Inorganic Geochemistry
Applications to Petroleum Geology

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Preface

During the spring of 1990 we were approached by a colleague, a geologist with a problem. He had read a paper in the latest issue of a major journal that presented fluid inclusion data from an area in which he was exploring. The paper had concluded that a Tertiary ‘thermal event’ had been responsible for generating petroleum; if this were the case, our friend assured us, it would have far reaching implications for the prospectivity of the basin. Could we read the paper and give an opinion as to the validity of the conclusion? We read the paper. Our view was that the data were probably fine but that they had been poorly and over-optimistically interpreted so that the evidence for a thermal event was very shaky indeed. Our friend was duly grateful.

It would be tempting to write that at this point we decided that we could make a lot of money by writing a book that would explain fluid inclusion and other geochemical techniques to petroleum geologists. In fact, we had been planning the project for a couple of months already but the incident did serve to confirm our view that there was room for a book that would enable non-specialists to make up their own minds about the large number of papers now appearing in print every month which include some facet of inorganic geochemistry as a major constituent. This book is the result. Its purpose is to bring together the most important inorganic geochemical methods in a single volume, to explain their potential and limitations in a form that is accessible to the non-specialist, and to demonstrate their application to a wide range of problems in petroleum geology, from exploration, through appraisal and development, to production. The book is therefore intended for geologists, geophysicists and production engineers in oil companies who wish to broaden their knowledge of the geochemical methods available for solving problems with which they are routinely faced. We hope that it will also be of interest to final year undergraduates, postgraduates with an interest in the inorganic geochemistry of sedimentary rocks and waters, and to those attending petroleum geology and related MSc courses.

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Andrew Aplin (Newcastle University) contributed the majority of Chapter 4 and Craig Smalley (BP Research) wrote the sections on Rb–Sr, Sm–Nd and U–Th–Pb in Chapter 5. The book is far better for these contributions. Numerous friends and colleagues have also contributed to the book by providing prize specimen photomicrographs, and by reviewing the text at the many and varied stages of its development. Thanks in no particular order to Chris Rundle (British Geological Survey), Jim Marshall (Liverpool University), Ian Hutcheon (University of Calgary), Christine Knox, Jon Gluyas, Jonathan Henton, Ed Warren, Tim Primmer, Norman Oxtoby, Andy Brayshaw, Shona Grant, Andy Leonard, Mike Bowman, Joyce Neilson, Steve Rainey, Max Coleman and Keith Mills.

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1.1 Background

Petroleum is not as easy to find as it used to be. Most of the accessible sedimentary basins in the world have been explored and a large proportion of the more obvious petroleum targets have been drilled. The more risky and costly exploration becomes, the more important it is to develop new discoveries as efficiently as possible and to extract a greater proportion of the petroleum in place from existing fields. The last 15 years have seen this imperative give birth to some important new topics within the earth sciences, most of which cross the boundaries between the traditional divisions of geology as taught to undergraduate students. For example, sequence stratigraphy – now a principal tool of the exploration geologist – has emerged from classical stratigraphy and seismic interpretation; and reservoir description has been born of a long overdue relationship between reservoir engineering, sophisticated geophysics, stratigraphy and sedimentology.

Inorganic geochemistry is one more relatively new weapon in the armoury of the petroleum geologist. In its broadest sense, the subject includes the study of all of the chemical constituents of rocks and subsurface fluids, excluding only organic components based on carbon. This book makes no attempt to cover this potentially vast field in its entirety. It may appear at first glance to contain rather a mixed bag of subject matter but the choice of what to include has not been arbitrary. The themes of the book are the characterization of fluids in sedimentary basins, understanding their interaction with each other and with rocks and the application of this information to finding, developing and producing oil and gas. This might include dating quartz cement growth in a sandstone in an attempt to predict porosity distribution, or determining the extent of seawater breakthrough into a reservoir during production. There is a considerable degree of overlap with the field of sediment diagenesis but this book covers important topics with a geochemical component which would never find their way into a diagenesis book, such as strontium isotope stratigraphy, correlation and production chemistry.

1.2 How is inorganic geochemistry applied to petroleum geology?

1.3 What is in this book

1.4 Overview

1.5 What is not in this book
The subject of inorganic geochemistry is not of course in itself new, but its application to sedimentary basins has lagged behind igneous and metamorphic geochemistry. There are a number of reasons for this. One may be the relatively unglamorous nature of a sandstone when set beside a peridotite. Perhaps more important is the fact that sedimentary, particularly clastic rocks are inherently difficult to analyse in any meaningful way because they contain constituents with many different origins which for most purposes must be analysed separately. The study of sediment geochemistry has however been stimulated in recent years by the increased availability of core from deeply buried sediments taken by petroleum exploration companies and by their readiness to finance research into controls on porosity and permeability (we are ourselves beneficiaries of this largess). The last few years have also seen the development of new methods – the use of lasers, for example which have helped to overcome sampling problems.

1.2 How is inorganic geochemistry applied to petroleum geology?

It is relatively easy to watch wave ripples form or to snorkel over a growing reef and study the deposition of sediments. It is a lot harder to study how sediments are modified during burial in a basin; processes cannot in the main be directly observed because they occur at substantial depths and in many cases may well have ended long ago. Only the products of fluid–rock interaction, diagenetic minerals and present day formation waters, are left to act as records. Inorganic geochemistry provides a means of interpreting these records. The main types of information it provides are as follows,

1 Timing. Relative and absolute ages of mineral growth and dissolution, and of the presence and migration of fluids (both water and petroleum).
2 Temperature. Temperatures at which minerals grew or dissolved and at which particular fluids were present in a rock’s pores. Temperature and timing are correlated for a sediment in a subsiding sedimentary basin and can be related by modelling burial and thermal history.
3 Chemical composition. The bulk and isotope chemistries of minerals and water contain information about the history of fluids, especially their interaction with rocks.

It is one matter to obtain this information from minerals and fluids but another matter entirely to interpret the processes involved. Given a sample of quartz cemented sandstone, the geochemist will quite probably be able to find out what temperature it grew at and say something about the origin of the water involved, but will not be able to say why the rock is cemented or what caused the quartz to precipitate. This is the level of current understanding of most diagenetic phenomena: we can characterize them but not explain them. The trick to using inorganic geochemistry to solve problems in the field of petroleum geology is to accept these limitations and do the best possible with the information that can be obtained. In many cases, this is quite a lot. At the very least, geochemical methods provide a means of integrating diagenetic phenomena into the temporal framework that forms the basis of basin analysis. For example, the timing of mineral cementation and dissolution, and consequent changes in porosity and permeability can be related to phases in the development of a basin and to oil migration. The models that emerge for porosity and permeability prediction invariably involve a large empirical component, but they represent an improvement over empiricism alone.

1.3 What is in this book

This book has two parts. Chapters 2–5 describe the groups of techniques that we have found to be most useful in petroleum geology and Chapters 6–9 describe case histories – mostly from our own work or that of our colleagues – grouped according to the nature of the problem that inorganic geochemistry helped (or in some cases, failed) to solve.

The chapters on geochemical techniques emphasize applications to sedimentary rocks and the fluids in sedimentary basins. Particular attention is paid to precision and accuracy and to the questions of what information can be plausibly obtained and under what circumstances: what do data mean and what do they not mean? Particular difficulties and pitfalls are illustrated by the use of examples which are made up of complete sets of real data. The case histories that make up the second half of the book cover a wide range of applications but inevitably reflect our interests and biases. They include clastic and carbonate rocks from many parts of the world but a number are from the North Sea (Fig. 1.1). Many of

Fig. 1.1 (Opposite page.) Location of North Sea oil and gas fields mentioned in this book.
the case studies are from rift basins but there is usually no reason why analogous problems in other geological settings should not be tackled in similar ways. Coarse grained sediments figure more than mudstones because they are of importance as reservoir rocks and because, in the main, they are easier to study and more information can be obtained from them.

All of the case histories are taken from real life and we have not tinkered with the data or modified the conclusions. Some were successful in solving the problem they set out to solve, rather more solved it partially, some solved a completely different problem and others proved scientifically fascinating but of no use whatsoever. We feel that it is far more instructive, and interesting, to present relative failures alongside relative successes. Negative results rarely get published but are often as instructive as positive outcomes. In most cases, careful and circumspect science can take a problem only so far. When that point is reached — and we try to make it clear when it is — we do not feel embarrassed to speculate. Petroleum geology, particularly exploration, involves making the best of incomplete understanding and is an essentially optimistic enterprise.

1.4 Overview

Chapter 2 (Textural and Mineralogical Analysis) describes five basic and three more advanced techniques for mineral identification and quantification. Inclusion of this topic in a book on geochemistry stretches the definition of the term, but analysis of a sample's mineralogy is vital if any sense is to be made of geochemical information obtained from it. The basic techniques include thin-section petrography, cathodoluminescence microscopy, fluorescence microscopy, scanning electron microscopy and X-ray diffraction. Examples are given throughout the text of the application of the techniques to mineral identification, differentiation of detrital grains from diagenetic cements, mineral quantification and the construction of paragenetic histories for reservoir rocks. The three more advanced techniques covered are transmission electron microscopy, thermogravimetric-evolved water analysis and pore image analysis, which are playing an increasing role in chemical analysis, clay mineral quantification and porosity analysis respectively. The chapter stresses the application of techniques at the expense of a detailed description of apparatus and sample preparation (for which see Tucker, 1988). Emphasis is also placed on the value of combining the techniques with standard petrophysical and engineering methods for describing the reservoir quality of rock samples.

Chapter 3 (Fluid Inclusions) explains how the study of these minute samples of fluid trapped during mineral growth or fracture healing can provide information about the temperatures of diagenetic reactions, and about the composition of fluids passing through sedimentary rocks and at what temperatures they did so. The study of fluid inclusions in igneous rocks and particularly, metallic mineral deposits, goes back more than a century but only over the last 10 years has much effort been put into the study of inclusions in sediments. Much of the earlier work, and some current studies, suffer from overinterpretation and this chapter attempts to redress the balance by underlining some limitations of the technique. Particular attention is paid to the question of leakage because if fluid inclusions in diagenetic minerals routinely leak — and a case can be made for thinking that they do — then they will be of limited value for the study of sedimentary rocks.

The applications of stable isotopes, the subject of Chapter 4, to petroleum geological problems range from stratigraphic analysis to better understanding and predicting reservoir quality and reservoir fluid type. Stable isotopes are used principally as natural tracers for subsurface reactions and — in the case of oxygen isotopes — can provide information about reaction temperature. The chapter first describes the principles and nomenclature of stable isotope systems (a necessary evil but surprisingly painless), the basic analytical techniques, and the uncertainties associated with isotopic measurements. This is followed by a description of the most important stable isotope systems in the context of the fluids and minerals in which they are found: oxygen in water, silicate, sulphate and carbonate minerals; hydrogen in water and clays; carbon in carbonate minerals, CO₂ and CH₄; and sulphur in sulphate and sulphide minerals and H₂S.

Chapter 5 explains the use of radiogenic isotopes to unravel geological history. It begins with a refresher in the simple physics that forms the basis of radiometric dating, which serves to stress the common features of all of the dating methods. Four isotope systems are described: K–Ar, Rb–Sr, Sm–Nd and U–Th–Pb. K–Ar dating is almost routinely used to date K-bearing mineral cements, principally illite. The chapter explains why this must
be done with great care even when the sample material is particularly suitable. Ar–Ar dating – a clever technique that also relies on the K–Ar decay series – is also covered. The other isotope systems can be used for dating sedimentary material only under rather restricted circumstances. However, radiogenic isotopes also have value as natural tracers. Strontium isotope ratios in particular can be used to trace the chemical evolution of natural waters. One consequence of this property is their use as a tool for dating marine carbonate and phosphate (strontium isotope stratigraphy).

Chapter 6 (Porosity and Permeability Prediction) is the first of four chapters that group case histories to illustrate a particular application of inorganic geochemistry. It is also the bulkiest because it has been up to now the most important application if the number of published studies is anything to go by. The introductory section explains how inorganic geochemistry contributes to porosity and permeability prediction by reducing risk (neither can be predicted using inorganic geochemistry alone). There follow six case histories which range from exploration in frontier areas where the amount of information available is very limited (Flemish Pass, Grand Banks) through progressively more mature exploration areas (offshore Louisiana and the Brent Province) to porosity prediction in appraisal, development and production in three North Sea fields (Magnus, Machar and Forties).

Chapter 7 (Fluid Migration) considers inorganic geochemical evidence for phases of water and petroleum migration. The value of knowing about petroleum migration need hardly be underlined but migration of waters is also of interest as these affect reservoir quality by interacting with rocks and can also alter oil through the processes of biodegradation and water washing. The four case histories cover the use of fluid inclusions for sorting out migration history in poorly and better known areas (Aquitaine and Weald Basins), the prediction of the occurrence of a rather odd diagenetic reservoir rock in the Central North Sea and the history of filling of a gas-condensate discovery (Waalwijk, Netherlands).

The next chapter (Correlation) describes how stable and radiogenic isotope systems can be used to correlate stratigraphic units, chiefly on a broad exploration scale, but also on the smaller scale of individual reservoir units within discrete oilfields. Four case studies are described. The first, from the Norwegian North Sea, shows how strontium isotope stratigraphy and radiometric dating can be used to refine the stratigraphic correlation of Tertiary clastic sediments, and assist in erecting a sequence stratigraphy. The second also uses isotope stratigraphy, but in this case oxygen isotopes are applied to provide a very high resolution stratigraphy of a few tens of thousands of years for Plio-Pleistocene sandstone reservoir targets in the Gulf of Mexico. The third and fourth case studies are both from oilfields in the Norwegian sector of the North Sea, the Ekofisk Chalk Field, and the clastic Gullfaks Field. In Ekofisk, strontium isotopes are used to correlate reservoir zones using data obtained from the rock matrix and from the formation waters. In Gullfaks, samarium and neodymium isotopic methods are used to predict the distribution of reservoir sand bodies by identifying changes in sand provenance.

Chapter 9 (Petroleum Recovery) outlines the basic principles of secondary and enhanced oil recovery, and the problems of corrosive fluid production (H₂S and CO₂). The first two case studies, from the Forties Field, UK North Sea, and from the Wytch Farm Field, onshore UK, demonstrate the value of oxygen and hydrogen isotopes as tracers for seawater breakthrough during oil production. The application of sulphur isotopes for understanding sour gas production in Wytch Farm is also outlined. The last two case studies are from the Cretaceous heavy oil sands of Alberta and Saskatchewan in western Canada. These demonstrate the importance of quantitative petrography linked to petrophysics for describing the effects of thermal recovery processes (steam injection and fireflooding) on shallow reservoir sandstones. The case study on steam injection also shows how carbon isotopes can be used to identify the source of CO₂ produced during thermal recovery.

1.5 What is not in this book

This is a book about the application of fluid–fluid and fluid–rock interaction to petroleum geology and as such contains only those methods which we have found to be useful in this field. We avoid describing methods of analysing whole rocks partly because we have found bulk chemistry to be of rather limited value in this respect and also because it is a subject in its own right that has been better covered than we could manage in other books. We have also avoided chemical modelling of water–rock interaction and modelling of fluid flow in sedimentary basins. These are used together by some (not by us) to predict
porosity; we believe them to have explanatory power and to be useful for understanding diagenetic processes but feel that their predictive power is limited (see Section 6.1). Although geohistory analysis — especially burial and thermal modelling — is repeatedly referred to in the text, it also constitutes a separate subject and we have not as a consequence dealt with fission track analysis which is principally a means of calibrating burial history.
Chapter 2  Textural and Mineralogical Analysis

2.1 Introduction

Mineralogical and textural analysis of samples is the essential first step in any inorganic geochemical programme and provides the critical link between the quality of a reservoir — chiefly its porosity and permeability — and more advanced geochemical techniques such as fluid inclusion analysis (Fig. 2.1). Mineralogical and textural analysis can provide several types of information:

1 mineral identification;
2 differentiation of detrital from diagenetic phases;
3 quantitative analysis of mineral abundance;
4 mineral paragenesis (the sequence of mineral growth and dissolution);
5 mineral chemistry;
6 description and quantification of porosity; and
7 identification of the main factors influencing porosity and permeability.

The most appropriate technique for providing each of these is shown in Table 2.1. Note that, to be most effective, certain techniques need to be applied in conjunction with others. Clay mineral X-ray diffraction is most effective as a tool for quantifying clay mineral content in rock samples when applied with thermogravimetric-evolved water analysis. Similarly, cathodoluminescence microscopy of limestone samples is most effective when applied with observations made using transmitted light.

The objectives of this chapter are to introduce mineralogical and textural analytical techniques, and their applications to understanding the post-depositional evolution of siliciclastic and carbonate rocks in petroleum provinces. We will concentrate particularly on the application of the variety of techniques described here, rather than on details of instrumentation and sample preparation. References covering these aspects in more depth are given in the text.

2.2 Transmitted light microscopy

2.2.1 Introduction

Transmitted light microscopy is a basic tool of the trade for the description of sedimentary rocks and
Chapter 2

Reservoir quality
- Porosity
- Permeability
- Water saturation

Petrography
- Mineral identification
- Differentiation of detrital/diagenetic phases
- Paragenetic history
- Mineral quantification

Further geochemical analysis
- Fluid inclusions
- Stable isotopes
- Radiogenic isotopes

- Identification of reservoir problem; porosity lower than expected before drilling.
- Identification of cause; up to 20% quartz burial cement.
- Identification of approximate timing of quartz by fluid inclusion analysis; quartz pre-dates petroleum fill.

Possible solution: Identify future prospects in this area where petroleum filling pre-dates quartz cementation.

Fig. 2.1 The link between reservoir quality, petrography and further geochemical analysis.

There are many texts which cover all aspects of sedimentary petrology. Folk (1974), Pettijohn (1975) and Tucker (1981) are good general petrographic texts, whereas Moore (1989) and Pettijohn et al. (1973) concentrate on carbonate and siliciclastic petrography respectively. The Atlas of Sedimentary Rocks by Adams et al. (1984), and the AAPG colour guides to sandstones (Scholle, 1979) and carbonates (Scholle, 1978) contain superb colour thin-section photomicrographs and are well worth referring to.

The objective of this section is to explain how transmitted light petrography can be used to describe the diagenesis of sedimentary rocks (rather than the depositional fabric). Petrographic description can provide five main pieces of information:
1. Mineral identification;
2. Differentiation of detrital from diagenetic phases;
3. Quantitative analysis of mineral abundance;
4. Mineral paragenesis; and
5. Description of porosity.

The problems associated with siliciclastic petrography are quite different from those associated with carbonates. Siliciclastic rocks tend to be polymineralic, with several different diagenetic phases such as clay minerals, quartz and carbonates and it is usually easy to distinguish these from the detrital components of the sediment. In contrast, carbonate rocks are composed of fewer minerals which tend to be relatively unstable during diagenesis so that much of the primary depositional fabric may be obliterated. Recognition of subtle changes in carbonate fabric and chemistry is therefore essential to differentiate primary constituents from diagenetic phases, and to allow different diagenetic carbonates to be recognized.

2.2.2 Sample preparation

The thin-section is the basic sample requirement for microscope petrography. It consists of a rock wafer 30 µm thick, mounted on a glass slide. The thickness of the rock wafer is standard to ensure uniformity of birefringence colours (which are determined in part by sample thickness). Similarly, to ensure comparability of samples, the rock wafer is usually mounted on the slide in a medium of uniform refractive index. Basic thin-section preparation is described in more detail by Miller (1988).

Before the section is cut, samples are commonly impregnated with a dyed resin. This fills and colours porespace in the sample, allowing easier identification of porosity types in the sample, and also
Table 2.1 Summary matrix of technique versus application.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Mineral identification</th>
<th>Differentiation of diagenetic¹ from detrital phases</th>
<th>Mineral quantification</th>
<th>Mineral paragenesis</th>
<th>Mineral chemistry</th>
<th>High resolution mineralogical and textural analysis</th>
<th>Porosity description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmitted light microscopy</td>
<td>•</td>
<td>•</td>
<td>³</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>³</td>
</tr>
<tr>
<td>CL Cold</td>
<td>C</td>
<td>•</td>
<td>⁵</td>
<td>•</td>
<td>•</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL Hot</td>
<td>S</td>
<td>•</td>
<td>•</td>
<td>⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CL SEM</td>
<td>S</td>
<td>•</td>
<td>•</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>UVF</td>
<td></td>
<td></td>
<td>⁵</td>
<td></td>
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</tr>
<tr>
<td>SEM SE</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td>•</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SEM BSEM</td>
<td>•</td>
<td></td>
<td>⁸</td>
<td>⁹</td>
<td>¹⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TEM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XRD Whole rock</td>
<td>• ¹¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XRD Fine fraction</td>
<td>• ¹²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TG-EWA</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>¹⁰</td>
<td></td>
</tr>
</tbody>
</table>

Key:
1 Includes sample screening
2 Includes cement stratigraphy and cement fabric analysis
3 With point-counting apparatus
4 Qualitative only for stained carbonates
5 Especially cement stratigraphy and cement fabric analysis in carbonates
6 Highly qualitative for Mn and Fe in carbonates
7 Qualitative with energy dispersive X-ray analysis
8 Software is available for BSEM quantification of very simple mineral mixtures
9 Semi-quantitative with energy dispersive X-ray analysis
10 BSEM-PIA provides quantitative porosity information only
11 Very rapid whole rock quantification
12 Especially for clay mineral identification

Prevents poorly consolidated rocks falling apart. Thin-sections are usually stained. Two stains are commonly used: a mixed stain for carbonates allowing the differentiation of ferroan and non-ferroan calcites and dolomites (Dickson, 1966); and a stain for feldspars allowing the differentiation of potassium feldspars, plagioclase, and quartz (Houghton, 1980). Table 2.2 summarizes the effects of the staining procedures on carbonate and silicate mineralogies. Note that it is essential to apply the feldspar stain before the carbonate stain, otherwise the latter will be removed!

2.2.3 Mineral identification and differentiation of detrital grains from diagenetic cements

The main theme of this section is the differentiation of diagenetic phases from depositional grains, which can be a source of considerable ambiguity in thin-section description. The following provides a guide to the recognition of the most common diagenetic phases in siliciclastic and carbonate rocks, and outlines the pitfalls and problems of distinguishing detrital grains and matrix from diagenetic phases. A detailed description of sedimentary mineral iden-
Table 2.2 Typical stain colours for carbonates and feldspars.

<table>
<thead>
<tr>
<th>Mineralogy</th>
<th>Stain colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-ferroan calcite*</td>
<td>Very pale pink to red</td>
</tr>
<tr>
<td>Ferroan calcite*</td>
<td>Ranging from mauve to purple to royal blue with increasing Fe content</td>
</tr>
<tr>
<td>Dolomite*</td>
<td>No colour</td>
</tr>
<tr>
<td>Ferroan dolomite*</td>
<td>Ranging from pale to deep turquoise with increasing Fe content</td>
</tr>
<tr>
<td>Plagioclase†</td>
<td>Pink, intensity is proportional to Ca content</td>
</tr>
<tr>
<td>Pure Na-Albite†</td>
<td>No colour with rhodizonate stain</td>
</tr>
<tr>
<td>Alkali feldspars†</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

* Carbonate stain colours using mixed stain of potassium ferricyanide and Alizarin red-S (Dickson, 1966).
† Feldspar stain colours using stain of sodium cobaltinitrate, followed by potassium rhodizonate (Houghton, 1980).

Identification is beyond the scope of this book. The reader is referred to texts by Kerr (1959) and Deer et al. (1977). Table 2.3 summarizes the optical properties of common minerals in sedimentary rocks and their occurrence. If the nature of a mineral is in doubt from microscopy alone, microbeam techniques can be applied (see subsequent sections in this chapter).

Quartz cement
Quartz cement is the most common diagenetic silicate mineral in sandstones (McBride, 1989). It occurs chiefly in two forms: as microcrystalline cement and as syntaxial overgrowths on detrital quartz grains (Table 2.3). Microcrystalline quartz, also known as microquartz, chert or chalcedony, is relatively easy to differentiate from the depositional fabric of the rock (Fig. 2.2a). Syntaxial quartz overgrowths are the most common form of quartz cement but are often difficult to distinguish from detrital grains because of the optical continuity of quartz across the grain–cement boundary. Quartz overgrowths can be clearly differentiated using optical microscopy only if the grain–cement boundary is visible. Figure 2.2b shows a sandstone largely composed of quartz in which grain margins cannot be identified even though the euhedral crystal faces show that quartz cement is present. If quartz cementation had continued to fill porespaces completely, only sutured contacts between areas of quartz would be visible. One possible interpretation would be that the sutured contacts could represent compromise boundaries between growing quartz crystals. Alternatively, we could infer that there is no quartz cement, and that the sutured boundaries are pressure-solution contacts along which quartz cement has been dissolved rather than precipitated (Houseknecht, 1988). Distinction between these two quite different interpretations must involve recourse to further techniques such as cathodoluminescence microscopy (Section 2.3). Fortunately, many sandstones have a thin coating of depositional or diagenetic material, commonly haematite, between the grains and cement which allows grain outlines to be identified (Fig. 2.2c). Fluid inclusions are also often concentrated along grain–cement boundaries (see Fig. 3.3f).

Feldspars
Feldspar cements are relatively common in arkosic sandstones but usually form only a minor or trace component of the total rock volume (Waugh, 1978). Like quartz, feldspar cements chiefly occur as syntaxial overgrowths on detrital grains and so present the same problems of identification. However, there is a further complication in feldspar petrography: certain types of feldspar, whether grains or cement, cannot be distinguished from each other or, in some cases, from quartz unless the section is stained (see Section 2.2.2).

Three types of feldspar are usually distinguished in sedimentary petrography: plagioclase, orthoclase and microcline (Table 2.3). Plagioclase is easily identified by common multiple or lamellar twinning which gives the mineral its characteristic striped appearance under crossed polars (Fig. 2.2d; Deer et al., 1977). Microcline, the low-temperature form of potassium feldspar, is also easy to identify owing to its cross-hatched 'tartan' twinning visible under crossed polars. Other feldspars are frequently untwinned. A common feature of feldspars, which also assists in their identification, is their diagenetic instability relative to quartz (Burley et al., 1985). Feldspars dissolve more readily, leaving ragged, etched grain remnants in oversized secondary pores, or skeletal grains with microporosity (Schmidt & McDonald, 1979). As well as being leached, feldspars are commonly altered to fine-grained clay minerals.
Fig. 2.2 Silicate cements in sandstones. (a) Microcrystalline quartz cement between quartz and feldspar grains, Jurassic sandstone, Central North Sea. Plane polarized light. Courtesy A. Hogg. (b) Quartz cemented sandstone, Northern North Sea. The boundaries between quartz grains and cements are invisible. Plane polarized light. Courtesy A. Hogg. (c) Quartz cemented sandstone, Rotliegend Group, Southern North Sea. Quartz grains and cements can be distinguished by the presence of a dust rim. Plane polarized light. Courtesy A. Hogg. (d) Syntaxial overgrowth of plagioclase feldspar on a detrital grain. The grain–cement boundary is marked by a rim of haematite. Crossed polars. Width of photograph is 400 μm.

Clay minerals
Clay minerals are best observed in the scanning electron microscope because of their small size (usually a few to a few tens of micrometres). Nevertheless, optical microscopy can still provide useful general information on certain clay mineral types. There are two main problems to be aware of in clay mineral identification from thin-section petrography: the identification of clay mineral type and differentiation of clay mineral cements from matrix clay.

The common diagenetic clay minerals are summarized in Table 2.3. Kaolinite forms characteristic booklets (Fig. 2.3a, b) or veriform aggregates with low birefringence (Fig. 2.3c). Chlorite, a ferromagnesian clay mineral, is also relatively easy to identify on account of its green hue in transmitted light and anomalous steely blue birefringence. It usually forms characteristic pseudohexagonal platelets or a complex meshwork. Illite, a potassium-bearing clay, commonly forms plates parallel to grain surfaces, or micrometre-thick fibres extend-
<table>
<thead>
<tr>
<th>Group/mineral</th>
<th>Crystal system</th>
<th>Colour</th>
<th>Cleavage</th>
<th>Relief</th>
<th>Birefringence</th>
<th>Other features</th>
<th>Cement</th>
<th>Form and occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>Trigonal</td>
<td>Colourless</td>
<td>None</td>
<td>Low+</td>
<td>Grey</td>
<td></td>
<td>Overgrowth cement common</td>
<td>As detrital grains and cement/replacive phase</td>
</tr>
<tr>
<td>Cherts</td>
<td></td>
<td>Colourless</td>
<td>None</td>
<td>Low+</td>
<td>Grey</td>
<td></td>
<td>Chalcedony and microquartz</td>
<td>Chalcedony and microquartz are diagenetic unless as detrital grain</td>
</tr>
<tr>
<td><strong>Feldspars</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Microcline</td>
<td>Triclinic</td>
<td>Colourless</td>
<td>Present</td>
<td>Low−</td>
<td>Grey</td>
<td>Crosshatch twins</td>
<td>Simple twins</td>
<td>Overgrowth cements</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>Monoclinic</td>
<td>Colourless</td>
<td>Present</td>
<td>Low−</td>
<td>Grey</td>
<td></td>
<td></td>
<td>Present as detrital minerals, but often altered or leached. Generally minor diagenetic phase, except in some arkoses</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>Triclinic</td>
<td>Colourless</td>
<td>Present</td>
<td>Low−</td>
<td>Grey</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Micas</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Muscovite</td>
<td>Monoclinic</td>
<td>Colourless</td>
<td>Prominent, planar</td>
<td>Mod+</td>
<td>Bright colours</td>
<td>Parallel extinction</td>
<td></td>
<td>Common detrital mineral</td>
</tr>
<tr>
<td>Biotite</td>
<td>Monoclinic</td>
<td>Brown−green</td>
<td>Prominent, planar</td>
<td>Mod+</td>
<td>Bright colours, masked by colour</td>
<td>Parallel extinction, pleochroic</td>
<td></td>
<td>Common detrital mineral</td>
</tr>
<tr>
<td><strong>Clay minerals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chlorite</td>
<td>Monoclinic</td>
<td>Green/blue green</td>
<td>Planar</td>
<td>Mod+</td>
<td>Grey/blue</td>
<td></td>
<td>Common as cements</td>
<td>Present as detrital minerals, as alteration products of silicates and as cements</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Triclinic</td>
<td>Colourless</td>
<td>Planar</td>
<td>Low+</td>
<td>Grey</td>
<td>Fine grained</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td>Monoclinic</td>
<td>Colourless</td>
<td>Planar</td>
<td>Low+</td>
<td>Grey-bright</td>
<td></td>
<td></td>
<td>Characteristic of low sedimentation rates, may infill foram tests etc.</td>
</tr>
<tr>
<td>Smectite</td>
<td>Monoclinic</td>
<td>Colourless</td>
<td>Planar</td>
<td>Low+</td>
<td>Grey</td>
<td>Commonly replace pellets</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glauconite</td>
<td>Monoclinic</td>
<td>Green</td>
<td>Planar</td>
<td>Mod, masked by colour</td>
<td>Grey, masked by colour</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zeolites</td>
<td>Most colourless</td>
<td></td>
<td>Low, most−</td>
<td>Commonly grey</td>
<td>Commonly</td>
<td>Common as cements in volcanics</td>
<td></td>
<td>Associated with volcanogenic sediments</td>
</tr>
<tr>
<td>Minerals</td>
<td>Crystal System</td>
<td>Colour Type</td>
<td>Habit</td>
<td>Cleavage</td>
<td>Hardness</td>
<td>Flotation</td>
<td>Remarks</td>
<td></td>
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<td>-------------------------------------------------------------------------</td>
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</tr>
<tr>
<td><strong>Carbonates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aragonite</td>
<td>Orthorhombic</td>
<td>Colourless</td>
<td>Rectilinear</td>
<td>Mod-high</td>
<td>High</td>
<td>Very high</td>
<td>Commonly acicular, present as detrital grains, cements and replacive phases in carbonates and siliciclastics</td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>Trigonal</td>
<td>Colourless</td>
<td>Rhombic</td>
<td>Low-high</td>
<td>Very high</td>
<td>Very high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dolomite</td>
<td>Trigonal</td>
<td>Colourless</td>
<td>Rhombic</td>
<td>Low-high</td>
<td>Very high</td>
<td>Very high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Siderite/</td>
<td>Trigonal</td>
<td>Colourless</td>
<td>Rhombic</td>
<td>Low-high</td>
<td>Very high</td>
<td>Very high</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ankerite</td>
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<td></td>
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<tr>
<td><strong>Evaporites</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>Monoclinic</td>
<td>Colourless</td>
<td>Planar</td>
<td>Low</td>
<td>Grey</td>
<td>Bright colours</td>
<td>Common burial cement, commonly crystalline, replacive after evaporites</td>
<td></td>
</tr>
<tr>
<td>Anhydrite</td>
<td>Orthorhombic</td>
<td>Colourless</td>
<td>Rectilinear</td>
<td>Mod</td>
<td>Grey</td>
<td>Bright colours</td>
<td>Burial cement, commonly partially replacive</td>
<td></td>
</tr>
<tr>
<td>Celestite</td>
<td>Orthorhombic</td>
<td>Colourless</td>
<td>Planar</td>
<td>Low-mod</td>
<td>Grey</td>
<td>Grey</td>
<td>Burial cement, burial cement in sandstones, may be associated with sulphide mineralization</td>
<td></td>
</tr>
<tr>
<td>Barite</td>
<td>Orthorhombic</td>
<td>Colourless</td>
<td>Planar</td>
<td>Low-mod</td>
<td>Grey</td>
<td>Grey</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halite</td>
<td>Cubic</td>
<td>Colourless</td>
<td>Rectilinear</td>
<td>Low</td>
<td>Isotropic</td>
<td>Isotropic</td>
<td>Only present if section prepared in oil Burial cement</td>
<td></td>
</tr>
<tr>
<td><strong>Iron minerals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite</td>
<td>Cubic</td>
<td>Opaque</td>
<td></td>
<td></td>
<td></td>
<td>Distinguished in reflected light Yellow</td>
<td>Common diagenetic mineral</td>
<td></td>
</tr>
<tr>
<td>Magnetite</td>
<td>Cubic</td>
<td>Opaque</td>
<td></td>
<td></td>
<td></td>
<td>Distinguished in reflected light Grey-black</td>
<td>Common diagenetic mineral in siliciclastic red-beds</td>
<td></td>
</tr>
<tr>
<td>Haematite</td>
<td>Cubic</td>
<td>Opaque, brown tinge</td>
<td></td>
<td></td>
<td></td>
<td>Distinguished in reflected light Red-grey</td>
<td>Occurs in ooids in ironstones and as partial pore-fills</td>
<td></td>
</tr>
<tr>
<td>Chamosite/berthierine</td>
<td>Monoclinic</td>
<td>Green</td>
<td>Mod</td>
<td>Grey masked by colour</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Collophane</td>
<td>Non-crystalline</td>
<td>Browns</td>
<td>Mod</td>
<td>Isotropic</td>
<td></td>
<td>Replacive textures, commonly in carbonates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bitumens</td>
<td>Non-crystalline</td>
<td>Opaque</td>
<td></td>
<td>Distinguished in fluorescence</td>
<td></td>
<td>Occurs in porosaces and in fluid inclusions</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ing away from the grain surface, and can also be identified from its relatively high birefringence. Pure smectite is less common as a cement in sandstones, but interstratified illite/smectites may form fibrous cements. These can be distinguished from pure illites using X-ray diffraction (Section 2.7). Glauconite is relatively easy to identify owing to its green hue in thin-section and its common occurrence as pellets in marine sandstones. Differentiating detrital from diagenetic clay may be more difficult. Frequently, what is described as a clay matrix consists of a dense brown mess which may contain any combination of original detrital material, recrystallized detrital clay, or true diagenetic precipitate. Under such circumstances, clay mineral identification is better left to scanning electron microscopy (Section 2.5), transmission electron microscopy (Section 2.6) and X-ray diffraction.

**Carbonates**

Identification of carbonate cements in siliciclastic rocks is relatively straightforward and may be as-
Table 2.4 Descriptive terms for carbonate cement morphologies. Modified from Harwood (1988).

<table>
<thead>
<tr>
<th>Cement terminology</th>
<th>Description and characteristic environment of precipitation (where appropriate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Needle</td>
<td>Thin (&lt;10 µm) cements of single or en-echelon crystals</td>
</tr>
<tr>
<td>Pendant or microstalactitic</td>
<td>Cement forms in droplets beneath grains in vadose zone (zone where porosity is partially air- and partially water-filled)</td>
</tr>
<tr>
<td>Meniscus</td>
<td>Cement forms at or near grain–grain contacts, also characterizes vadose zone</td>
</tr>
<tr>
<td>Acicular</td>
<td>Thin, straight form (aspect ratios of 20–40, ≈10 µm width). Characterizes marine phreatic (pores wholly water-filled) environment</td>
</tr>
<tr>
<td>Peloidal</td>
<td>Dark, microcrystalline coating to grains and pores. Characterizes marine phreatic environment</td>
</tr>
<tr>
<td>‘Micritic’ or micocrystalline</td>
<td>Microcrystalline cement which may coat grains and form bridges between grains. Characterizes marine phreatic environment</td>
</tr>
<tr>
<td>Columnar</td>
<td>Broad cements (≈20 µm + ) commonly longer than broad</td>
</tr>
<tr>
<td>Circumgranular isopachous acicular</td>
<td>Equal thickness of acicular cements surrounding grains. Characterizes marine phreatic environments</td>
</tr>
<tr>
<td>Equant</td>
<td>Equidimensional crystals (commonly ≈100 µm + ). Characterizes freshwater or burial phreatic environments</td>
</tr>
<tr>
<td>Circumgranular equant</td>
<td>Equidimensional cements surrounding grains. Characterizes meteoric phreatic environment</td>
</tr>
<tr>
<td>Overgrowth</td>
<td>Cement is in optical continuity with substrate</td>
</tr>
<tr>
<td>Sparry</td>
<td>Coarse (≈300 µm + ), commonly equidimensional crystals</td>
</tr>
<tr>
<td>Poikilotopic</td>
<td>Coarse cement crystals enclosing grains and pre-existing cement phases</td>
</tr>
<tr>
<td>Baroque (or ‘saddle’)</td>
<td>Coarse cement displaying undulose extinction. Characterizes burial environments</td>
</tr>
</tbody>
</table>

In carbonate rocks, the major problems are in distinguishing unaltered carbonate grains from those which have been diagenetically modified, and in differentiating genuine cements from neomorphic carbonate. Again, staining the thin-section helps. Under normal marine conditions, all organisms secreting a calcite test will precipitate non-ferroan calcite with a low manganese content. Accordingly, the presence of any dolomite or ferroan calcite immediately indicates that the skeletal particle has undergone diagenetic alteration. However, the presence of non-ferroan calcite in itself is insufficient evidence to guarantee that no diagenetic alteration has taken place. Further screening for the presence of manganese in the calcite by cathodoluminescence (Section 2.3) should be carried out, as well as detailed observation of skeletal fabrics by scanning electron microscopy (Section 2.5).