, AAS analysis, is accurate and the CaO and MgO data obtained is valuable for resource assessment purposes. However, the many stages of preparation and analysis make the method prone to systematic errors.

Table 31. Laboratory results for measurement of carbonate content and estimation of calcite and dolomite content.

BGS Sample No.	DMR L.O.I (%)	BGS L.O.I (%)	BGS TGA L.O.I (%)	BGS Insoluble Residue (%)	BGS TGA Calcite (%)	DMR AAS Calcite (%)	BGS XRD Calcite (%)	BGS TGA Dolomite (%)	DMR AAS Dolomite (%)	BGS XRD Dolomite (%)
BST 8	37.9	37.9	38.8	25.6	59.1	60.3	55.0	26.8	23.6	24.3
BST 9	42.8	36.9	37.5	12.8	85.3	90.8	75.3	0.0	6.0	2.7
BST 10	29.9	41.7	44.3	7.1	91.5	50.2	90.0	7.1	16.9	13.3
BST 11	41.5	41.1	42.9	3.7	97.6	92.3	96.9	0.0	2.0	0.0
BST 12	34.8	40.5	41.5	6.7	93.0	77.6	80.3	0.0	1.7	0.0
BST 13	42.2	40.8	43.0	3.9	97.8	93.8	82.5	0.0	2.4	0.0
BST 14	44.9	46.0	48.8	1.0	12.6	26.4	18.9	90.5	69.6	118.5
BST 16	43.2	42.5	44.8	0.0	101.8	96.9	99.9	0.0	1.3	0.0
BST 17	43.0	42.5	44.1	0.0	100.3	97.0	78.5	0.0	0.9	0.0
BST 18	43.0	42.5	44.3	0.0	100.6	96.7	96.6	0.0	0.9	0.0
BST 19	42.7	42.6	42.9	0.0	97.6	95.8	81.9	0.0	1.2	1.7
BST 20	42.9	42.5	44.4	0.0	101.0	96.8	81.1	0.0	0.9	0.0
BST 21	43.2	42.3	43.6	0.9	99.2	97.9	93.4	0.0	0.8	0.0
BST 23	34.9	34.0	34.4	21.7	78.2	76.0	53.0	0.0	2.1	0.0
BST 25	46.3	46.6	47.5	2.5	6.4	16.6	1.3	92.6	82.6	118.2
BST 26	43.3	43.1	33.9	1.5	77.1	94.5	84.6	0.0	3.5	1.0
BST 29	46.7	46.4	47.5	0.5	9.8	9.5	8.8	90.5	89.6	98.7
BST 30	42.8	43.1	44.3	0.2	98.8	95.6	75.3	1.7	1.4	0.4
BST 34	43.4	42.8	44.4	1.1	97.6	94.6	89.3	2.1	3.6	0.4
BST 35	43.6	42.8	43.7	1.9	91.3	97.3	73.4	7.3	1.6	6.6
BST 36	46.9	47.0	52.0	1.9	7.3	5.4	1.8	88.8	94.0	133.6
BST 37	47.2	46.6	49.0	0.1	11.6	6.6	9.3	87.6	92.6	119.0
BST 40	43.4	43.1	44.7	0.4	99.4	94.7	100.7	2.1	2.8	0.0

Table 32. Summary of laboratory trials for measurement of carbonate content.

BGS Sample No.	Carbonate BGS Insoluble Residue (%)	Carbonate DMR AAS (%)	Carbonate BGS TGA (%)	Carbonate BGS XRD (%)
BST 8	74.4	83.9	85.9	79.3
BST 9	87.2	96.9	85.3	78.0
BST 10	92.9	67.1	98.7	103.3
BST 11	96.3	94.3	97.6	96.9
BST 12	93.3	79.3	93.0	80.3
BST 13	96.1	96.2	97.8	82.5
BST 14	99.0	96.1	103.1	137.4
BST 16	100.0	98.2	101.8	99.9
BST 17	100.0	97.9	100.3	78.5
BST 18	100.0	97.6	100.6	96.6
BST 19	99.9	97.0	97.6	83.6
BST 20	99.9	97.7	101.0	81.1
BST 21	99.1	98.6	99.2	93.4
BST 23	78.3	78.2	78.2	53.0
BST 25	97.5	99.2	99.0	119.4
BST 26	98.5	98.0	77.1	85.7
BST 29	99.5	99.1	100.3	107.4
BST 30	99.8	97.0	100.5	75.7
BST 34	98.9	98.2	99.7	89.7
BST 35	98.1	98.9	98.6	80.0
BST 36	98.1	99.4	96.1	135.4
BST 37	99.9	99.2	99.2	128.3
BST 40	99.6	97.5	101.5	100.7

Table 33. Statistical analysis of laboratory carbonate content results.

	Method A	Method B	Method C	Method D
Statistical parameter	Carbonate BGS Insoluble Residue (%)	Carbonate DMR AAS (%)	Carbonate BGS TGA (%)	Carbonate BGS XRD (%)
Mean (%)	95.9	94.1	96.2	94.2
Standard Deviation	6.9	8.5	7.3	20.7
Standard Error Mean	1.4	1.8	1.5	4.3
95% Confidence limits	2.8	3.5	3.0	8.4

F test, one-tailed	F test value
Method A - Method B	0.339
Method A - Method C	0.791
Method A - Method D	0.000
Method B - Method C	0.488
Method B - Method D	0.000
Method C - Method D	0.000
Variance equal as:	F test values all <2.01 5% level of significance

T test, two-tailed	Ttest value
Method A - Method B	0.438
Method A - Method C	0.910
Method A - Method D	0.701
Method B - Method C	0.391
Method B - Method D	0.995
Method C - Method D	0.665
Population mean equal as:	T test values all <1.684 5% level of significance

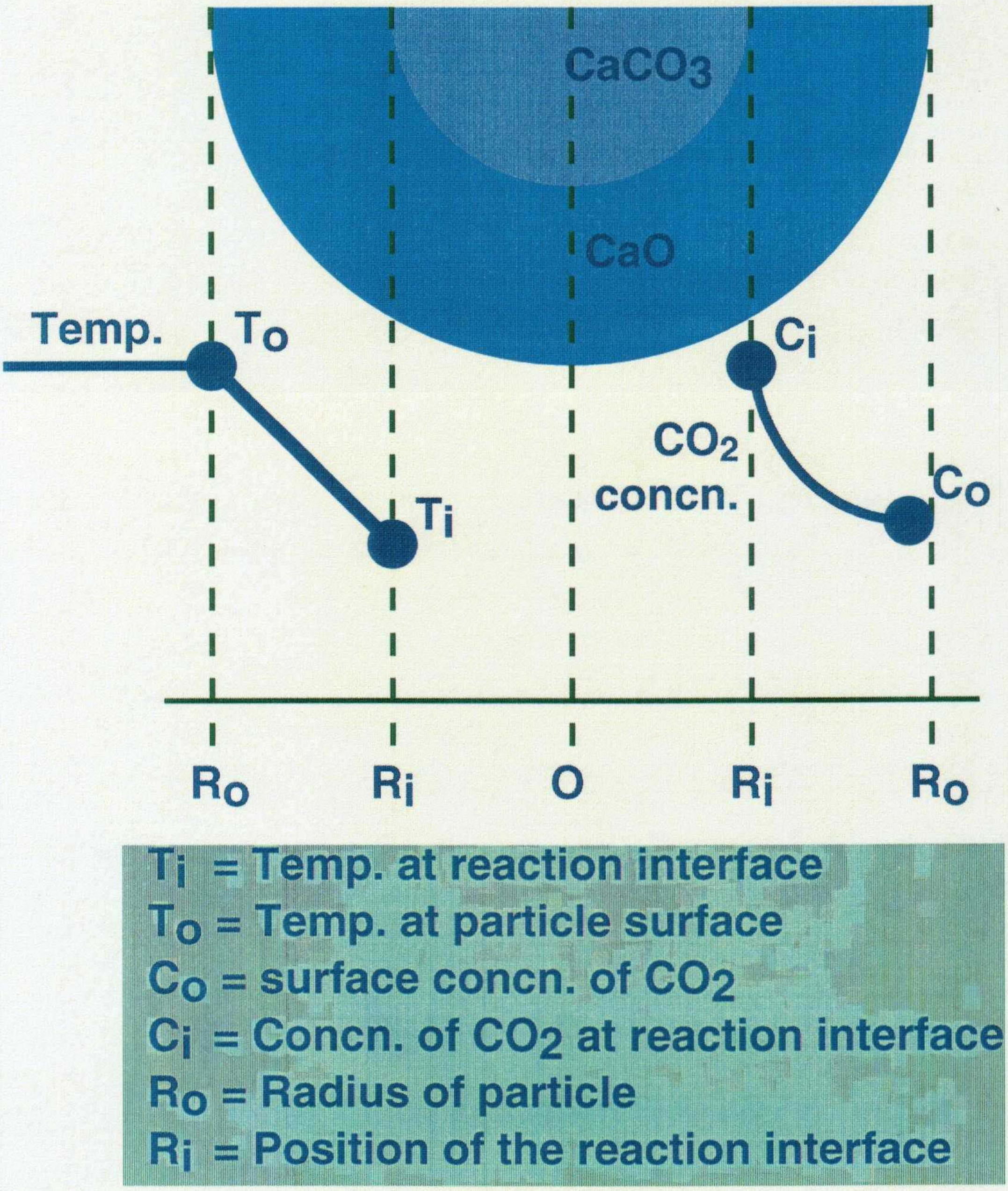
Table 34. The sensitivity, precision, accuracy and throughput of five selected methods of carbonate analysis.

	(A) XRD	(B) TGA	(C) AAS	(D) Insoluble Residue	(E) LOI
(1) Sensitivity (%)	3 approx	1.5	?0.01	0.005	0.005
Precision:					
(2) Carbonate (%)	6.6	1.2	1.4	0.2	0.1
(3) Calcite (%)	8.1	2.4	ND	NA	NA
(4) Dolomite (%)	5.2	1.0	ND	NA	NA
(5) Accuracy (%)	+2.0	-1.0	+0.6	-1.8	NA
Throughput:					
(6) Preparation time (min)	20	5	ND	0.5	None
(7) Analysis time (min)	15	60	24	5/20	15
(8) Calibration (min)	120	None	ND	None	None

Row (1): All % carbonate basis, except for column (C) which is % oxide basis.
Row (6): Per sample basis.
Row (7): Per sample basis.
Row (8): Per month basis.
Column (C): Data from Siesser and Rogers (1971). Analysis time includes preparation and calibration.
Column (D): Analysis times quoted for limestone/dolomite, respectively.
NA: Not applicable
ND: Not determined

Table 35. Precision and accuracy of laboratory methods for determination of carbonate content.

Two standard mixture 50% calcite : 50% dolomite	L.O.I (%)	TGA L.O.I (%)	Insoluble Residue (%)	TGA Calcite (%)	XRD Calcite (%)	TGA Dolomite (%)	XRD Dolomite (%)	Carbonate Insoluble Residue (%)	Carbonate TGA (%)	Carbonate XRD (%)
Test 1	44.5	44.6	1.6	50.9	49.4	46.5	50.7	98.4	97.5	100.2
Test 2	44.6	45.4	1.8	51.4	45.5	47.8	47.9	98.2	99.2	93.4
Test 3	44.6	45.3	2.1	52.2	52.8	46.7	52.8	97.9	98.9	105.5
Test 4	44.5	46.0	1.9	51.4	54.9	49.0	54.0	98.1	100.4	108.9
Standard deviation	0.0	0.6	0.2	0.5	4.1	1.2	2.7	0.2	1.2	6.8
Mean (%)	44.6	45.3	1.8	51.5	50.7	47.5	51.4	98.2	99.0	102.0
Coefficient of variation (%)	0.0	1.3	10.7	1.0	8.1	2.4	5.2	0.2	1.2	6.6



T_i = Temp. at reaction interface

T_o = Temp. at particle surface

C_o = surface concn. of CO_2

C_i = Concn. of CO_2 at reaction interface

R_o = Radius of particle

R_i = Position of the reaction interface

Figure 22. Simultaneous calcination and sintering model, after Fuertes and others (1993).

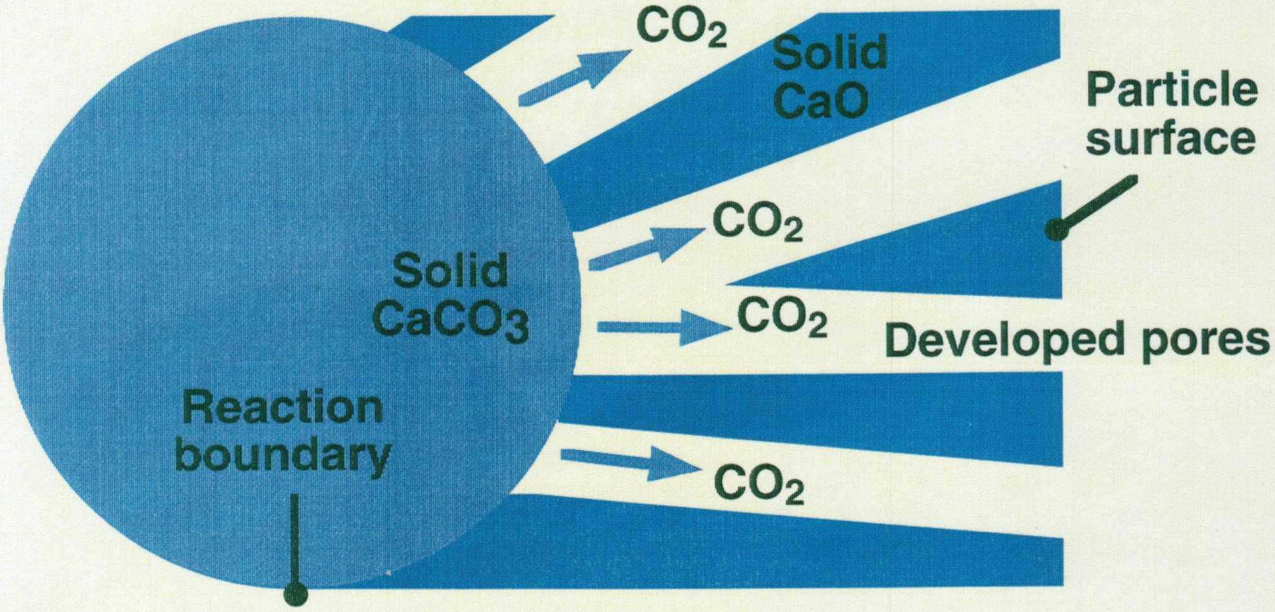


Figure 21. Shrinking core model of calcination, after Keener & Khang (1992).