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LIMESTONE : DOLOMITE FIELD DISCRIMINATION TEST

C J Mitchell

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British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK

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INTRODUCTION

The aim of this document is to outline field test procedures for the rapid assessment of limestone. The background to these field tests will be discussed. The relative advantages and disadvantages of each method will be discussed. Step-by-step guides to the test methods will be given. This work forms part of the BGS/ODS Research & Development project 'Development of procedures for the rapid assessment of limestones'.

BACKGROUND

In Thailand limestone is primarily used for the manufacture of cement. The production of limestone is growing fast. Resource studies are required in order to ensure adequate land planning, the appropriate use of high purity limestone and that resources are developed in an environmentally acceptable manner. As a contribution to a current limestone resource study by DMR the development of a simple method for the discrimination of limestone from dolomite was considered appropriate. This would enable the rapid production of resource data and maps.

The identification of dolomite is crucial in the assessment of carbonate rocks for cement manufacture. Most specifications for ordinary portland cement (OPC) require that the cement should not contain more than 6% MgO (less than 3% in the limestone). Dolomite, $CaMg(CO_3)2$, contains 45.7% $MgCO_3$ or 21.9% MgO. Therefore limestone with more than 14% dolomite mineral is unsuitable for the manufacture of cement. If an excessive amount of dolomite is present in the raw material, periclase (MgO) forms during the cement manufacture, which hydrates after setting and causes expansion.

Dolomite can often be identified by its physical appearance. It occurs mainly as massive, finely to coarsely crystalline rock, brown, grey, white or bluish in colour and resembles limestone. It has a specific gravity of 2.85 g/cm^3 and a hardness of 3.5-4 on Mohs scale. Dolomite is usually formed as a replacement of limestone. This may have occurred very soon after deposition by "metasomatism while the calcium carbonate crystals were still influenced by the composition of surface waters in their environment of origin". This is referred to as primary dolomite. However, most dolomite is formed by the replacement of limestone rock. Relicts of limestone textures and fossils often occur. This produces a dolomite with a sugary or "sucrose" texture of dolomite rhombs separated by pore space. Magnesium ions are smaller than calcium ions, therefore a replacement of limestone by dolomite leads to a volume reduction and hence porosity forms.

However, in the field it may be difficult to distinguish between calcitic and dolomitic carbonates due to their fine grain size. This is where field testing can make an important contribution

FIELD DISCRIMINATION TESTS

Hydrochloric acid

The simplest method to discriminate between limestone and dolomite is by the use of cold dilute hydrochloric acid. Limestone reacts vigorously whereas dolomite barely reacts at all. The following is a simple method, using rock chips (5mm x 2 mm) and cold dilute HCl acid (10-15% solution), of identifying limestone and dolomite:

Limestone	-	Violent effervescence, audible frothing; chip bobs about and floats to the surface.
Dolomitic limestone	-	Brisk effervescence; chip skips about bottom of container and may rise slightly off; continuous stream of CO_2 bubbles.
Calcitic dolomite	-	Mild emission of CO_2 bubbles; chip may vibrate but stays in place.
Dolomite	-	No effervescence; slow formation of CO_2 on rock surface; reaction may slowly accelerate until a thin stream of CO_2 bubbles arise.

Critically this method uses cold acid, making it effective in cool, temperate climates; however in hot climates (such as in Thailand where the mean air temperature does not drop much below 80°F) this method is less effective. This is because dolomite reacts more vigorously with warm acid.

Staining

Staining of limestones to determine their carbonate mineralogy is a common petrographic technique. The recommended staining method uses a solution of potassium ferricyanide and alizarin red S in 0.5% HCl acid. This is a valuable dual staining technique that allows differentiation between dolomite, ferroan dolomite, ferroan calcite and calcite to be carried out in one operation. The proposed field staining method is as follows:

Carbonate staining method

i) Staining solution preparation. Add 0.6g of alizarin red S to 300 ml of 0.5% HCl solution and stir to dissolve. Add 8g of potassium ferricyanide to 200 ml of 0.5% HCl solution and stir to dissolve (with use of electric stirrer). Filter potassium ferricyanide solution into alizarin red S solution (Whatman filter 1). This makes 0.5 l of staining solution.

ii) Limestone surface preparation. Locate a relatively even, horizontal surface (grind flat with carborundum block if possible). Etch surface with dilute HCl acid (10% solution) and rinse well with water to remove layer of calcium chloride. Do not wipe surface, draw off excess water with tissue paper from side of prepared area.

iii) Staining. Add stain solution to surface, ensuring even coverage. Waft with fan to agitate solution. Leave in contact with limestone for several minutes, then drain off excess solution and allow to air dry.

iv) Results. The following are the stained colours expected:

Calcite - Very pale pink to red.

Ferroan calcite - Very pale pink to red. Pale blue to dark blue. Purple to mauve to royal blue.

Dolomite/Ferroan dolomite - No colour

Ferroan dolomite - Pale to deep turquoise (depending on iron content)

Calcite / Ferroan calcite - Very pale pink to red

The staining solution should ideally be made fresh for each field trip. This method is untried in the field as yet. Anticipated problems include locating suitable limestone surfaces and discernible stain colours. This method is purely qualitative, it can not give an indication of the relative amount of dolomite present in the carbonate.

Density

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 limestones consisted of 100% calcite and all dolomites 100% dolomite. However this is not the case and a complete spectrum exists from limestone, through dolomitic limestone and calcitic dolomite, to dolomite. Therefore any density test would need 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.

Several methods were considered for density measurement:

a) Pycnometer

The weight and volume of a small sample of ground carbonate would be determined using a pycnometer bottle and from this the specific gravity could be determined. The field method considered is as follows:

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 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).

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

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.

A recent example of the use of sodium polytungstate was in a magnesite resource evaluation programme conducted in Canada. Magnesite (3 to 3.2 g/cm^3) is significantly denser than calcite and dolomite. Three sodium polytungstate solution were used, with the following densities: 2.85 g/cm^3, 2.89 g/cm^3 and 2.94 g/cm^3. Samples that floated in the 2.85 g/cm^3 solution consist of calcite or a calcite - dolomite mixture. Samples that sank in the 2.85 g/cm^3 solution but floated in the 2.89 g/cm^3 solution consist of a dolomite - magnesite mixture. Samples that sank in the 2.89 g/cm^3 solution but floated in the 2.94 g/cm^3 consist of a magnesite - dolomite mixture. Samples that sank in the 2.94 g/cm^3 solution consist of magnesite.

The following is a field method, adapted from the Canadian method, for limestone dolomite discrimination:

Sodium polytungstate density method

i) Sampling. Representative rock chips (~1 cm cubes), at least 5 per sample. Examine each chip in order to ensure that no non-carbonate minerals 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 small flat area to use as a temporary field laboratory (eg back of Land Rover). Check equipment before testwork (see separate list).

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. Dry chip carefully (avoid removing number) and place into correspondingly numbered compartment in aluminium sample tray. (NB ensure all bags and tissues disposed of responsibly).

iv) Pour sodium polytungstate solution (2.8 to 2.85 g/cm^3) into plastic beaker. Check density range with beads. Using tongs place first sample chip into solution. Record whether it sinks, floats or is suspended. Gently agitate solution to dislodge any air bubbles that may be adhering to the surface of the sample.

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

vi) Repeat steps iv) and v) using sodium polytungstate solutions of 2.75 to 2.8 g/cm^3 and 2.7 to 2.75 g/cm^3.

vii) Results. The dolomite content of the samples can be quantified using the following table:

Density (g/cm^3)	**Dolomite content**
> 2.8 - 2.85	At least 65%
2.75 - 2.8 to 2.8 - 2.85	Between 30 and 65%
2.7 - 2.75 to 2.75 - 2.8	Between 10 and 30%
< 2.7 - 2.75	Less than 10%

Field trials of this density method have been carried out in Midlands and SW of the UK, in areas of Lower Carboniferous limestone (very similar to the Permian limestones in Thailand). These trials were successful in discriminating between limestone and dolomite. This method will be tested further in the field during visits to Thailand.

This method would be 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).

CONCLUSIONS

Field methods for the discrimination of limestone from dolomite have been considered. These include reactivity with acid, chemical staining and density determination by pycnometer and using heavy liquids. The field method chosen for further trials is that using sodium polytungstate as a heavy liquid.

Clive J Mitchell
1st December 1995

Equipment for sodium polytungstate field test

Geological hammer
Hydrochloric acid (10% solution)
Deionised water
Tweezers
Paper tissue
Beakers (x 5)
Density beads (2.7, 2.75, 2.8, 2.85)
Aluminium sample tray
Sample bags
Disposable nitrile plastic gloves
Marker pen
Plastic stirring rods (x 3)
Washings bottle
Sodium polytungstate solutions (approx. 250 ml of each in the ranges 2.7-2.75, 2.75-2.8 and 2.8-2.85)
Plastic box to contain most of equipment