

# Geological prospecting

## 2.2.1 Photointerpretation, remote sensing, digital cartography, integrated mapping

### Introduction

This section describes the important and rapid impact of space and computer technology, particularly in the last two decades of the 20<sup>th</sup> century, on oil and gas exploration and development, both on and offshore.

In order to explore for and extract hydrocarbons, the most detailed knowledge of the Earth's geology, geography and oceanography is essential. The geological evolution of a region must be known to ascertain whether source rocks exist buried at a suitable depth to generate hydrocarbons, if the right kind of reservoir rocks are present and whether suitable structures allow migration and later entrapment of the hydrocarbons. The surface geography and topography is important not only in terms of access for geophysical exploration and then drilling, but also later for extraction, building of pipelines and facilities, etc. Although our knowledge of most of the Earth's surface and oceans today is fairly mature, much of this is due to detailed mapping carried out mainly in the second half of the 20<sup>th</sup> century using first airborne and later space techniques. This work continues in the 21<sup>st</sup> century with yet more sophisticated spaceborne systems and universal use of computer mapping techniques to replace the older printed maps and photographs. However in the 19<sup>th</sup> and early 20<sup>th</sup> centuries such regional mapping did not exist and until very recently we had better and more consistent digital topographic maps of other planets than we did of our own.

More recent developments, especially in the exploitation of space and in the dramatic development of powerful microcomputers, have had an even more profound effect on the evolution of the geosciences. Today, orbiting spacecraft transmit geographically precise data to the user on the ground who can interpret their complex spectral content on a laptop computer to map structure, lithology and even mineralogy. Orbiting satellites map natural hydrocarbon seeps and variations in the Earth's gravitational field over the oceans and the satellites of the Global Positioning System (GPS) provide the means to exactly locate the geologist's position on the ground.

### Photogeology

Photogeology, the method of geological mapping through interpreting aerial photographs, developed as a viable and rapid means of geological mapping during the period between the two world wars.

Large format (25×25 cm film) cameras were developed, capable of taking overlapping stereo-pairs of black and white aerial photographs. These would be interpreted using a mirror stereoscope allowing the geologist to view the terrain in three dimensions. Large areas of previously poorly mapped terrain were surveyed in this way, particularly by the former colonial powers in Africa and Asia, and also throughout the United States of America. These aerial surveys were primarily for topographic mapping purposes (good topographic maps being a prerequisite for any kind of socio-economic development in remote areas). However, geologists soon recognised that different rock types and lithologies erode in different and quite

characteristic ways in various geographic and climatic environments, so that very detailed and accurate geological maps can be made with a minimum amount of field checking. Stereoscopic or 3D viewing is especially useful in helping the interpreter recognise different landforms and map drainage patterns (which often reflect underlying rock types), geological bedding, strike and dip, as well as fault offsets. In this way the geology of many of the main producing oil regions of the world, such as the Zagros mountains of Iran, the interior basins of North America and the giant structures of Algeria, were first mapped in detail. Today, as we will see below, photogeology has largely been replaced by satellite image interpretation and stereo-viewing has been replaced by 3D representation and visualisation techniques of Digital Elevation Models (DEMs) made possible by computer graphics. However, the basis of satellite image interpretation remains as it was with photogeology: careful visual analysis by experienced geologists with good field understanding. Another great advantage of photogeology and particularly later developments in satellite imaging, is the wide overview provided by these techniques relative to working on the ground. Not only does this greatly speed up the task of geological mapping, but it allows the geologist to make observations outside the immediate area of interest – for example, source rocks often do not outcrop within a basin of interest, but are actually exposed some distance away, possibly across political borders. Furthermore, broad scale structures, which could be very difficult or impossible to detect close-up on the ground, can be observed.

Considering they evolved in a pre-computer period, aerial photography and photogrammetry became a very sophisticated and accurate process for the production of detailed topographic maps. Ingenious optical, mechanical and photographic methods were used to mosaic together photographs and remove distortions inherent in the camera process. These were further developed during the Second World War, when aerial reconnaissance became an extremely important strategic intelligence tool. At this time, colour photographic materials started to emerge, including infrared films for camouflage detection, and radar technology, both of which would later prove extremely significant for geological reconnaissance representing major inputs into future space developments.

### **Infrared or false-colour photography**

Following the Second World War, aerial photography reached maturity and most parts of the world were surveyed in this way, although the photos and resulting maps were often considered secret or classified by national governments for security reasons. One significant development was the use of camouflage detection or colour infrared film. This film is sensitive to reflected infrared radiation just beyond the capability of the human eye. In this part of the spectrum, vegetation reflects very strongly and there is a very wide range of response between different types of vegetation. This is the reason the film was developed for detecting unnatural false vegetation used for military camouflage, but the result is that subtle variations in natural vegetation can also be clearly seen in an enhanced way and this is often geologically related. Different combinations of plant communities favour soils derived from different rock types. All of this serves to help the photogeologist map different and varying rock types, especially in regions generally obscured by vegetation and soil cover. A further advantage is that in the near infrared part of the spectrum, penetration of atmospheric haze is improved so that false-colour photos often appear sharper, especially when acquired from a high altitude. These benefits were later put to good use in the development of satellite imaging instruments.

### **Radar imaging**

Difficulties remained, however, in high latitude and tropical and equatorial regions where persistent cloud cover precluded the acquisition of consistent and cloud-free photos. This problem was solved by the development of radar systems since they are capable of imaging the terrain surface through cloud cover. These are active systems operating in the microwave part of the spectrum, which illuminate the ground with an oblique swath and then record the reflected radiation to generate an image; adjacent overlapping swaths can be viewed stereoscopically. Although such radar images are generally more difficult to interpret than conventional photographs due to their oblique illumination angles, they also sometimes enhance topographic and geomorphic features revealing surprising additional geological detail. In the 1970s, before the advent of satellite imagery, many areas of the tropics of interest for oil exploration such as in Central and South America, West Africa and Southeast Asia, were mapped with airborne radar for geological interpretation.

### Remote sensing from space

The so-called cold war led to the increased use and awareness of remote aerial intelligence. The subsequent vulnerability of manned high-altitude reconnaissance aircraft stimulated the development of space for strategic purposes. Thus space became the next arena both for exploration and for the acquisition of images of the Earth. Both the US and URSS developed photo-reconnaissance satellites in the 1950s and 1960s, but the results were rarely, if ever, seen by civilians, although by the late 1960s photographs of the Earth taken by astronauts in the US Apollo missions had shown how valuable consistent satellite imagery might be to geoscientists. It was not until 1971 that the US launched ERTS1 (later renamed *Landsat*) and consistent, geographically rectified images started to become available to researchers worldwide.

Although the initial Landsat images had a resolution of only 80 m, they were in infrared false-colour and could be enlarged to 1:250,000 scale, moreover they were available for most of the world with the exception of cloud covered areas. Their availability coincided with, and contributed to, the developing understanding of plate tectonics throughout the 1970s and 1980s, particularly in terms of brittle tectonic features such as faults and lineaments, which could now be mapped on a continent-wide scale. In this respect, offshore satellite gravity (see below) also made a major contribution. Oil companies rapidly started to exploit the use of newly available satellite imagery for regional tectonic studies, basin analysis, seismic planning and even crude structural target selection. Some remote parts of the globe which had never been surveyed with aerial photographs were now mapped for the first time. The Landsat series have continued to be developed with 30 m resolution imagery appearing with the Landsat ETM in 1986, together with additional middle infrared spectral bands especially useful for discriminating different clay minerals and hence improving geological mapping capability. The last satellite in the series, Landsat 7, launched in 1999, which however failed in 2003, provided 15 m ground resolution and the feasibility of mapping up to 1:50,000 scale (**Fig. 1 A**).

As a result of this failure, the ASTER imager (built in Japan but mounted on NASA's Terra satellite, launched in 1999) has come to prominence as a short-term alternative. This is interesting to the geologist because it offers 15 m resolution with 14 spectral bands and the

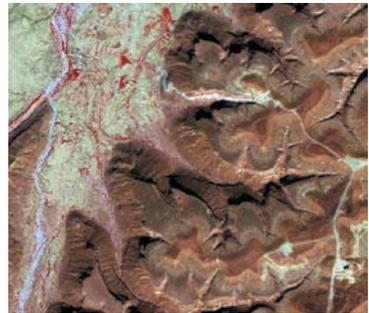
capability of generating DEMs (see below). Unfortunately the spectral bands on ASTER are on the whole more suitable for examining igneous and metamorphic rocks and minerals than for oil exploration geology. ASTER, however, has generated considerable geological interest leading towards the two other hyperspectral satellite sensors, NASA's Hyperion (launched on EO-1 in 2000, 220 spectral bands with 30 m resolution) and the European Space Agency's CHRIS (launched on PROBA in 2002, 18 spectral bands with 18 m resolution). Because of the small

**Fig. 1.** Comparison of Landsat ETM, SPOT and Ikonos data-sets (Yemen).

**A.** 15 m Landsat ETM



**B.** 5 m SPOT



**C.** 2.5 m SPOT



**D.** 1 m Ikonos

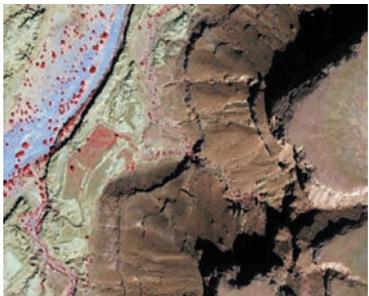


image areas of these two sensors and the limited coverage available, as well as the unsuitability of CHRIS's bands for geology, both satellites remain primarily of research rather than operational interest.

A Landsat follow-on mission is to be planned by the United States, but most observers believe there will be a new programme, possibly with international cooperation. The future drivers for such programmes will be primarily concerned with environmental monitoring, forestry, agriculture and land-use mapping, but the science of geology will also be a beneficiary. Although much geological analysis still remains to be done with images archived over the last 20-30 years, geological interpretation generally does not necessarily need the most up-to-date images.

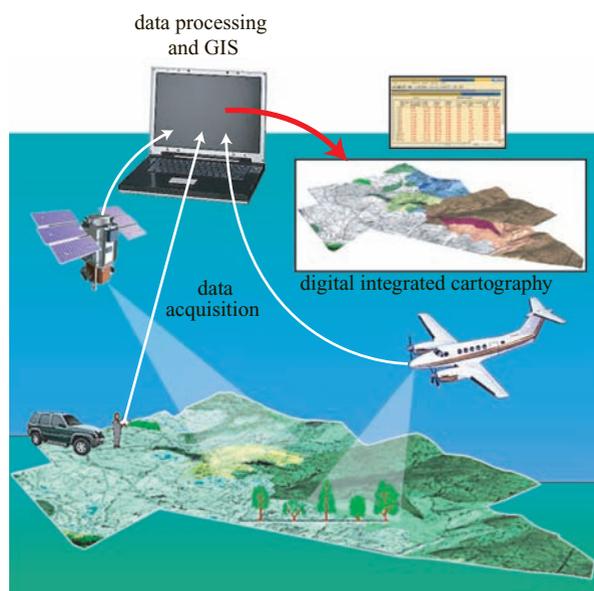
### **Computer Image Processing and mapping**

The images from Landsat (and most other imaging satellites) are transmitted to ground as electromagnetic signals and so are highly suited for computer manipulation and enhancement. In the 1970s, low cost digital computers were still being developed and the necessary input, mass storage and output devices to handle the complex and large data volumes of satellite images were scarce and expensive. This situation started to change dramatically in the late 1980s with the advent of affordable microcomputers so that the true value of this important source of geological information could finally be realized. Today it is possible for a geologist to download from the Internet 15 m resolution imagery of just about anywhere in the world onto his personal computer, merge it with digital elevation data, render the results in a 3D view and then 'paint' his interpretation of the geology onto the image and extract that as geological map for colour printing. Furthermore, he can import and register many kinds of ancillary data such as potential fields (magnetics and gravity), subsurface (seismic and wells) and general information to elaborate and enhance the final interpretation.

*Image Processing* (IP) techniques allow images, and particularly those with multiple spectral bands, to be enhanced and displayed to best effect to help the interpreter in his work. The images can be sharpened and filtered in various ways and the brightness and contrast adjusted to optimise the interpretability. IP can also be used in some areas to carry out certain mapping operations semi-automatically, for

example selecting all areas of a particular rock type or vegetation cover. However, most geologists agree that visual interpretation, using the human brain and its amazing capacity to make optical associations and recall all the experience of field training, remains paramount. Thus IP systems contain functionality to annotate the images with the interpreter's mapping, such as bedding traces, structural symbols and lithological boundaries. IP also facilitates the merging of differing data sets, so that the texture or terrain detail of a satellite image can be coloured, for example, with the co-registered elevation data or with an aeromagnetic contour map to make a composite image. Investigating such comparisons may help the geologist both in his surface interpretation and in understanding the relationship of the surface morphology to the subsurface geology. Finally, these merges may be displayed in 3D or perspective view to give an additional dimension. IP becomes particularly important when dealing with multiple spectral channels, such as with the ASTER satellite, because it is only with the help of the computer that the different combinations of spectral response can be analysed to map out the various contributions of mineral spectra. This will become even more critical in the future when interrogating data from the next generation of truly hyperspectral satellites.

*Geographical Information System* (GIS) on the other hand, is basically the modern replacement for printed maps with the additional dimension that all the information is stored digitally and ordered in relational databases. GIS allows the mapmaker to bring together disparate information to form many different sources and ensure that it is all geographically co-registered, and to present the results with a high degree of flexibility (**Fig. 2**). Typically a GIS will allow the use of different map projections and data and will contain functionality that allows inter-comparison of the feature content and links between the different elements making up the data set. Ultimately, maps can be printed on demand at a wide range of scales and projections with appropriate backdrops of imagery or geophysical data as required. The obvious great advantage of the GIS approach is that maps can be continually updated and revised in terms of content and inter-relationships displayed. The trend is for this to be achieved almost exclusively on the computer screen rather than with printed media.



**Fig. 2.** GIS system: production of digital and geo-referred thematic maps and 3D models.

The technology of IP and GIS is still developing just as rapidly as the power and ability of microcomputers themselves. IP works on raster data (comprising a matrix or grid of data values such as a photographic or other image), often with a high degree of colour depth (for example, 24 bits in the case of most satellite data), whereas GIS is dominantly oriented around relational databases and vector graphics (comprising point values, often linked together making up lines and polygons). At the present time these two approaches do not converge or integrate quite as readily as would suit the geological user, but this will change as the technologies mature. Furthermore, there is still a considerable gap between the specialised processing and display systems used for subsurface data such as seismic information and those used in IP and GIS; however, these can be expected to converge in the near future.

### **GIS, integration of thematic maps, digital databases and three-dimensional models**

Maps and data obtained either on the ground or with the methodologies and instruments described above can be integrated with one another in a GIS to produce specific final maps in either 2 or 3D to meet the various requirements of oil exploration. For example, topographic maps can be integrated with geological maps, aerial photographs and satellite images (**Fig. 3**).

The merging of various types of remote-sensed data, e.g. Landsat images with SPOT images or radar (see below), enables maps to be produced that describe particular features of the terrain (lithology, structural lineaments, vegetation, soil moisture) revealed by a different spectral resolution or sensor (e.g. Radar) or characterized by high spatial resolution (for example, obtained with SPOT images). Other information such as roads, national boundaries, vegetation, buildings, can be superimposed on application-specific maps (morphological, geological, relating to engineering facilities, etc.). The final geographical database thus comprises various 'layers' (see again Fig. 3).

Using GIS software, cartographic and other data can be analyzed and integrated to obtain both topographic maps and also digital thematic maps, including, for example, morphology, geology, lithology, stratigraphy and chronostratigraphy, structure and tectonics, hydrology, slope stability, vegetation, wetlands, pollution. Furthermore computer techniques facilitate the overlaying and intercomparison between these various themes or layers. GIS systems also allow all the associated information in the relational database, such as elevation values, names, symbols, rock type, structural orientations, geochemical values, to be displayed, edited, analysed or updated.

Thus modern digital maps are derived from a series of inter-related digital databases, and diverse data such as well locations, exploration concession boundaries, seismic lines, oil pipelines, field and reservoir outlines can be imported and exported. Increasingly sources of these databases are distributed in different locations such as with oil companies, geophysical contractors, government agencies, and the great power of the Internet comes into play in searching for data and bringing together the various elements which constitute the specific map required for a particular application.

Finally the latest techniques in visualization decrease the need for printed maps and enhance the way in which data, particularly in 3D such as thematic maps draped over DEMs, can be viewed. In the past maps were drawn with pen and ink and, finally, lithographically printed in colour; an expensive and time consuming process. Today, large format colour printers connect direct to computers and print out customized maps rapidly on demand. However, printed maps are used less and less as geologists and geophysicists undertake their analysis on computer work-stations, many of which have 3D display capability, either through the use of special viewing glasses or with screens which provide direct 3D rendition to the naked eye. Where geo-scientists need to consult together, special 3D 'visionariums' or

immersion studios have been developed so that all participants can see surface and sub-surface models in 3D and even walk about to discuss the geology in 3D space, with seismic lines shown on the terrain surface and the seismic sections and exploration wells projected into the sub-surface!

**VHR and future optical satellites**

Other satellites, which have contributed to the available database of optical imagery include the French SPOT series, which since 1986 have provided 10 m ground resolution and stereo capability allowing the production of digital elevation models and 3D geological interpretation. SPOT 5, the latest in the series, provides 2.5 m resolution (**Fig. 1 C**) and a special DEM generating sensor. Most recently Very High Resolution (VHR) imaging satellites have appeared, which provide a ground resolution of 1 m (Ikonos, since 1999, **Fig. 1 D**) or 0.65 m (Quickbird, since 2002). Although these satellites are primarily used for military intelligence, their imagery is now generally available for most areas of the world, and they can be very useful in the oil exploration field for mapping terrain access, infrastructure and even production facilities (**Fig. 4**). However, the small area covered by each frame (11 km×11 km) means that images such as SPOT (60 km×60 km) or Landsat (185×185 km) are generally preferred for pure geological mapping (see again Fig. 1). Optical satellites have also been launched by Russia, India, Japan and Israel, amongst others, and are used where appropriate in geological mapping. A new generation

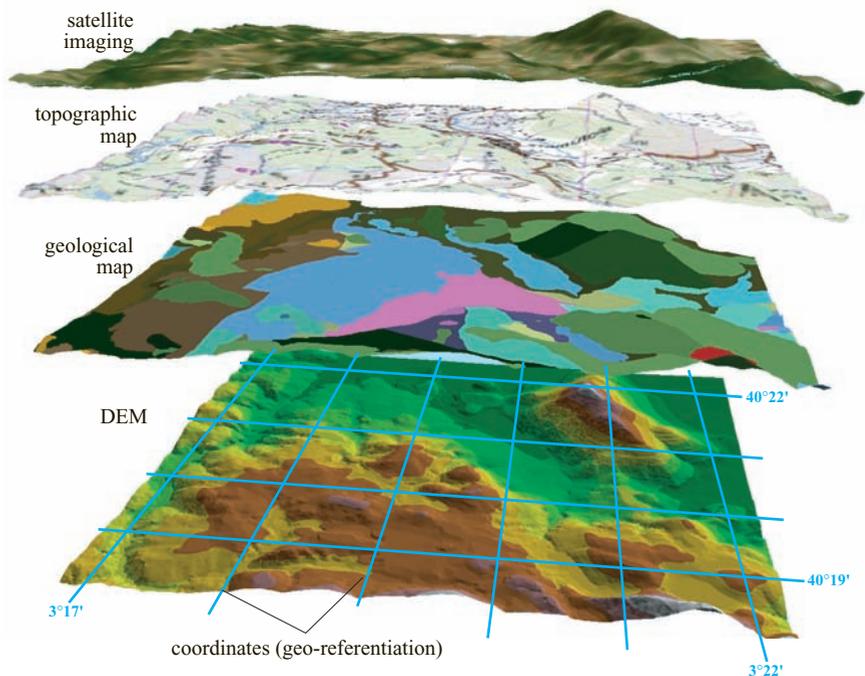
of low cost micro-satellites have been developed in the UK, and a constellation of five has been launched specifically for disaster monitoring. Because of the military and security demand, it is certain that there will be no shortage of future optical data.

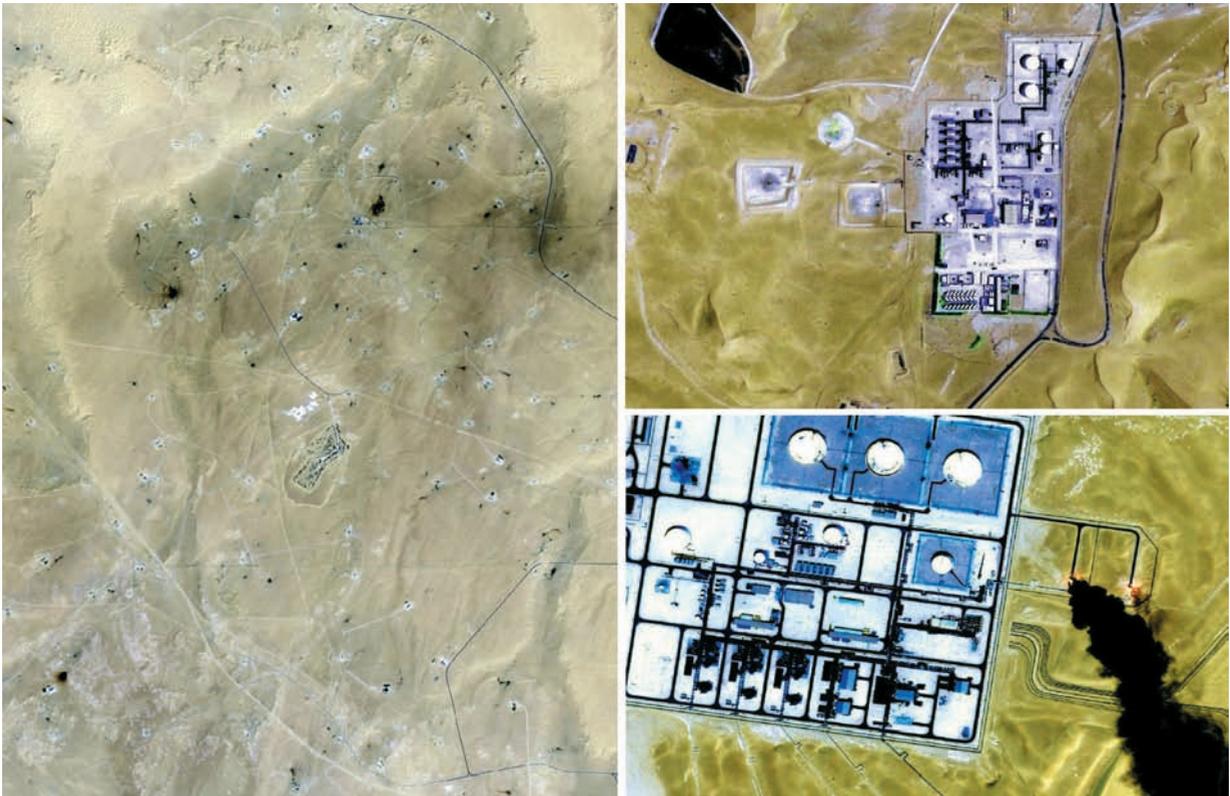
**Radar satellites**

Alongside optical satellites, Synthetic Aperture Radar (SAR) imaging satellites have also been developed. These were designed primarily for observation of the world's oceans, but have also been found useful for onshore geological interpretation in areas of high cloud cover.

The first consistent global radar coverage came from the European Space Agency's ERS1 satellite launched in 1991, followed by ERS2 in 1996. These were designed to observe the state of the global oceans as an environmental indicator (since the oceans are the driver of continental meteorological patterns), but knowledge of ocean conditions is also critical for many aspects of offshore exploration, production and transport of hydrocarbons so that there has been an important spin-off for this industry. Furthermore, the radar sensor also provides excellent imagery of the land, which can be used both for geological interpretation and a wide range of environmental applications (cf. **Fig. 5**, where the ERS radar imagery, of the same area covered by the Landsat data, shows a greater amount of continuous structural detail than available on the optical data.

**Fig. 3.** Geographical Information System (GIS): integrated cartography.





**Fig. 4.** Ikonos image showing production installations around Hassi Messaoud (Algeria; NPA Satellite Mapping).

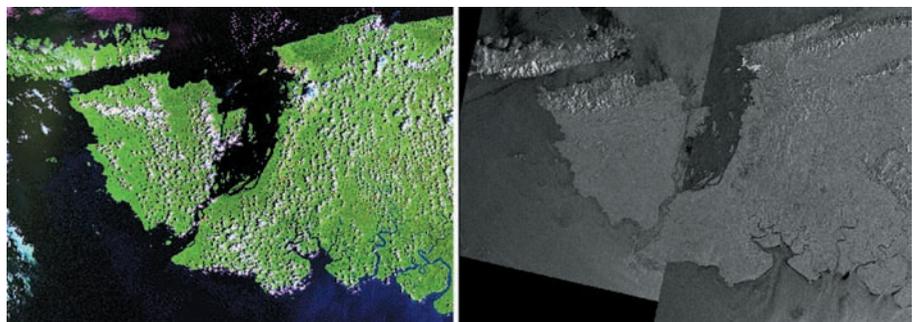
The cloud-free nature of the radar has enabled faults, linears and anticlines to be mapped over tens of kilometres). Canada launched a similar, but more versatile satellite (Radarsat) in 1995, with the primary objective of monitoring sea-ice (another area of environmental concern for offshore exploration and production activities in high latitudes). Radarsat, with its variable pointing capability, can also be used to make topographic contour maps through ‘radargrammetry’ and has provided some of the first digital elevation models for remote cloud covered areas of the world. Whereas ERS and its successor, Envisat, have a ground resolution of around 20 m, Radarsat also

has a ‘fine’ beam mode with a resolution of 10 m. Other satellites are planned with 1 m resolution (by Radarsat and by Terrasar).

#### **Digital Elevation Models (DEMs)**

Digital Elevation Models are for the geological interpreter in many respects the modern equivalent of stereo air photographs, and so are in strong demand for exploration in remote areas. They can be used alone for both geomorphologic and geological interpretation as well as for the assessment of access or logistics. Furthermore they can be merged with satellite imagery to produce data sets which can be computer rendered for 3D

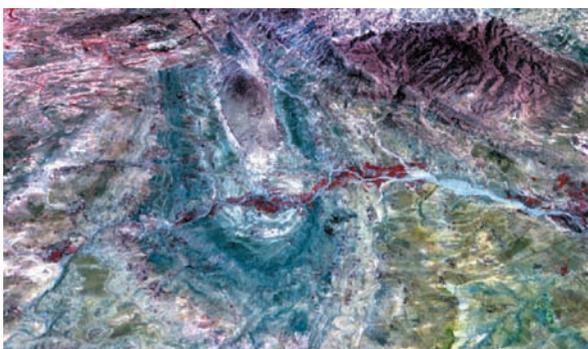
**Fig. 5.** Comparison of optical Landsat ETM and ERS radar data (Irian Jaya; NPA Satellite Mapping).



or perspective viewing, including the production of simulated fly-throughs. DEMs can be made from stereo air photos, digitising existing topographic maps, stereo satellites images or with radar interferometry (InSAR), either airborne or spaceborne. One such InSAR system, the SRTM (Shuttle Radar Topographic Mission) was operated on a Space Shuttle mission in 2000 and has produced a high definition (30 m horizontal spacing, 15 m vertical accuracy) set of data for most of the world within 60° South and North. At present the highest level of definition of SRTM data is militarily restricted in most areas outside the USA because of its value for logistical navigation, so only data with a 100m horizontal grid is available.

Optical satellite systems for DEM generation include SPOT 5 with a 6-10 m vertical accuracy on a 20 m horizontal spacing and ASTER with a 30 m vertical accuracy on a 15 m horizontal spacing (Fig. 6 shows a 3D false-colour image created from the ASTER DEM using three of its spectral bands (3-2-1, R-G-B), looking north-east up the nose of the fold. The more resistant and cooler central core of the fold is a lower Eocene carbonate, surrounded by marls and shales).

Airborne systems can provide even higher levels of accuracy, and an airborne interferometric radar system has been used to cover complete territories such as the UK and Indonesia providing a DEM with around 0.5 m vertical accuracy. The ultimate level of terrain detail available today is acquired with airborne Lidar systems capable of producing vertical accuracy down to a few centimetres. These have been successfully applied to create DEMs for onshore seismic planning in several different types of terrain including desert sand dunes and coastal mangrove swamps.



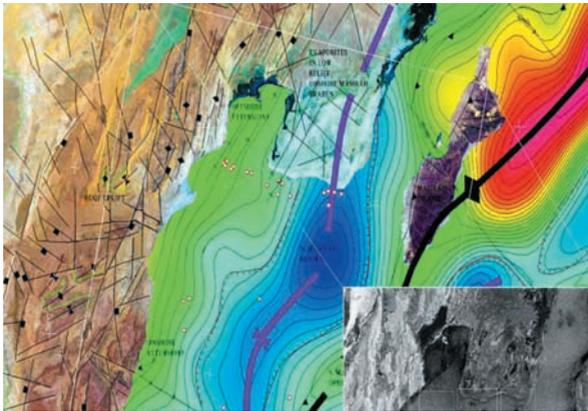
**Fig. 6.** ASTER DEM (Tunisia; NPA Satellite Mapping).

### Offshore exploration. Seep detection and satellite gravity

The uses of satellite techniques are not restricted to onshore regions. An unexpected benefit of radar satellites to the oil exploration community has been the ability to detect traces of oil on the sea surface with satellite radar imagery. The presence of small amounts of oil on the sea surface modifies naturally occurring wavelets or ripples induced by wind on the sea surface, creating ‘slicks’ or areas of calm sea. These show up quite clearly on radar images because the wavelength of the ripples is very close to that of the radar (5.6 cm). Many of these surface indications derive from pollution effects, but some are the result of natural hydrocarbon seepage from the sea floor to the sea surface. Careful study of the ‘slicks’, coupled with analysis of their shape and knowledge of the prevailing weather, makes it possible to separate pollution from natural seepage with a good degree of confidence (Fig. 7). Thus it has been possible to study almost all the world’s offshore basins for signs of natural seepage in a consistent way, and this has proved an inexpensive and valuable tool in screening frontier basins, particularly in deep water, to prioritize them before companies commit to the much more expensive geophysical methods that are necessary for the next stage in exploration. Not only does this technique indicate whether there is a working hydrocarbon system in the basin or not, but the relation of the seepage pattern to the basin architecture may reveal important information about depocentres, source kitchens and migration pathways.

Offshore oil exploration geology has benefited from yet another military innovation achieved from space: the requirement for submarine navigation. Underwater, beyond the sight of stars or without the aid of artificial navigation satellites (e.g. GPS), submariners required a map of the ocean floor comparable to a topographic map of the land surface. Charting the world’s oceans in sufficient detail with conventional means is an operationally and politically inconceivable task. However, it was clear that either a map of bathymetry (water depth) or the Earth’s gravitational field would provide the necessary navigational aid, and this could be achieved by radar altimeters measuring the ocean surface height from orbiting satellites.

One might think the Earth should be a near perfect spheroid, whose exact shape is known. In practice the ocean surface does not precisely conform to this, but has a complex pattern of small undulations induced by a combination of the local water depth and gravity field, which is related to the density of the surrounding rocks. By systematically observing the height of the ocean geoid from satellites over many hundreds of



**Fig. 7.** Satellite image, offshore gravity interpretation and seepage detection (Oman; NPA Satellite Mapping).

orbits and extracting the mean result showing subtle ocean surface gradients, highly detailed maps revealing ocean bathymetry and offshore gravity can be derived. Although these do not replace highly accurate swath bathymetry and shipborne gravity surveys carried out later in the exploration process, they nevertheless permit low cost reconnaissance surveys in the world's last remaining frontier offshore basins, especially when coupled with the satellite radar offshore seep detection method described above (see again Fig. 7). The first ocean altimeters were US military missions such as Geosat launched in the 1980s and not declassified until the 1990s, but the density of global observations has been greatly increased by more recent civilian missions such as Topex/Poseidon and the altimeters mounted on the two ERS satellites (which also have created the bulk of the archives of radar imagery of the ocean surface used for oil seep detection).

### Global Positioning and Communications Systems

Discussion of the contribution to exploration from space would be incomplete without mentioning Global Positioning Satellites and Communication Satellites. Handheld or even wristwatch GPS devices capable of pinpointing latitude and longitude to a few metres are now commonplace, but we should not forget that geologists often had to rely on astronomical observations to be sure of their position in the field, even as recently as the 1970s. Furthermore satellite telephones now allow the field party not only to talk to base and home, whether from onshore or offshore, but also to transmit maps, images, field data, reference material to and from central archives via the Internet. Of course, once again, we might not have these convenient tools were they not developed first for military use.

### Environmental applications

All the aerial, satellite and computer mapping techniques discussed above clearly have many important applications in the environmental field, with the added dimension that monitoring temporal changes is far more significant in the environmental domain than it is for geology. Satellites are highly efficient and cost-effective for repeated imaging and long-term monitoring. Furthermore, their design is generally much better adapted to detecting vegetation and soil changes or mapping coastal ecology, for example, than it is for geology. With the rapidly growing awareness of the need for environmental responsibility, we can be sure that many projects in sensitive areas will work against an environmental baseline developed using historically archived satellite data and will be monitored with the latest satellites as they become available. These techniques are also applicable to exploration and production facilities, and to pipelines and processing plants, where physical security from ground movement or incursion is as important as the environmental aspects.

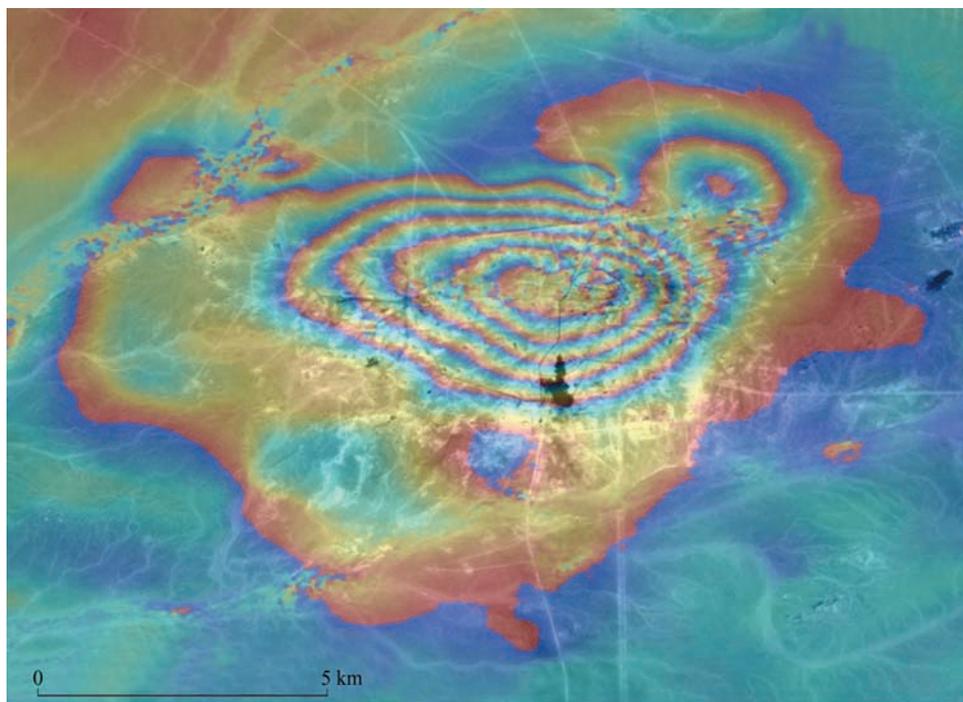
The latest developments in satellite radar interferometry (**Fig. 8**) provide the ability to measure ground movements or relative changes in the Earth's surface down to the millimetric level, which is much better than we can currently achieve with GPS. As a consequence, not only may we detect the incipient movement of soil creep as a precursor to landslips affecting pipes or industrial facilities, but we can measure the ground subsidence above reservoirs as they are depleted and monitor the possible environmental effects. This may lead to pipelines and other installations in sensitive or unstable areas being equipped with special reflectors or transponders to facilitate the satellite measurements and monitoring. There are also possible applications in the reservoir engineering field, since this kind of mapping may help understand the stochastic response of the reservoirs.

### The future of the remote sensing instruments and technologies

Many new Earth observation satellites are planned for launch, particularly high resolution optical and radar imaging systems. There will undoubtedly also be more 'hyperspectral' imaging satellites with hundreds of spectral bands which will greatly improve our ability to distinguish and map different rock types, although vegetation and soil cover will remain a problem. We can also expect to see increasingly detailed digital elevation models of the Earth's surface which will help with geological interpretation, planning access and environmental protection.

However, hydrocarbon accumulations are generally found at some depth below the Earth's

**Fig. 8.** Subsidence pattern over the Jibal oil field (Oman), produced from satellite radar interferometry: each colour fringe represents 28 mm of subsidence (Oman; NPA Satellite Mapping).



surface, yet for the time being the tools we have view only the surface. Ideally the aim would be to have some spaceborne or airborne tool capable of revealing hydrocarbons at depth. This still seems some way off. We know that hydrocarbons do seep to the surface in most if not all basins, but onshore most obvious surface manifestations are already known. One significant outcome of the global offshore radar seepage detection method mentioned above is that offshore, seepage patterns are much more widespread and pervasive than we might expect from onshore evidence alone, as – onshore – it is clear we are not seeing the full picture because of the intervening mask of overburden, soil and vegetation. The more subtle effects, such as gas seepage, are still extremely difficult to detect even with painstaking methods on the ground, let alone from the air or space. Even well exposed rocks strongly altered by the long term effects of seeping gaseous hydrocarbons have proved extremely difficult to distinguish with existing spectral or thermal sensors. We should expect to see some progress in this area as more sophisticated satellites, particularly hyperspectral, are put into operation, but it should be borne in mind that the main applications for such satellite are unlikely to be oil exploration alone. In terms of remote mapping of the subsurface (i.e. non seismic) we could expect that there will be improvements in the sensitivity and capability of airborne techniques such as magnetics and gravity, but these are unlikely to be achieved from the altitude of orbiting satellites and so will

remain airborne developments. One area which might have some promise is the use of satellite radar interferometry to detect millimetric changes in Earth surface elevation with time. As mentioned above, existing radar satellites are already being used in this way to monitor small amounts of subsidence over oil and gas fields as they are depleted. The technique is so sensitive (capable of resolving changes down to the millimetric level) it might provide clues to subsurface reservoirs and their likely contents (oil or gas) by pinpointing differential surface changes with Earth tide state. Environmental satellites are already compared with medical technology as providing a ‘health-check on planet Earth’. In geological terms we can expect that future space missions will provide both spectroscopic and tomographic analysis of the Earth’s surface, all contributing to our knowledge of the sub-surface where oil and gas still lie hidden. A futuristic vision perhaps, but not so far-fetched considering the leap we have already made from hill top visual observation to the space age of the early 21<sup>st</sup> century.

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### 2.2.2 Geological surveying

Geological surveying is the earliest investigation method in oil exploration. It was first used in the mid 19<sup>th</sup> century when researchers began to realize that the presence of reservoirs was linked to the geometry of the rocks (traps) and their lithological characteristics, and that at times it was possible to find the evidence of deep geometries in outcrops. Most areas with these characteristics have now been fully explored, even if mapping structural lineaments on a large scale from satellite images is still useful for regional studies. Geological surveying is now performed chiefly to support geophysical surveys, especially for exploration in areas where only indirect data (seismology, gravimetry, etc.) are available.

In this type of survey, geological data are systematically collected to obtain information about the geological features of a given area. The results of observations on the ground must be supplemented with stratigraphic, structural, petrographic, sedimentologic and palaeontologic analyses, which allow for synthetic charts and diagrams to be produced (geological maps and sections, stratigraphic columns and drawings) in order to trace the rocks present in the area in question, their surface distribution and their spatial relationships.

Geological surveying is fundamental to hydrocarbon geology because it defines the stratigraphy of the region and therefore the presence of potential source rocks, reservoir rocks and sealing rocks, as well as the structural configuration of the area to explore. Since most structures containing hydrocarbons are buried and cannot be observed from ground level, geological surveying can be performed in areas close to the hydrocarbon exploration zone when there are similarities (lithologic, stratigraphic, structural, etc.) between buried and outcropping rocks. Information obtained from the geological survey must then be extrapolated to the exploration area. For example, potential reservoir rocks, which contain hydrocarbon reservoirs in the Po Valley, and the relative sealing rocks, outcrop extensively in the Alps. Geological surveying, carried out along the Alpine chain by generations of geologists, has provided a full picture of the stratigraphic sequence widely used for deep

exploration of the subsurface structures in the Po Valley.

The main aim of a geological survey is to produce a map which shows the distribution of outcropping rocks (geological map). Geological maps are generally plotted on existing topographic bases; if no topographic base exists for the area in question, one will have to be produced *ad hoc*. This is presently done using remote surveying methods (satellite images, aerophotogrammetry, etc.).

Outcropping rocks, identified mainly on the basis of their lithologic characteristics by means of surveying techniques (Low, 1957; Lahee, 1961; Cremonini, 1973; Damiani, 1984), are shown on the geological map.

#### The concept of formation

A formation is a geological body whose lithologic characteristics observable on the field, which are not necessarily uniform, allow for its identification and characterization. Rocks with sedimentary origin are particularly important in hydrocarbon exploration. The lithology of a sedimentary body is the result of the sedimentation environment, therefore the geologist's task is to study the correspondence between sedimentation environments, their vertical evolution and their lateral changes.

The stratigraphic position of a formation is of fundamental importance: rocks with the same lithologic and sedimentologic characteristics but of a different age are attributed to different formations; coeval rocks with different lithology, formed within different sedimentary environments, are also attributed to different formations.

There are numerous criteria which distinguish one formation from another. Lithology may differ even within the same formation: some formations have fairly uniform lithology (such as the Dolomia Principale), while others have two alternating lithologies (e.g. the Marnoso-Arenacea Formation). Other distinctive criteria include: bedding characteristics, which may be massive (e.g. Dolomia dello Sciliar in reef environment) or more complex (like the Dolomia Principale in shelf environment as mentioned above); colour (Scaglia Rossa, which is different from Scaglia Cinerea); sedimentologic characteristics (the Arenarie di Serravalle are much

more cemented than the Sabbie di Asti); age (the last two formations date to the Miocene and Pliocene respectively). At times age may not be identifiable directly on the field studying macrofossils, but only by means of micro-palaeontologic lab examination. Some of the formations mentioned above were named adopting lithological criteria, using the name of the location where the formation has its best characterisation. It is in this location that the formation is generally described in lithologic, sedimentologic and palaeontologic terms, measuring its thickness, and interpreting the environment and vertical and lateral variations.

Hydrocarbon exploration can reach formations which do not outcrop or which in any case can be assessed more effectively in the subsurface; many formations have recently been identified and described during hydrocarbon exploration. In many cases a formation is known better in the subsurface, when it has been drilled by wells during exploration activities, rather than from its outcrops. Moreover, a formation is often not as deformed in the subsurface so it can be defined better; as an example, the Frio Formation in the Oligocene rocks of Texas (Galloway *et al.*, 1982), or the Cellino Formation in lower Pliocene rocks of central Italy (Casnedi, 1983) can be considered.

### Geological maps

A geological map is the output of a systematic process generally involving different steps.

Firstly, a preliminary study is carried out with quick surveys throughout the studied area; a geologist can identify the main outcropping formations and their stratigraphic relationships.

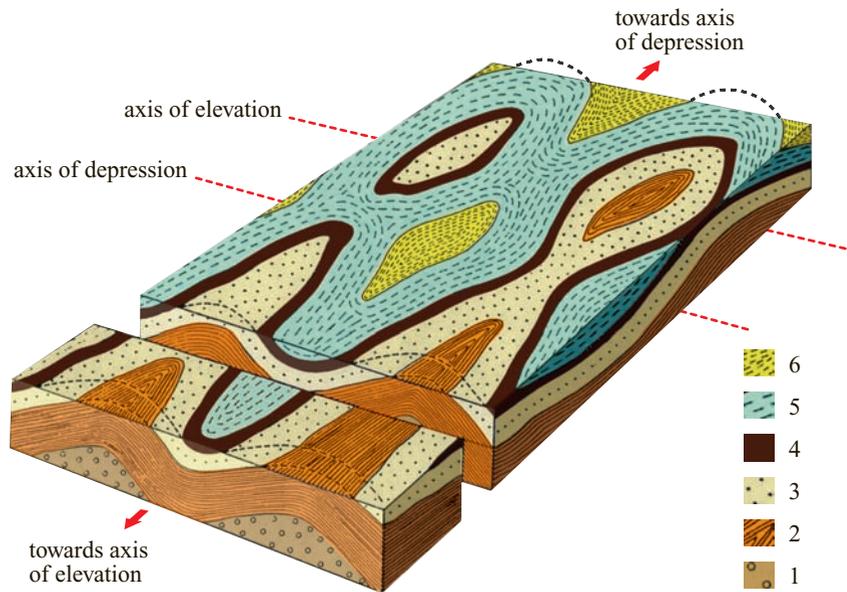
The area is then mapped in increasing detail. During this stage the geologist obtains more information about the formations present in the area, identifies units inside them in more detail (formations can be divided into members) and establishes the relative stratigraphic relationships, i.e. superposition or lateral transition if the formations are coeval. At the same time stratimetric data are collected (strike, dip and inclination of the formations); these data are used when establishing the formation superposition relationships and the structural setting of the area. The map must indicate, as accurately as possible, the boundary between formations when they are in contact. When the boundary lines are traced, it is important to specify whether the contact between the two formations is stratigraphic, corresponding to a normal chronological sequence or if it is tectonic, caused by a deformation (fault), which displaces the rocks in an irregular manner.

In the case of stratigraphic contact, the surface separating the two formations is represented by a line which indicates the intersection of said surface with the topographic surface: if the layers are horizontal, the line runs horizontally, that is, parallel to the contour lines; if the layers dip in an opposite direction to that of the slope, the line follows the contour lines, rounding their curvature; if the layers dip in the same direction as that of the slope, but with reduced inclination compared to that of the slope, the line accentuates the curvature of the contour lines. If the lines dip in the same direction as that of the slope, but with greater inclination to that of the slope, the line curves in the opposite direction to the contour lines. Finally, in vertical formations the line is straight and follows the strike of the formations. Palaeontologic data (mainly macrofossils), sedimentologic data (such as the bottom marks of the formations which allow the direction of provenance of clastic sediments to be determined), petrographic, structural and geochemical data can also be collected on the field.

Finally the data collected are processed; this step, which either follows or alternates with field work, is essential for an exhaustive geological survey. A geological survey can be completed with delimitation of the formations when their contact on the field cannot be observed due to vegetable cover or inaccessibility. Stratimetric data are used to trace or complete boundary lines because they allow interpolation and extrapolation of the relative orientation of the formations, bearing in mind, as already mentioned, the trend of the beddings compared to the dip of the slope. A network of interpretative geological sections provides useful indications to check the precision of the field survey.

During this stage the nature of the tectonic surfaces surveyed on the field is interpreted: if the sequence is stratigraphically normal and the erosion phenomena have acted above all on raised areas, a fault will cause the older formations to outcrop on the raised side. Correct tracing of the fault surfaces will allow the dip of the fault plane, to be identified, therefore distinguishing between tension faults, where the lowered side coincides with the dip of the fault plane and compression faults, where the opposite situation occurs. Fold phenomena, if not directly identified in the field (as in the case of large scale folds) can also be reconstructed during the map production stage: in an anticlinal fold the bedding planes dip away from the fold axis and in most cases older rocks outcrop along the core of the fold, normally corresponding to the axis. A fold where the opposite situation occurs is called synclinal. Fold geometries are also determined by analysing the geological map, especially if

**Fig. 1.** Block diagram of a folded region with undulating fold axes (elevation or culmination axes and depression axes); 1-6, strata in age sequence (Jaroszewski, 1984).



accompanied by the relative block diagram (**Fig. 1**): an anticlinal fold can have zones where folding is more pronounced (structural culmination) or less pronounced (structural depression); the same occurs for synclinal folds. Structural culminations are a favourable site for hydrocarbon accumulation (see Chapter 1.3).

Finally, petrographic and sedimentologic studies are performed in the laboratory to obtain the chemical-mineralogical compositions of the formations; sedimentologic studies are carried out at the same time to define the environment in which sedimentation took place and to define the texture of the sediments (size, shape and arrangement of the constituent elements). These studies are useful in hydrocarbon exploration as they are informative of the petrophysical characteristics of potential reservoir rocks and mainly of their porosity. Palaeontologic analyses are of utmost importance: while a macrofossil can be identified directly in the field, the study of microfossils and their associations, the cornerstone of stratigraphy, is carried out on thin sections and residue of appropriately chosen washed samples using a microscope. Geochemical analyses can be performed on samples of source rock (for oil-source rock correlation studies) or on oil and gas samples when surface shows occur.

A well-planned geological survey is based on the collaboration of surveyors, working in the field or in the office studying the data collected, and analysts such as petrographers, above all sedimentary petrographers, and micropalaeontologists, working in the laboratory.

### Thematic maps

Geological cartography can provide thematic products, which refer to specific aspects of scientific interest or of application to hydrocarbon exploration. The maps used in hydrocarbon exploration, which include surface and subsurface data, for three-dimensional evaluation of rock bodies, are: structural maps, isopach maps, isolith maps, lithofacies maps, palaeogeographic maps and palinspastic maps.

There are two types of structural maps: those representing outcropping areas of the major structural units (for example, the structural map of the Alps, which indicate the outcropping cartography of Helvetides, Pennides, Austrides, etc.) and those with greater detail and of higher hydrocarbon interest which indicate the structure of each formation in the subsurface by means of contours. These more detailed maps are used to represent the structure of a reservoir rock, allowing hydrocarbon-bearing areas to be identified in the structurally higher parts of the reservoir rocks.

Isopach maps represent the distribution of the thickness of a given formation using isolines; if it is reservoir rock, the map gives information about the volume of the reservoir.

In formations with different lithologies, isolith maps represent the thickness of a single lithotype by means of isolines; each isoline indicates a given thickness of the lithotype in question; in hydrocarbon exploration this is generally the porous-permeable fraction (e.g. in an interbedded sand and shale formation only the thickness of the sand that can contain hydrocarbons is indicated).

Lithofacies maps represent the lithofacies of formations for a given chronological interval, highlighting porous-permeable lithofacies, supplementing surface data with data obtained from drilling. This lithofacies map provides a picture of potential reservoir areas. Superposing on it the lithofacies map of the chronologically higher interval helps identifying areas where impervious lithofacies, which may represent seals (sealing rock), overlie those with porous-permeable lithofacies (potential reservoir rock); this stratigraphic requirement is necessary for the presence of hydrocarbons in the reservoirs.

Palaeogeographic maps represent the geography of a region in the reference period and therefore the distribution and altitude of emerged areas, coastlines and submerged areas, with the depth of the sea in the period in question. These maps are used in hydrocarbon exploration to identify stratigraphic traps (see Chapter 1.3).

Palinspastic maps indicate the original position of formations, before subsequent dislocations modified the primary relationships.

Traditional tools such as compasses and altimeters can be supplemented with more modern instruments such as GPS (Global Positioning System) for direct georeferencing of points surveyed – using a network of geostationary satellites – and electronic compasses with digital memory, which allow immediate storage of measured data. These instruments facilitate data entry in digital form.

Particular features of the ground (morphology, rock fracturing) can be acquired by means of stereophotogrammetry in which three dimensional photographs of significant outcrops such as quarries, rock walls and landslides are reconstructed. Cartography produced directly on the field can also be supplemented with information obtained from remote measuring (aerophotogrammetry, satellite images, etc.).

The data can be processed using GIS (Geographic Information System), a system developed to manage, handle and analyse spatial data (digital numerical cartography); thus data for which the geographic coordinates (latitude, longitude and, when available, altitude) are known or can be calculated are used.

DEM (Digital Elevation Model) processing, where mapped data correspond to the average elevation of the ground at that point, is important in cartography. Models can be obtained from remotely measured images or by digitalising existing topographic maps.

Thematic maps (topographic, geological, morphological, structural, etc.) produced with the aid of the methods and tools described above

(georeferencing, electronic compasses, digital models of the ground, stereophotogrammetry, satellite images, etc.) allow digital databases to be created in order to supplement cartographic products (often three-dimensional) with the relative lithologic, structural, petrographic data, etc.

### 2.2.3 Petrography

Petrography is the study of the genetic processes of rocks, their structure and composition. Since, with rare exceptions, hydrocarbons are closely linked to sedimentary rocks in terms of origin, migration and accumulation, only the petrography of sedimentary rocks (Pettijohn, 1957; Bosellini *et al.*, 1989; Blatt, 1992; Tucker, 2001), and in particular their nature, composition and classification, will be discussed.

In the oil industry, quantitative analyses and petrographic studies are carried out using optical and electronic microscopy, diffractometry and X-ray fluorescence allow to determine the composition of the constituent parts of rocks, identify autigenous elements (cements) formed during the burial of the rocks, highlight dissolution phenomena of given constituents, reconstruct the succession of the cementation-dissolution events affecting the sediment to determine its present structure and, finally, through image analysis, specify the geometric characteristics of the porous component of the sediment.

Petrographic studies are carried out on samples of rocks obtained from well cores and outcrops and on drilling cuttings (small fragments of rock produced by the bit and carried to the surface along with the drilling mud). The data are then entered in the sedimentologic and geological model of the basin to predict the quality, in terms of reservoir characteristic (porosity and permeability), of the sedimentary rocks also in zones where no drilling is being carried out.

Important information is obtained which, along with other data, is used to assess whether an exploration well should be drilled or a programme prepared to develop the reservoirs identified.

#### Frequency of sedimentary rocks

Endogenic processes are responsible for the origin of the magmatic rocks while sedimentary rocks originate from exogenous processes. Consequently, the frequency of the latter increases gradually approaching the Earth's surface. While the Earth's crust contains less than 5% of sedimentary rocks and metamorphic rocks of sedimentary genesis, most (around 75%) outcropping rocks are of sedimentary origin.

The main reason for the abundance of outcropping sedimentary rocks is chemical instability, or metastability, of magmatic rocks in the presence of atmosphere. Indeed, rocks and minerals are in equilibrium only in the physical-chemical conditions in which they are formed. The formation temperatures and pressures of magmatic rocks are much higher than those measured on the Earth's surface. Moreover, the deep environments in which they form contain smaller quantities of oxygen, water, carbon dioxide and organic material, substances which enrich the sedimentary rocks through oxidation, hydration, hydrolysis and salification processes.

**Classification of sedimentary rocks**

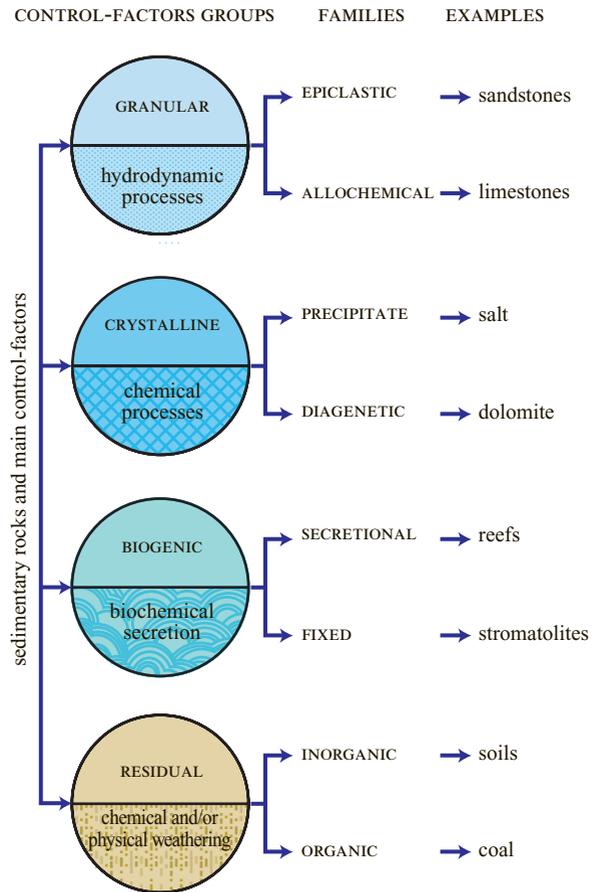
There are two main classification criteria: the first is based on the genesis of the rocks, the other on their chemical-mineralogical composition. The two criteria often relate to the same types of rock, because the genesis of a sediment affects its composition.

*Genetic criterion.* The original rock, exposed to the action of atmospheric agents, is degraded through physical processes (disaggregation) and chemical processes (alteration). Most disaggregation products (clasts) are removed and transported (in suspension or by rolling) by water courses and the wind, giving rise to epiclastic rocks made up of particles which sediment through settling; other particulate or granular rocks include pyroclastic rocks, of volcanic origin, and allochemical rocks such as oolitic limestone and limestone formed by fossil fragments.

Chemical alteration creates products generally transported in solution in meteoric water which sediment through precipitation, following evaporation or variation of chemical equilibriums, to form crystalline rocks of sedimentary origin. These rocks should not be mistaken for those of metamorphic origin. After sedimentation, diagenesis of the limestone, which takes place upon ionic exchange with the sea water, can give rise to the formation of dolomites.

The part of rock not removed after degradation or decomposition remains *in situ* and forms the residual rocks. The action of living organisms forms organogenous or bioconstructed rocks consisting entirely of skeletons or fragments of shells of animals or vegetables (reefs formed mainly of corals and algae) or by carbonatic fixation by vegetables (stromatolites) (Fig. 2).

*Compositional criterion.* The main components of sedimentary rocks are terrigenous rocks, allochemicals and orthochemicals (Bosellini *et al.*, 1989, Fig. 3).



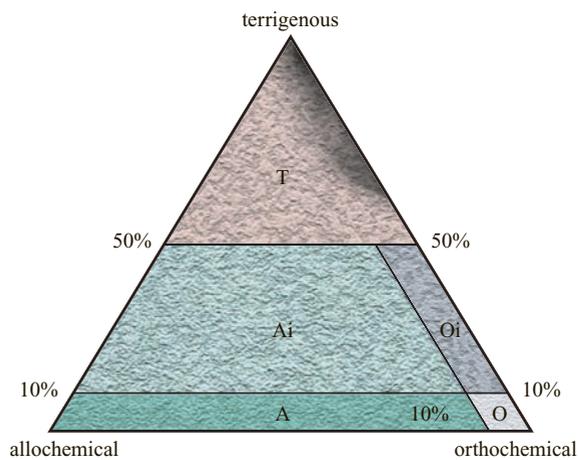
**Fig. 2.** General chart of sedimentary rocks based on their genetic-textural characteristics (Bosellini *et al.*, 1989).

The terrigenous components comprise particles generated by the disaggregation and fragmentation of existing rocks, eroded and transported individually in the sedimentation basin. Alteration takes place over time, modifying the chemical-mineralogical composition of the rock (Fig. 4). The most important terrigenous rocks are quartz (35-50%), feldspars (5-15%), clay minerals (25-35%), micas and heavy minerals (less than 1%), fragments of rocks and chert (5-25%).

The allochemical components consist of particles formed through chemical precipitation or organic secretion directly in the sedimentation basin where they can move and accumulate.

Orthochemical components are chemical precipitates formed in the sedimentation basin, such as evaporites, or products of solutions circulating within the same sediment, such as cement.

Genetic criteria (sandstone), compositional criteria (carbonate rocks) or both (shale) are used to describe the different sedimentary rocks.



T. Terrigenous rocks - example: many argillites, sandstones and conglomerates. They form the 65-75% of the sedimentary rocks; the main part falls in the dark area.

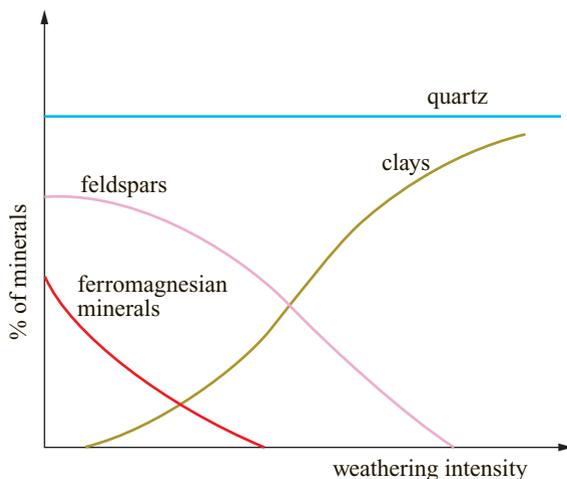
Ai. Impure allochemical rocks - example: very fossiliferous clays, sandy limestones, marls. They form the 10-15% of the sedimentary rocks.

Oi. Impure orthochemical rocks - example: clayey gypsum. They form the 2-5% of the sedimentary rocks.

A. Allochemical rocks - example: oolitic and fossiliferous limestones. They form the 8-15% of the sedimentary rocks.

O. Orthochemical rocks - example: salt, anhydrite, chert. They form the 2-8% of the sedimentary rocks.

**Fig. 3.** Triangular diagram to classify sedimentary rocks on the basis of their three main components (Bosellini *et al.*, 1989).



**Fig. 4.** Variation in the mineralogical composition of a sand of granite origin subject to gradual alteration in a temperate climate (Bosellini *et al.*, 1989).

### Types of sedimentary rocks

The main types of sedimentary rocks are: shale (60%), sand, sandstone, gravel and conglomerates (20%), carbonate rocks such as limestone and dolomites (15%); along with these there are, in much smaller percentages, evaporites, particularly halite and sulphates.

Shales are formed by particles with a diameter of less than 4  $\mu\text{m}$ ; alongside silts, with dimensions of between 4 and 62  $\mu\text{m}$ . For this reason, these particles can be easily kept in suspension also by very weak currents. Larger accumulations of shale are found on the continental shelves or, interbedded with sandstone, at the foot of continental slopes where

sequences with thicknesses of up to several kilometres form in the turbidite fans. Shales mainly comprise clay minerals, originating from hydrolysis of silicates with quartz and feldspars prevailing in the silts. They are extremely porous but impervious and are therefore an excellent sealing rock but do not offer accumulation possibilities as a reservoir rock. When subject to overburden and pressure in general they are compressed, losing their porosity, and are called argillites (or pelites or lutites).

Sandstones include all detrital rocks consisting of particles with a diameter of more than 62  $\mu\text{m}$ ; when the sandstones are not compact they are called sands. If the particles are more than 2 mm, sandstones are classified as conglomerate (gravel if not coherent, breccia if consisting of elements with angular edges). Their composition depends on the rocks they originate from: quartz and feldspars, especially acid ones, dominate and are the most stable minerals. Alteration processes tend to transform less stable minerals, such as amphiboles, pyroxenes, olivine and, in general, the more basic ones which are therefore less frequent. Sandstone is called mature when the chemical alteration has acted over a long period of time and with greater intensity both in the area of origin and during transport. In parallel, physical agents such as transport have an effect: rolling has an abrasive effect and tends to smooth the edges, rounding the particles. After sedimentation, the most important diagenetic process is cementation through precipitation, due to solutions circulating in the rock pores. Cementation is decisive in calculating porosity values.

Sandstones are classified on the basis of the dimensions of the particles or as a function of their mineralogical composition. Distinction according to

dimensions uses a geometric scale: from 1/16 mm (62.5 μm) to 1/8 mm, very fine sand (or sandstone); from 1/8 to 1/4 mm fine sand; from 1/4 to 1/2 mm medium sand; from 1/2 to 1 mm coarse sand; from 1 to 2 mm very coarse sand. The same classification is used for rocks with larger grain-size such as conglomerates. Classification based on mineralogical composition is more complex: instead of the complex classical terminology, with numerous terms to represent the various types of sandstone, the classification method introduced at the beginning of the 20<sup>th</sup> century by Amadeus William Grabau is preferred, where rocks are defined with a compositional prefix and dimensional suffix (Grabau, 1913). Of the sandstones, siliceous arenites, for example, have a silicate composition and suffix deriving from the Latin *arena* “sand” and are differentiated from calcarenites, dolarenites, gypsumarenites, etc.

This terminology can be extended to all detrital or clastic rocks, from the finest (for example siliceous lutites, from the Latin *lutum* “mud”) to the coarsest (for example siliceous rudites, from the Latin *rudus* “pebble”). Despite the fact that their genesis is different from that of carbonate rocks with chemical or organogenous origin, clastic rocks with carbonate composition (such as calcarenites) are generally described together with the latter, giving more importance to their composition than their genesis.

Carbonate rocks originate from direct chemical precipitation of CaCO<sub>3</sub> or through fixation by organisms with carbonate shell or skeleton. The formation of limestone is often followed, due to ionic exchange with salt water containing magnesium, by their transformation into dolomites whose constituent

mineral, dolomite, has the formula CaMg(CO<sub>3</sub>)<sub>2</sub>. Scientific interest for carbonate rocks is accentuated by their fossil content: indeed, it is above all through palaeontologic study of remains contained in carbonate rocks that the history of the Earth and its biological evolution has been traced.

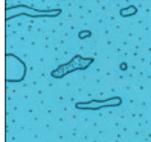
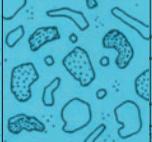
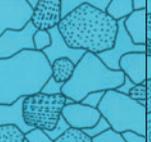
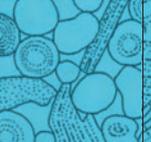
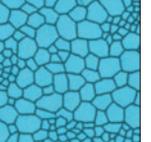
Along with their link to the biological world, carbonate rocks are different from other sedimentary rocks because they deposit *in situ*, without the significant contribution of transport processes (except for the case already mentioned of clastic carbonate rocks), because of their premature diagenesis and their composition which is often mono-mineral. Indeed its constituent minerals are calcium carbonate (in the forms of calcite and aragonite, often determined by a different crystalline status of the shells of the organisms) or dolomite, originating from secondary processes following sedimentation; carbonate may on rare occasions be iron (siderite) or magnesium (magnesite). Clay minerals are fairly frequent; their presence gives rise to typical mixed rocks like marlimestone and marl.

Carbonate rocks are more complex to classify than clastic rocks because not only their mineralogical composition, but also their textural and diagenetic characteristics, which best characterize the type of rock, have to be taken into consideration. The most widely adopted classifications (Bosellini, 1991) are those proposed by R.L. Folk in 1959 (Fig. 5) and the one developed by R.J. Dunham in 1962 (Fig. 6). Folk’s classification is based on textural components: allochems, i.e. the various constituent particles; the matrix, comprising carbonate mud (micrite); the cement, formed by sparry calcite or sparite. Dunham’s classification is

**Fig. 5.** Classification of carbonate rocks according to the terminology proposed by Folk (1959), based on textural components (Bosellini *et al.*, 1989).

main allochemicals					other categories
fossils and bioclasts	ooids	peloids	intraclasts		
BIOMICRITE	OOMICRITE	PELMICRITE	INTRAMICRITE	matrix > 2/3	MICRITE WITH VUGS (dismicrite) (fenestra, birdseye)
BIOSPARITE	OOSPARITE	PELSPARITE	INTRASPARITE	cement > 2/3	BIOLITITE

**Fig. 6.** Classification of carbonate rocks according to the terminology proposed by Dunham (1962), based on depositional texture (Bosellini *et al.*, 1989).

depositional texture: recognizable					not recognizable
primary constituents (grains) not bound during deposition				primary constituents bound during deposition	CRYSTALLINE CARBONATES
mud present (grains < 30 μm)		mud absent			
mud-supported texture		grain-supported texture			
grains < 10%	grains > 10%				
MUDSTONE	WACKESTONE	PACKSTONE	GRAINSTONE	BOUNDSTONE	
					

more widely used and is based on the original depositional texture in relation to its hydrodynamic significance. This introduces the distinction between particles without mud, deposited in a high energy environment (reef), and mud supported particles, deposited in a relatively calm environment (lagoon). The terms already described (calcarenite, etc.) can also be used for carbonate rocks of clastic origin. In carbonate rocks, porosity and permeability characteristics relate mainly to secondary processes, particularly dolomitization.

Rocks with evaporitic origin, less frequent than the others, play an important role in the oil industry because they are impervious and can be typical sealing rocks. They take their name from their origin, linked to evaporation processes, particularly active in hot, arid climates. Being highly soluble, these rocks can be dissolved easily by meteoric water.

Evaporation of salt water in a closed system causes the gradual precipitation of salts in reverse order to their solubility. The first to precipitate is calcium carbonate, whose poor solubility gives rise to the formation of carbonate rocks; these can also form with poor evaporation (precipitation is linked to the release of carbon dioxide into the atmosphere). The deposition of calcium sulphate, in the form of anhydrite at high temperatures, or gypsum and halite, with a much higher salt concentration, follows. The last minerals to form, in smaller quantities due to their low concentration in salt water, are magnesium sulphate and potassium chloride (silvite).

Evaporation often does not take place in a closed system: occasional contributions of salt water can cause innumerable repetitions and interbeddings. In the Mediterranean and surrounding areas for example, the Upper Miocene evaporite sequences are

particularly important; these have been related to the drying up stages of the sea, following the closure of the Strait of Gibraltar.

Sedimentary rocks also include siliceous deposits of biogenic origin, produced by the accumulation of organisms with siliceous skeleton (sponge spicules, diatoms, radiolaria) and of diagenetic origin (chert nodules, lenses and beds), often present in the carbonate sequences; iron-manganese, phosphate and coal deposits are also frequent. In hydrocarbon geology, anoxic sediments resulting from the sedimentation of organic matter in a reducing environment are also important: for further information about these sediments, closely linked to hydrocarbon source rocks, see Chapter 1.2.

## 2.2.4 Principles of stratigraphy and sedimentology

### Stratigraphy

Stratigraphy studies the chronological sequence of events influencing the Earth's history, determining the space and time relationships of the rocks. Closely related to sedimentation, stratigraphy also analyses other phenomena such as magmatism, metamorphism, deformations, climatic variations and changes in the distribution of seas and emerged lands.

As most of the chronological attributions are due to the study of fossils and the biological evolution of sedimentary rocks, stratigraphy offers valid support to palaeontology and sedimentology. Methods for defining the chronology of a stratigraphic sequence are based on relative and absolute criteria.

*Relative chronology.* The concept of sequence is a relative criterion, linked to vertical, and therefore

**Fig. 7.** The Grand Canyon sedimentary sequence of Colorado shows a succession of formations from the Precambrian to the Tertiary for a chronological interval of more than 600 million years (by courtesy of RIT, New York).



time-related relationships of the stratigraphic units. The basic principle of relative chronology is the principle of sedimentary superposition which assumes that increasingly recent units progress from bottom up, except in a few, easily recognisable cases of intensely deformed or overturned sequences. The most spectacular example of application of the sedimentary superposition principle can be seen in the Grand Canyon in Colorado (**Fig. 7**), where the formations outcrop in regular succession from the Precambrian to the Tertiary for a time interval of more than 600 million years. This principle is confirmed by palaeontology, which identifies increasingly evolved fossils in the vertical succession.

The second principle is that of correlation, where the chronological equivalence between units of different stratigraphic sequences is identified. This can be established by comparing the lithological characteristics of the sequences (lithostratigraphy) and distinguishing the various units (formations) and sub-units (members). Oil exploration has combined surface lithological analysis on the Earth's surface with subsurface analysis: with electric and radioactive logs of formations in boreholes it is possible to make correlations based on similarities between their characteristics; in the same way, seismic surveys have allowed sections to be traced which can be interpreted using stratigraphy (seismostratigraphy), with the possibility of reconstructing the geometry of sedimentary bodies. A unit generally has a limited horizontal development because its lithology changes with changes in the sedimentation environment; the palaeontologic criterion (biostratigraphy) which allows comparisons even between one continent and another is preferred for wide-ranging correlations. This criterion has resulted in the definition of a

chronological scale (chronostratigraphy), valid at a global level, which represents the basis for the history of the Earth.

Chronostratigraphy allows rock layers to be dated and relative time relationships to be established. The geochronological unit refers exclusively to the time interval in which a certain sequence of rocks deposited; in the chronostratigraphic unit geological time is represented by the same sequence. Chronostratigraphic units therefore offer a representation of the Earth's history: in decreasing hierarchical order eras, periods, epochs and ages depending on their importance and relative duration (see the data offered by the International Commission on Stratigraphy; Hedberg, 1976); geochronological units on the other hand only provide the time numerical datum.

Other correlations are based on palaeomagnetism: ferromagnetic minerals, if placed in a magnetic field, are magnetised and remain so during cooling; this fixes the characteristics of the magnetic field at the moment of crystallisation of said minerals. As the characteristics of the magnetic field vary over time, their determination on oriented samples allows magnetostratigraphy evaluations.

*Unconformities.* The Earth's surface is subject to erosion due to the action of atmospheric agents: the continual movement of materials from the continents to the oceans leads to the peneplanation of the surface at the end of an orogenic cycle until the invasion of the sea in the previously emerged area (transgression) triggers the next cycle. The products of erosion, deposited in a submarine environment, can give rise to a continual succession of stratigraphic units without interruptions in sedimentation. In other cases, events generally linked to deformation stages, lead to an

interruption of sedimentation, shown by the lack of corresponding units, often well documented by palaeontology (sedimentary-chronological *hiatus*). The most common case is that of the rise of one part of the sequence with ensuing emersion (regression). During this stage, sedimentation can continue into the continental environment but more often a partial or total dismantling and denudation process takes place due to the erosion agents.

Subsequent transgression can give rise to new sedimentation and superposition of horizontal formations on deformed ones (unconformity). Cases of stratigraphic unconformities are varied.

Oscillations in the level of the sea have above all affected the continental margins, giving rise to variations in the coastline, with ensuing different palaeogeography. The causes of these oscillations can be global (eustatism) such as the increase in temperature which leads to the melting of glaciers or local, such as volcanism or the deformation of the Earth's crust. Eustatic variation curves have been reconstructed at a global level (Vail *et al.*, 1977); these are of major interest in the geology of hydrocarbons as a lowering of the sea level (low-stand) activates erosion phenomena and progradation into the sea of sedimentary bodies where hydrocarbons can accumulate.

*Absolute chronology.* While the principles of relative chronology derive from direct study on the field, those of absolute chronology are based on the decay of radioactive elements present in the rocks. Each radioactive element transforms, emitting radiation, into one or more non-radioactive elements; i.e. stable elements. The time needed for a certain quantity of radioactive element to decay to half (half-life) is constant for each isotope. Measuring this time gives the absolute age of the rock. Thorium and uranium decay (to lead and helium respectively) measurements are used to date very old rocks; the transformation of thorium 232 into lead 208 has a half-life of  $2 \cdot 10^{10}$  years. Measuring the ratio between common lead ( $^{204}\text{Pb}$ ) and radiogenic lead, i.e. originating from the decay of thorium and uranium ( $^{206}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$ ) allows absolute age to be determined. Uranium rich minerals such as pitchblende were used for the first datings; it was noticed immediately that the rocks were much older than the estimates, based on sedimentation rate, made previously.

Other old dating methods use the decay of rubidium, which transforms into strontium (half-life of  $9 \cdot 10^{10}$  years) and potassium, which transforms into calcium and argon.

In the oil sector stratigraphy is fundamental because it classifies sedimentary sequences

encountered in the subsurface, source and reservoir rocks in particular, in time and space. It also provides information for other studies such as correlations between wells, interpretation of seismic data, basin modelling and reservoir characterisation.

Micropalaeontology (the study of microfossils) is used to date sediments drilled and identify their original sedimentation environment; these micro-organisms are very small and so can be identified even in small quantities of sediment or fragments of rocks (e.g. cuttings). Microfossils are studied in different types of samples (washed samples, thin sections, etc.) using an optical microscope; the sequence is dated and the stratigraphic column of the well is reconstructed with the age and names of the stratigraphic units drilled.

Stratigraphy is also applied during drilling because the position reached by the bit can be established by identifying the formations drilled on the basis of the lithology and microfossils present, thus allowing subsequent operations to be planned more efficiently and above all giving a more precise forecast of the times needed to reach the reservoir rock.

Stratigraphy is therefore a very useful tool when drilling directional wells. Finally, in-depth knowledge of formations being drilled allows direction variations to be set in order to intercept and follow the hydrocarbon-bearing formations.

### Sedimentology

Sedimentology studies the nature and composition of present and past sediments (sedimentary rocks) to identify their origin, the environment in which they are formed, their transport and depositing processes and other processes which modify and transform the sedimentary accumulations (Ricci Lucchi, 1978; Reineck e Singh, 1980; Selley, 1988; Zimmerle, 1995).

Transport, deposition and sedimentation processes and subsequent transformations affect porosity and permeability, the main parameters for hydrocarbon accumulation.

In the oil industry this discipline is used mainly to determine the areal distribution and geometry of rocks that may constitute source rocks, migration paths, reservoirs, sealing rocks, facies variations and therefore potential traps.

At a regional basin scale, information obtained from wells already drilled and information from surface geological surveys is important. Well data give spatially limited information, while reconstruction of the sedimentary structures visible in outcrops allows geological-sedimentary models to be created and used as reference for interpretation of similar situations in the subsurface. At the smaller

reservoir scale, sedimentology allows detailed study of how the reservoir facies are distributed, providing information which improves knowledge of the reservoir.

### 2.2.5 Tectonics and structural geology

Tectonics and structural geology study the movements which have deformed and modelled the Earth's crust.

Movement can take place through the simple transport of a rock body from one place to another or, more commonly, through a deformation which breaks the rock or changes its shape and dimensions. Tectonics studies the history of these movements and deformations from a regional to a global scale while structural geology ranges from a regional scale to microscopic deformations (Boccaletti and Tortorici, 1987; Twiss and Moores, 1997).

In the oil industry, tectonics is used to study deformations which have characterised the geological evolution of a sedimentary basin and which may have contributed to creating favourable conditions for the accumulation of hydrocarbons.

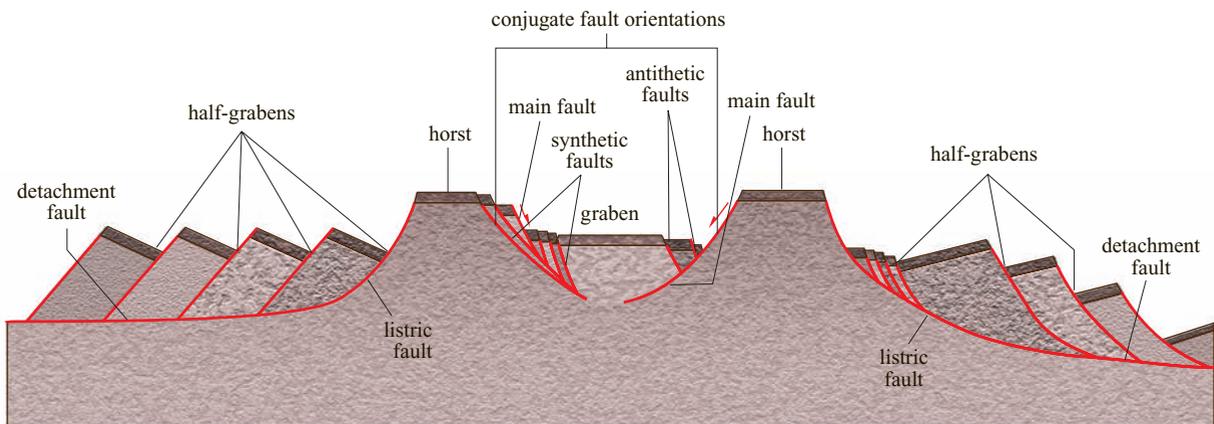
Structural geology is used in more restricted areas to establish trap formation processes and times. With structural geology studies it is possible to define the current configuration, reconstruct the progressive evolution of the deformations over time (cinematic synthesis) and establish the relationships existing between the forces applied and the resulting deformations (dynamic synthesis). This discipline also studies the fracturing processes which may, in carbonate rocks for example, have led to favourable petrophysical conditions for the formation of reservoirs.

Deformations of sedimentary rocks (Maltman, 1994) are interesting for hydrocarbon geology; when the rocks are subject to forces they undergo a strain and provide a stress which depends on their physical state and geometrical shape. An incoherent cement can therefore assume a particular strain state in response to a light force with a limited stress, while a lithified sediment will require a more intense force, with major stress, to assume the same strain state.

The first force acting on a sediment is gravity, which, depending on the compressibility of the sediment, produces a compaction strain associated with a vertical stress, both increasing with depth according to a relationship which links geostatic load to density and depth.

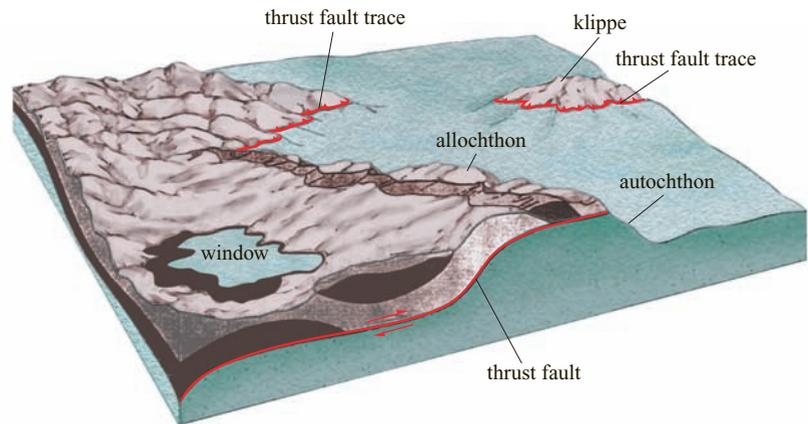
Tangential forces determine different deformations depending on the physical state of the sedimentary rock, its elasticity, homogeneity, intensity with which the force acts as a function of time and pressure and temperature conditions. A first distinction is made between brittle deformations and ductile deformations. The former occur in compact rocks (limestone and sandstones), which react with fractures and faults, the latter occur on plastic and incoherent rocks (shale and sands) which deform through folding.

If the force acts with low intensity but over long periods of time, a compact rock can deform plastically; in the same way, high temperatures and pressures favour plastic deformations (for example, folds in limestone and compact sandstone). On the contrary, high intensity forces over short periods of time can produce brittle deformations in plastic rocks (e.g. fractures and faults in shales). An influential factor is the homogeneity of the sedimentary sequence: limestone and sandstone



**Fig. 8.** System of direct faults normally characterised by a main fault associated with secondary faults and by low angle detachment faults (Twiss and Moores, 1997).

**Fig. 9.** Diagram of an overthrust nappe (*allochthon*) in compression style which overlies the autochthon sequence with thrust fault. The autochthon sequence is exposed in a tectonic window and a klippe represents the most external allochthon sequence, separated from the nappe by erosion (Twiss and Moores, 1997).



incur almost always brittle deformations if they are in massive bedding; if they interbed with shale, as in turbidite sequences, the entire sequence will tend to deform plastically in folds even with short bend radius.

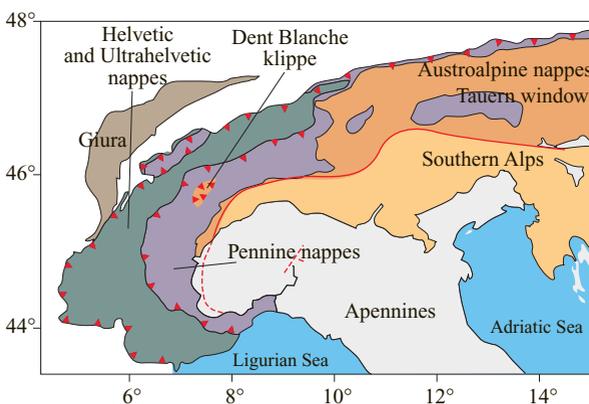
The deformation style is fundamental in hydrocarbon geology, as is the sealing rock/structural trap system (see Chapter 1.3). There are many cases of deformations with faults, of tensional (direct faults, **Fig. 8**) and compressional (reverse faults) origin, whose most evident effect is the nappe structure which characterises the mountain ranges (**Fig. 9**), in particular the Alpine chain (**Fig. 10**). Fold phenomena also result in structural traps which can be identified by the morphology of the folds, in particular of their axial culminations (Fig. 1).

Other techniques provide all the information needed to define fractured systems and reconstruct the structural

deformations. The data obtained can be on all scales: for example, well samples and logs provide information at a scale of a few mm to just over 1 m, while data obtained from seismics or satellite images are obviously on a larger scale, from some tens of m to several km. Three-dimensional geological-structural models can be reconstructed when a full set of data is available.

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**Fig. 10.** Structural map of the Alps with the distribution of the main formations. The Austroalpine nappes overlie the Pennines – outcropping in two tectonic windows (Engadina and Tauri) – which in turn overlie the Helvetides. Outside the chain the folded autochthon Giura sequence (Twiss and Moores, 1997).

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## 2.2.6 Subsurface geology

### Introduction

Subsurface geology is the study of drilled geological formations and the fluids they may contain (gas, oil, and/or water). Such studies take place on a rig site, where the oil company geologist supervises the work done by a service company specialist (a mud logger or a diagraphist). In the geology laboratory unit on the rig site, the geologist studies the cuttings available for the entire drilled length of the well, the cores which are taken from places of interest and the sidewall cores which are taken after drilling in important zones where no cores were taken before. A gas detector and a gas chromatograph linked to a mud degasser provide information about the output of gas from the mud stream. Gas detection is extremely important for security reasons and in order to determine the type of hydrocarbons in potential reservoirs. Other information regarding drilling parameters and mud characteristics, such as density, resistivity and temperature, are sent to the laboratory from sensors situated on the drilling rig.

The above information allows the geologist to establish an interpreted lithology column of the well, to make correlations with neighbouring wells and,

using the gas interpretation, to determine the presence of hydrocarbon reservoirs.

### Cuttings

The cutting size depends on the type of bit used, i.e. the longer the bit teeth, the bigger the cuttings. For example, Polycrystalline Diamond Compact (PDC) bits scratch the formation, making very small cuttings which are quite difficult to analyse. Once at the surface, the mud goes from the flowline to the shale shakers where the cuttings are separated from the mud. A container or board may be placed under the shale shaker in order to recover part of the cuttings which will be collected and analysed by the geologist or the mud logger (**Fig. 1**).

Large-sized cuttings (more than 5 mm), called cavings, fall from the hole wall and are not drilled from the bottom by the bit. Caving is a sign of well instability and can create major problems, from stuck pipes to collapse of the well.

Air drilling, also known as dusting the hole, produces very fine cuttings, and a large quantity of sample must be taken in order to recover some useful cuttings from the dust.

Mud loss in a well is another potential source of difficulty, as part of the cuttings are either lost or arrive late with respect to their theoretical lag time.

**Fig. 1.** Cuttings under microscope (courtesy of Geoservices S.A.).



The addition of lost circulation materials to the mud, and the difficulty in eliminating them, makes analysis more complicated.

#### *Lag time*

The time it takes the mud flow to carry the cuttings from the bottom of the well to the surface is known as the lag time. The general lag time formula is:

$$\text{lag time (min)} = \text{well annular volume (l)} / \text{mud flow rate (l/min)}$$

The annular volume is computed from:

$$\text{annular volume} = \text{open hole/s volume} + \text{casing internal volume} + \text{linear internal volume} + \text{riser internal volume (for floating rigs)} - \text{external volume of the drill string}$$

The flow rate is given by:

$$\text{flow rate} = \text{pump stroke volume} \times \text{pump efficiency} \times \text{number of pump strokes per minute}$$

It may also be useful to know how many pump strokes are needed to get the mud flow up from the bottom:

$$\text{lag strokes} = \text{annular volume} / (\text{pump stroke volume} \times \text{pump efficiency})$$

In deep offshore drilling a booster pump is sometimes needed to increase the mud velocity in the large diameter riser. When this is the case, the time required for the mud to go from the bit to the wellhead and from the wellhead to the surface must be calculated separately and then added together.

A problem arises from the fact that the lag time depends on the open hole diameter that is, in theory, the same as the bit diameter. In reality, however, caving may increase the hole volume quite a lot making the calculated lag time less than the actual lag time.

There are several techniques for checking the accuracy of the lag time. Originally, this was done by pouring red-dyed rice into the pipe at the surface, and letting the rice be carried to the bottom by the mudflow and then back to the surface. Measuring the time it took for the rice to arrive on the shale shaker gave an accurate value of the so-called short cycle, which is the lag time plus the time that the mud takes to go from the surface to the bottom inside the drill string.

Nowadays, it is common to use calcium carbide (which creates acetylene when in contact with water), or propane to avoid nozzle plugging. These gases are then monitored by the gas detector. With this technique, it is imperative to take into

consideration the transit time of the gas from the degasser to the gas detector.

#### *Sampling*

Different types of samples are taken by the diagraphist and sent to clients for further analysis:

- Unwashed wet: 500 cm<sup>3</sup> of raw samples (straight from the shale shaker) in a closed plastic bag.
- Washed wet: 150 cm<sup>3</sup> of washed samples in a sealed plastic bag.
- Washed and dried: 20 cm<sup>3</sup> of washed samples which have been oven dried, and stored in sealed paper bags.
- Geochemical: 750 cm<sup>3</sup> of raw samples, stored in a can and then covered with a bactericide solution; this type of sample is used for geochemical studies.

A spot sample is a small quantity of cuttings taken for analysis only. Spot samples are taken at the end of the circulation before a trip or when any drastic variation in the rate of penetration indicates a lithological variation.

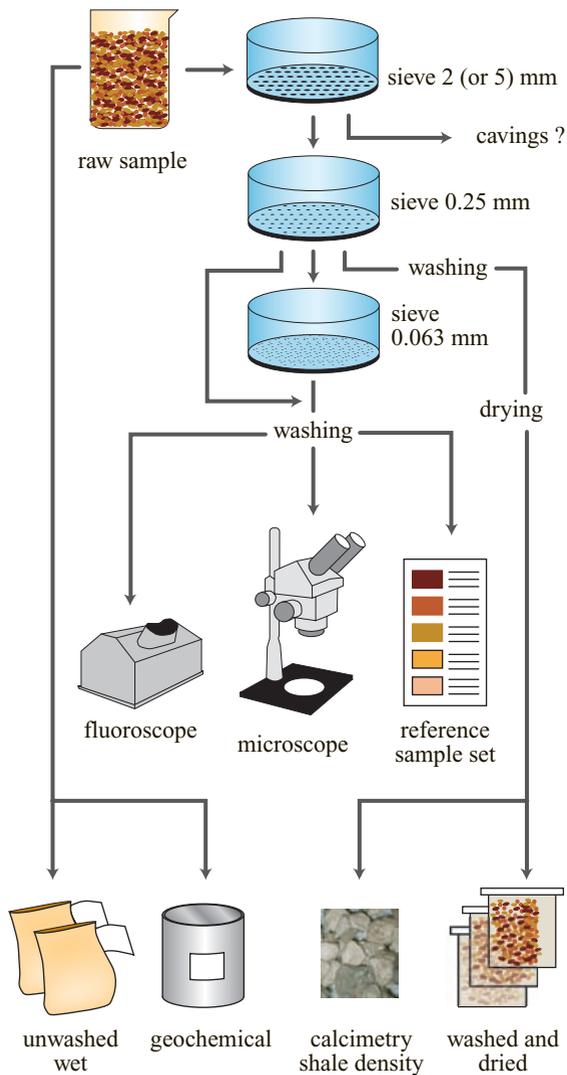
#### *General analysis procedure*

According to the geological program, the mud logger will take a sample of cuttings at a given rate (e.g. every 5 m). For example, if the bit is drilling at a depth of 1,000 m at 12.00, knowing the lag time (e.g. 45 min) the mud logger will take a sample on the shale shaker at 12.45. It should be noted that what is recovered corresponds to the entire interval from 995 m to 1,000 m.

Back in the mud-logging unit, the first thing that needs to be done is to check for fluorescence which may indicate oil staining: with this goal a small amount of cuttings is viewed under an ultraviolet lamp called a fluoroscope.

To obtain an accurate analysis, a constant volume of cuttings must be washed through three sieves (of 5 mm, 0.25 mm, and 0.063 mm), as shown in **Fig. 2**. With water based mud, the samples are washed with water; with oil based mud, they are washed with diesel or oil from the mud, then the samples are rinsed with detergent. A constant volume of samples is important when drilling soft clay; the argillaceous material is very small and will go through the 0.063 mm sieve, getting completely washed out. The remaining part will be predominantly sand and its volume will be measured in a graduated tube in order to determine the relative percentages of sand and clay.

The coarse part remaining in the upper sieve is considered to be caving. The part remaining in the two lower sieves is observed under a microscope



**Fig. 2.** The sampling procedure.

and the different types of rocks are described. Several chemical tests are available to help with rock determination. It is also important to determine the percentages of the different types of lithology. The samples taken correspond to a depth interval from 1 to 10 m and, in the case of rhythmic deposition, will contain different rock types.

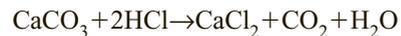
#### Cutting analysis kit

The materials needed to analyse cuttings are: *a*) tweezers to handle the cuttings; *b*) a teasing needle to test the hardness; *c*) a porcelain spot tray used to perform the chemical tests; *d*) a binocular microscope to observe the wet cuttings; *e*) a calcimeter to determine the quantity of calcium carbonate and dolomite. The chemicals used for the tests are: *a*) a solution of 10%

hydrochloric acid; *b*) a solution of 10% nitric acid; *c*) barium chloride; *d*) silver nitrate; *e*) alizarin dye and phenolphthalein.

#### Calcimetry

Calcimetry is used to measure the calcium carbonate content of a rock, thus allowing the quantitative determination of limestone and dolomite. The method consists of treating a standard weight of finely crushed sample with hydrochloric acid and measuring the volume of carbon dioxide produced by chemical reactions such as:



Recording the speed of reaction provides information on the presence of the substances mentioned above, especially that of dolomite. A quick reaction (less than 1 min) indicates limestone, whereas a slow reaction is characteristic of dolomite. In the case of dolomitic limestone, the curve is divided in two parts: the first is related to the reaction of limestone (up to 1 min); the second to the reaction of dolomite (from 1 min to the end of the process). Observation of the residue can also provide interesting information as it gives an indication of the presence of sand, clay or accessory minerals present in the carbonates.

Quantitative calcimetry also allows clay-carbonate combinations to be taken into account: *a*) a calcareous shale contains from 10 to 35% carbonates; *b*) a marl ranges from 35 to 65%; *c*) a shaly limestone from 65 to 90%; *d*) a pure limestone contains more than 90% carbonates.

#### Shale density

It is also possible to measure shale density in order to predict overpressures due to shale under compaction. Normally, compaction increases with depth, and formation water is expelled as porosity decreases. In some cases, however, the water cannot be eliminated in time and it remains trapped in the sediment. Water elimination from shale depends on three factors: the very low clay vertical permeability; the sedimentation and burial rates (if the sedimentation rate is very high, the shale is buried very deep before the water has time to escape and so remains trapped in the sediment, e.g. in deltaic areas); the drainage efficiency (sand layers act as a drain and help water elimination, for example, a shale which contains less than 15% sand will experience a lack of drainage). The excess of water provokes a decrease in the density of the shale. When the shale density is plotted against depth, an inversion in the density trend shows the top of the zone which is under-compacted.

The principle of the shale density measurement is to divide the weight of a shale cutting in the air by the weight in the air minus the weight of the cutting immersed in water.

#### *Preparation and use of the most common analytical solutions*

10% nitric acid is used to differentiate coal and lignite due to the fact that, in acid, lignite produces a brownish solution. 10% hydrochloric acid is used to detect calcium carbonate and dolomite. In contact with acid, calcium carbonate reacts quickly producing an effervescence due to carbon dioxide emission, whereas dolomite has a slower reaction.

Sulphates (present in gypsum and anhydrite) are detected using a barium chloride solution which is prepared by dissolving 61 g of this salt in 1,000 cm<sup>3</sup> of distilled water. In this solution sulphates produce a milky precipitate.

The presence of halite is determined using a silver nitrate solution. In such a solution halite gives rise to a milky precipitate in which turns black if exposed to light.

To highlight the dolomite crystals in a dolomitic limestone it is necessary to use a solution of alizarin red dye which is made with 1g alizarin red dissolved in 998 cm<sup>3</sup> distilled water and 2 cm<sup>3</sup> concentrated hydrochloric acid. The alizarin dye will stain limestone red but will not affect dolomite.

The presence of industrial cement can be revealed using a phenolphthalein solution made with 1 g of phenolphthalein powder in 50 cm<sup>3</sup> of methyl or ethyl alcohol. Such a solution is used after a casing cementation in order to determine the quantity of cement in the samples. The phenolphthalein works by staining the industrial cement red.

#### *Cutting analysis*

The first step in cutting analysis involves using a needle to assess whether a rock is soft, firm or hard. A soft and sticky white rock which dissolves completely in acid is chalk; when the sample does not chemically react with acid it is clay; while a small reaction indicates marl which has been defined by quantitative calcimetry to contain 35 to 65% calcium carbonate.

Loose grains are defined as sand, but may also be interpreted as sandstone that has been crushed by the drilling bit. If the sample shows little or no reaction with acid, can be easily scratched with a nail, is transparent and white to pink in colour and gives a positive barium chloride test, it is gypsum or anhydrite. Furthermore, gypsum is more fragile and lighter than anhydrite.

Halite (salt) has little or no reaction with acid, is transparent and white to pink in colour, dissolves in water, has a salty taste and reacts positively to a silver nitrate test. Lignite is a black and fibrous rock which reacts positively to the nitric acid test. A shale is a firm cutting which exhibits little or no reaction with acid, is easily scratched and breakable with a needle, and gives a negative result to any chemical test. As for the hard rocks, a strong reaction to acid and a calcium carbonate content greater than 65% is characteristic of limestone. Dolomite gives rise to a significant reaction which starts after some time. Furthermore an alizarin dye test will differentiate dolomite crystals in a dolomitic limestone. A weak reaction with acid but with a lot of very fine residue is indicative of marl.

A very hard rock that cannot be scratched with a needle, but scratches glass is a chert (called flint if it is black; while green or red cherts are jasper or radiolarites). A siliceous limestone will react with hydrochloric acid. Occasionally, some igneous rocks, e.g. basalt, may be drilled.

A lot of grains cemented together may be interpreted in different ways: if it is possible to visually separate the grains, and if there is loose sand present in the sample, it is sandstone. After a casing cementation, the cement looks like sandstone in the samples, but can be identified by testing with phenolphthalein. However, if the grains interlock and are randomly arranged with a lot of mica, we have granite or another plutonic rock.

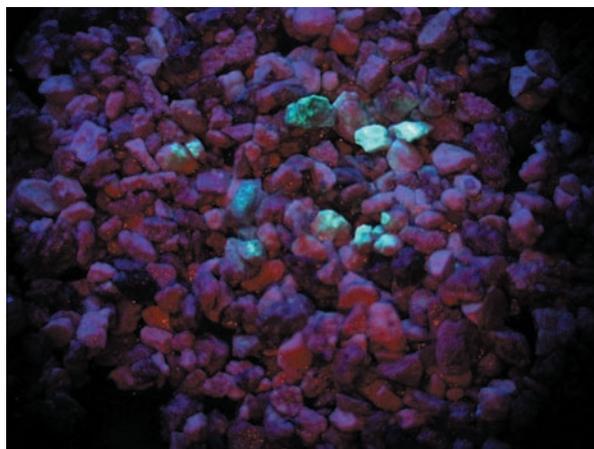
#### *Making thin sections*

Thin sections are made in order to diagnose the rock type (especially useful for carbonates), to provide qualitative information concerning pore size and interconnection and to aid in the identification of microfossils. Such sections can be performed on cuttings or on core fragments.

There are two methods of making thin sections: the conventional method, where the samples are glued directly to a glass slide; while in the second method the samples (not coherent or very fragile) are placed in a moulded matrix made from a transparent resin. The first method is best used when the rocks are coherent and not very fragile and the cuttings are ground on a glass plate covered with grit abrasive powders until they become transparent and they can be observed with a microscope.

#### *Hydrocarbon detection*

Oils are fluorescent under an ultraviolet lamp. Natural oils have a dull 'dirty' fluorescent colour



**Fig. 3.** Oil direct fluorescence (Geoservices S.A.).

(**Fig. 3**), while artificial oils and greases have a bright, ‘flashy’ colour. It is important to distinguish between the two because grease from the drill string may be present in the cuttings and must not be mistaken for a hydrocarbon manifestation.

A ‘cut fluorescence’ test is performed on a dried sample: some drops of solvent are poured on the cuttings and then placed under an ultraviolet lamp. This test will eliminate the risk of interpreting mineral fluorescence (e.g. calcite and fluorite are fluorescent) as oil fluorescence (**Fig. 4**). Dead oils and asphalts have no direct fluorescence but show a strong cut fluorescence.

#### *Sample description*

The sample is always described in a standard way: rock name, colour, hardness and fissility, elements or grains. The description of this last item depends on the type of rock. For example, for carbonates, the grain nature and size are reported, while for clastic rocks, the description is more complete and includes grain size, roundness, sphericity and sorting. The description continues with the type, nature and crystallization of the cement or the matrix; accessory minerals (pyrite, calcite, quartz, and so on); fossils; visual porosity estimation; and hydrocarbon indications: visual (stains, bleeding), direct fluorescence (extent, intensity, colour), cut fluorescence (rate, intensity, colour). Other features may be added at the end of the description.

#### *The masterlog or mud log*

The masterlog is the final document containing all of the data regarding the well. An interpreted lithology column on the masterlog is created with the help of all available information (cutting

percentage, rate of penetration, gas shows, gamma rays and so on).

A standard masterlog contains the following columns (from left to right): *a*) the date; *b*) the rate of penetration curve, electrical logs data (gamma ray, resistivity), depth, bit characteristics, trip indications, casing diameter and shoe depth; *c*) the percentages of the cuttings; *d*) direct and cut fluorescence of the cuttings; *e*) the total gas curve; *f*) all of the gases detected after chromatography (from methane to pentane); *g*) lithology interpretation; *h*) mud data; *i*) the geological description and deviation surveys.

#### *The interpretation of the lithological column*

The creation of an interpretative lithology column is done with the help of different sources of information: first of all, the percentages and descriptions of the cuttings. These percentages represent a drilled interval (1 m if drilling is slow but may be up to 10 m at the beginning of the well or in the case of a fast rate of penetration) and so they may contain several lithologies mixed together. The presence of gas shows will help to determine where the porous/permeable levels are (generally sandstones or fractured limestones). Variations in the rate of penetration are helpful to situate the tops and bottoms of layers of different hardness or drillability. The calcimetry curve indicates levels of carbonates (limestone, dolomite and marls). The presence of salt is indicated by a decrease in mud resistivity. Other useful indications are given by gamma ray and resistivity logs when electrical Logging While Drilling (LWD) is available. Gamma rays show shale levels, and resistivity can detect different types of



**Fig. 4.** Oil cut fluorescence (Geoservices S.A.).

fluids (high for fresh water and hydrocarbons, low for salt water).

### Cores

The analysis of the cuttings is limited as it is very difficult to find macroscopic elements to evaluate. These can be studied on a *core*, that is, on a cylinder of rock drilled with an annular drilling bit (the cylinder is trapped in a core barrel situated above the bit). Two types of core can be taken: for lithology studies or to know the reservoir characteristics. The lithology core will give information on sedimentary structures, fractures, macrofossils, inclination and thickness of the stratification, granulometry in conglomerates, etc. A core taken in a reservoir allows for the evaluation of its porosity, its permeability, and the extent of its oil and water saturation.

The minimum core analysis performed at the well site includes a physical examination of the core surface, the taking of chips for lithological description, and testing for the presence of hydrocarbons (under normal and UV light). If the core is sleeved, samples can only be taken from the extremities of each section. At the end, the well site geologist compiles a core description log based on this examination.

If the core is unsleeved, it is possible to observe the brightness and colour of the fluorescence. Furthermore, the entire core should be described in detail in the following way: the appearance, the lithology features of the strata and the sedimentary structures. A small sample is taken every time there is a noticeable change (facies, lithology, hardness, apparent porosity, granulometry and colour). If the lithology is uniform, a sample is taken every metre.

If detailed analysis of the core itself is to be made off-location, the core must be packaged as soon as possible after taking samples. Once the packaging is complete, further analysis is done on the samples: *a*) study under a binocular microscope; *b*) calcimetry analysis; *c*) cut fluorescence test; *d*) creation of thin sections. Once the analysis is complete, a core description report is compiled, with the following information: *a*) cored depth interval and recovery percentage (most of the time, part of the core is lost in the hole when the core barrel is pulled out); *b*) sampling depths; *c*) lithology description; *d*) calcimetry results; *e*) qualitative fluorescence (direct and cut).

### Sidewall cores

Sidewall cores are useful in order to obtain information after a well or a portion of a well has been drilled without any coring. They are taken with

a special gun run with a wire line. The mini core barrels are shot with explosives that penetrate the formation. As the core barrels are linked to the gun by a wire, pulling the gun out brings up all of the cores.

Sidewall cores are taken at the discretion of the well-site geologist, usually after the completion of drilling in a given phase. Numerous sidewall 'shots' are made, with the aim of scanning the zone of interest (reservoir or other critical zone).

To prevent loss of recovered fluids, the cores are placed in glass storage jars immediately after recovery. On the rig site, sidewall core examination is therefore limited to a visual description only, with no microscopic examination.

### Drilling mud

An analysis of the drilling mud is also a rich source of information. A decrease in the resistivity of the mud coming out from the well can indicate the presence of salt which can have two origins: drilling of salt layers or salt water produced by a high pressure formation. If the salt is in thin layers, it may dissolve completely in water-based mud and will not be possible to detect in the cuttings. Variations of the mud density will allow these various types of salt origin to be distinguished: the addition of water to mud will decrease its density. This density decrease is also valid for any type of fluid invasion, like gas or oil.

### Gases

#### Hydrocarbons

The most important hydrocarbons detected are alkanes or paraffins. Methane to pentane are detected with standard equipment, but the use of mass spectrometers associated with a degasser/heater allows the detection of the alkanes from methane to octane and of the aromatics (benzene, toluene, xylene). All these substances are highly flammable and potentially dangerous in case of eruption.

Depending on the gas-oil ratio in the reservoir, we can define several types of gas: a *dry gas* contains less than 1.3 l of condensable liquids per 100 m<sup>3</sup> of gas; a *wet gas* has more than 4 l of condensable liquids per 100 m<sup>3</sup> of gas. In an undersaturated pool, the gas is dissolved in oil. A saturated pool has a gas cap called *free gas* which occupies the upper part of the pool. It should be noted that gas may also be dissolved in water. Lastly, hydrocarbons can be contained within frozen water cages as clathrates (hydrocarbon hydrates) which look like snow and are stable at high pressure and low temperature. Clathrates have been found in certain sediments in Alaska and Siberia but also in deep sea drilling projects.

### Other gases

A gas containing hydrogen sulphide ( $H_2S$ ) is called *sour gas*. Hydrogen sulphide smells like rotten eggs at low concentrations, but at high concentrations the smell diminishes. It is extremely toxic and lethal from levels of 500 ppm in the atmosphere. It is also flammable and very corrosive to metal (the drill string becomes black and breaks easily). A hydrogen sulphide eruption is considered to be the worst hazard on a rig.

*Carbon dioxide* ( $CO_2$ ) is not flammable, but its high solubility in water provokes a significant volume expansion and when it arrives at surface can cause eruptions.

*Hydrogen* ( $H_2$ ) is very flammable but its presence in a well is often due to the action of metal against metal or to electrolytic reactions between metal and mud products.

*Helium* (He) is an inert gas created in the form of alpha radiation by the disintegration of radioactive elements found in the Earth's crust; this gas then travels through the lithosphere in the fractures of rocks.

### Gas evaluation

A gas that reaches the surface may exist in a different phase in the reservoir, depending on the reservoir temperature and pressure, the hydrocarbon composition, the amount of gas dissolved in the oil and water and the reservoir type (saturated or unsaturated). During its trip to the surface, the gas volume will increase with the decrease of pressure. This expansion follows the equation:

$$V_S = (V_R \times Z_S \times T_S \times P_R) / (Z_R \times T_R \times P_S)$$

where  $P_R$  represents the gas pressure in the reservoir (kPa),  $P_S$  the gas pressure at the surface (kPa),  $T_R$  the gas temperature in the reservoir (K),  $T_S$  the gas temperature at the surface (K),  $V_R$  the gas volume in the reservoir ( $m^3$ ),  $V_S$  the gas volume at the surface ( $m^3$ ),  $Z_R$  the gas compressibility factor in the reservoir, and  $Z_S$  the gas compressibility factor at the surface.

*Liberated gas* is the gas contained in the pores of the drilled volume of rock, as a result its quantity depends on the rock porosity. The volume of liberated gas increases with the formation permeability and porosity, the hole diameter and the bit rate of penetration.

The *produced gas* occurs when the formation gas pressure is greater than the hydrostatic pressure of the mud column. In that case, the gas flows from the formation into the hole and provokes a *kick* (i.e. the sudden flow of a fluid into a well) or worse, a blow-out.

*Recycled gas* is a gas that has not been eliminated by surface equipment and that is pumped back in the hole. The heavier the gas, the more difficult is its extraction from the mud. With a degasser located in the suction pit, it is possible to evaluate and remove the recycled gas from the liberated gas. In that case, it is necessary to know the mud long cycle time, which is the time it takes for the mud to complete a complete cycle from/to the suction pit.

We call *trip gas* a gas produced by swabbing during the trip. As the gas migrates during the trip time, the trip gas may arrive earlier than the lag time (especially if the trip is long).

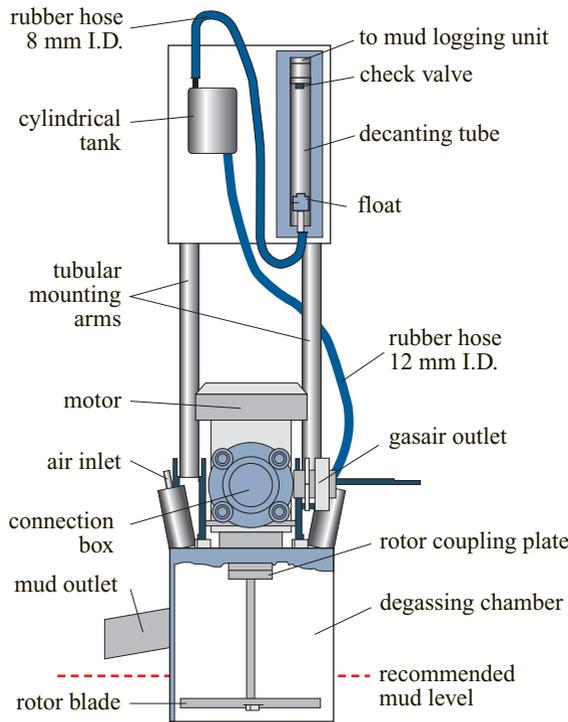
Swabbing during the pipe connection produces a *pipe connection gas* which should arrive after a certain lag time. If the this gas arrives late with respect to the lag time, it is an indication of caving.

### Practical data acquisition

#### Detection

The degasser is an important part of the gas analysis chain. It is situated on the shale shaker box or on the flow line and extracts, in solution form, a part of the gas from the mud, which is then mixed with air in the degassing chamber. A standard degasser consists of a degassing chamber immersed in the mud flow: a 'T' shape agitator rotates and removes the gas from the mud, a gas line starts from the top of the chamber and is connected to a vacuum pump in the gas detector situated in the geology unit (**Fig. 5**). The problem with this instrument is that the gas percentage reading depends on the variations of the mud level in the degassing chamber. To eliminate this problem, a constant level degasser can be used. The basic principle is the same, but the degassing chamber does not need to be immersed in the flow because a pump transports the mud, through a suction probe, from the flow line to the degassing chamber. It is important to position the suction probe close to the bell nipple to avoid the spontaneous degassing of the mud during its travel in the flow line. The gas detector gives the percentage of gas in the air/gas mixture. The most common gas detection system is the Flame Ionization Detection (FID).

The combustion of hydrocarbon gas with a hydrogen flame will produce positively charged carbon-hydrogen ions which can be collected by a cathode. Subsequently, an electrometer counts these ions. The whole process is equivalent to a carbon counter. The burning of one molecule of methane ( $CH_4$ , called  $C_1$ ) will produce one ion, i.e. will show a value of 1 on the carbon counter. For ethane,  $C_2H_6$  (called  $C_2$ ), the counter will register a value of 2 for 1 burnt molecule, and so on for other



**Fig. 5.** Standard degasser.

gases with a number of carbon atoms greater than 2 ( $C_3$ ,  $C_4$ , etc.). Therefore, the total gas detection based on the counting of carbons in a mixture of gases is made in terms of a *methane equivalent* (methane being considered the base unit, as it has 1 carbon atom only). This detection is continuous and gives a good idea of the gas percentage variations, which is of great importance for the purposes of security.

A quantitative result of the different gas percentages can be obtained using chromatography, which consists of a separation of the gases in a column filled with a material that will adsorb the gases with a strength relative to their molecular weight. As a result methane will spend less time in the column than ethane and so on. The gases will leave this column one by one and in this way they can be burnt and measured in the FID. The entire process of chromatography takes 3 min. This type of detection can show few ppm of gas, but only allows the detection of the alkanes (methane to pentane).

Replacing the FID by a mass spectrometer will allow faster analysis, a higher precision (from 1 ppm) and a larger range of analysable gases (alkanes from methane to octane, aromatics, carbon dioxide, helium, hydrogen sulphide, and so on).

Gas sampling is performed by using two metal cylinders connected parallel to the gas line, between

the degasser and the detector vacuum pump. A manifold allows one tube to be closed and the other to be opened. The closed tube contains a gas sample and can be removed, the open tube is filled by the gas flow. This system avoids the interruption of the gas flow to the detector.

**Gas normalisation**

The Corrected Gas Index (CGI) represents a normalized gas percentage corrected for variations of flow rate, Rate Of Penetration (ROP) and bit diameter. The CGI is given by the formula:

$$CGI = (\text{gas-in-air} \times \text{flow rate} \times ROP) / \text{hole metric volume}$$

where CGI is expressed in decimal percentage, *gas-in-air* in decimal percentage, *flow rate* in  $m^3/\text{min}$ , ROP in  $\text{min}/\text{m}$ , and *hole volume* in  $m^3/\text{m}$ .

The volumetric normalization tries to give the relation between the gas values actually read to a standard set of drilling conditions for the same depth:

$$G_n = [G_a \times R_n \times (D_n)^2 \times Q_a] / [R_a \times (D_a)^2 \times Q_n]$$

where  $G_n$  represents the normalized gas in percentage,  $G_a$  the actual gas percentage read by the total gas detector,  $R_n$  the normal rate of penetration in this type of formation in  $\text{ft}/\text{h}$  or  $\text{m}/\text{h}$  (the usual rate of penetration in productive zones is 20 to 30  $\text{m}/\text{h}$ ),  $D_n$  the normal bore hole diameter in inches (the usual diameter, where productive zones exist, is 8.5 by default),  $Q_a$  the actual flow rate in  $\text{gal}/\text{min}$  or  $\text{l}/\text{min}$ ,  $R_a$  the actual rate of penetration in  $\text{ft}/\text{h}$  or  $\text{m}/\text{h}$ ,  $D_a$  the actual bore hole diameter in inches,  $Q_n$  the normal flow rate in  $\text{gal}/\text{min}$  or  $\text{l}/\text{min}$  (the usual flow rate when a productive zone is drilled, is 900-1,000  $\text{l}/\text{min}$ ).

**Gas saturation**

The Surface Potential Index (SPI) represents the volume of gas recovered at the surface per  $m^3$  of rock drilled (this index requires knowledge of the percentage of gas in the mud). The SPI is given by the formula:

$$SPI = (\text{gas-in-mud} \times \text{flow rate} \times ROP) / (100 \times \text{hole volume})$$

where SPI is dimensionless, *gas-in-mud* is given in decimal percentage, *flow rate* in  $m^3/\text{min}$ , ROP in  $\text{min}/\text{m}$ , and *hole volume* in  $m^3/\text{m}$ .

The Calculated Gas Saturation (CGS) represents the volume of gas per  $m^3$  of rock drilled rock under bottomhole conditions of temperature and pressure:

$$CGS = (100 \times SPI \times P_a \times Z \times T_u) / (P_u \times T_a)$$

where CGS is given in percentage,  $P_a$  (the surface pressure) in kg/cm<sup>2</sup>,  $Z$  (the gas compressibility) is taken from a Katz diagram,  $T_u$  (the formation temperature) is given in K,  $P_u$  (the formation pressure) in kg/cm<sup>2</sup>, and  $T_a$  (the surface temperature) is 288 K.

### Gas ratios

Gas ratio analysis has many applications including: *a*) determination of the fluid origin (thermogenic or biogenic); *b*) possible mixing or diffusion in the reservoir; *c*) alteration processes (biodegradation, water washing, etc.); *d*) fluid contacts; *e*) independent diagnostic about pay zone locations (fresh water context, thin beds, presence of tight zones); *f*) marker identification for geosteering, connectivity study; *g*) cap rock efficiency; *h*) criteria for reservoir fluid sampling; *i*) origins of compositional changes, and so on.

Comparing the gas ratios of different wells provides a good correlation tool. Many gas ratios are available for this type of analysis, for example, light/heavy,  $C_1/C_3$ , and isomer ratios. The  $iC_4/nC_4$ ,  $iC_5/nC_5$  ratios allow the detection of biodegradation, caused by bacteria which preferentially attack normal alkanes.

If the fluid has not been biodegraded, several authors consider that a ratio of  $C_1/C_2$  ranging from 2 to 15 indicates an oil-bearing zone, while a ratio from 15 to 65 indicates a gas rich zone. The lower the  $C_1/C_2$  ratio, the richer the gas (or the lower the oil gravity). A  $C_1/C_2$  ratio less than 2 or greater than 65 is indicative of non-productive zones.

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## 2.2.7 Applied geochemistry

The assessment of hydrocarbon source rocks begins in the field or well-site where samples are collected (outcrop samples). Outcrop samples should be selected with care in order to correctly identify the geological horizon and location, and to avoid highly weathered rock samples. Generally, avoiding sloughed shale samples and chipping or coring deeply into an outcrop will minimize oxidative effects of weathering (Clayton and Swetland, 1978). Oxidation is documented by chemical analysis and by visual kerogen assessment.

Archived sample cuttings or core samples are suitable for geochemical analyses, although coals may suffer some oxidation. Though many of the lightest hydrocarbons will be lost during storage, depending on lithology and storage conditions, the kerogen is protected in the rock matrix and good results can be obtained from archived samples.

### Surface seepages and petroleum exploration

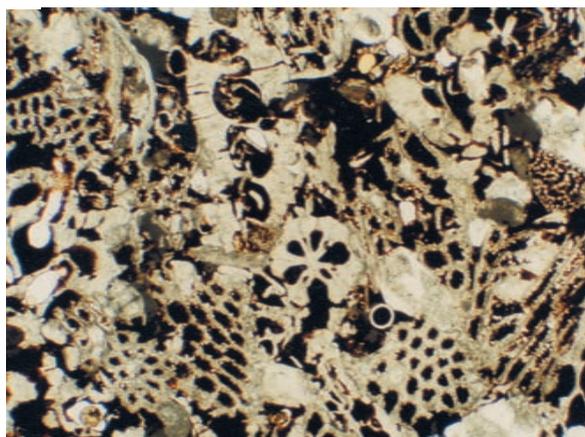
The study of the geochemical characteristics of hydrocarbons that occur in surface shows is of primary importance, especially in virgin areas or areas little investigated in exploration, in order to make inferences regarding the petroleum.

Large-scale deposits of asphaltic rocks are often an expression of palaeo-accumulations, affected by erosion, while the fractured facies along a fault, with invasive asphalt, are an indication of ancient migration or dismigration pathways (**Fig. 1**). Bituminous impregnations are frequent also in palaeo-pathways, i.e., permeable rocky levels that facilitate the migration of hydrocarbons from the source rock to the reservoir rock (**Fig. 2**). Sources in which oil and gas are present bear witness to on-going dismigrations, which take place for various reasons (fractured cover, faults, surface occurrence of a permeable level linked with the reservoir, etc.).

Emissions of gaseous hydrocarbons are very common, but are evident only in particular environmental conditions, e.g., through the presence of water or mud springs, where bubbling can be observed, or when, due to occasional ignition, the

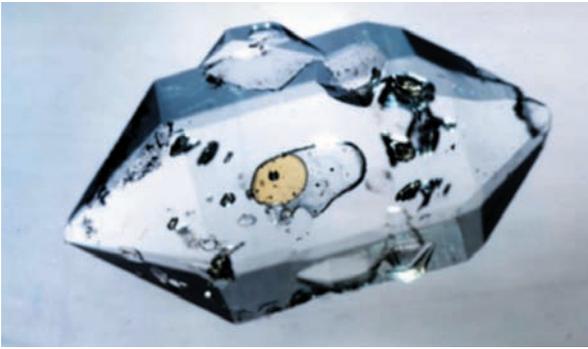


A



B

**Fig. 1.** A, bitumen/asphalt percolating along fractures in the limestone Lettomanoppello (Abruzzo). In the Pescara valley there are some imposing lenses of asphaltic rocks, with mineralizations concentrated along faults and associated fractures. The exploiting of asphaltic limestones started in 1869. B, from the same locality, a thin section of calcareous rock with its pores impregnated with bitumen (Eni).



**Fig. 2.** Quartz crystal (9 mm) with a fluid inclusion macroscopically visible (consisting of water, oil with a mobile gas bubble and solid bituminous residues), collected in 1991 in Valle di S. Lucano (Dolomites) in a cavity of a dolomitic layer. The dolomitic layer is interbedded in a Middle Triassic source rock and represents a palaeo-pathway. The fluids that impregnated the rock pores were entrapped by the crystal during its growth phases (collection P. Scotti, photo Eni).



**Fig. 3.** Natural gas shows feeding persistent tongues of flame (Baku, Azerbaijan) (Eni).

natural emissions feed long, persistent tongues of fire (**Fig. 3**). Gaseous hydrocarbons consist exclusively or predominantly of methane. Gas of biogenic origin (generated by bacterial degradation of organic matter at a low temperature) always consists of pure methane. The presence of other hydrocarbons (ethane, propane, butane), in addition to methane, suggests a thermogenic origin of the gas (thermal degradation of the kerogen and/or secondary cracking of the liquid hydrocarbons). The possibility of finding more or less pure methane in cases of high thermal maturity also exists, in which case an isotopic analysis of the carbon enables it to be easily distinguished from biogenic methane.

Sampling gases from surface macro-occurrences can be completed with very simple techniques, using,

for example, an ordinary funnel to convey the gases into a small, inverted, glass test-tube.

At the end of the 18th century, Alessandro Volta was one of the first people in history to have studied ways of sampling, and postulated some interesting hypotheses regarding the origin “of the inflammable native marsh air” (only a few years later identified as methane), sampled in a number of locations in the Verbano-Lariano area. A famous sampling was made on 3 November 1776 in the presence of numerous witnesses, in a canebrake near Angera (**Fig. 4**). The publication in 1777 of the *Lettere del Signor Don Alessandro Volta sull’aria infiammabile nativa delle paludi* (“Letters of Signor Don Alessandro Volta on the inflammable native air of the marshes”) is regarded, at an international level, as an original manifesto of the biogenic origin of methane.

A curious natural phenomenon linked with occurrences of gaseous hydrocarbons is known as ‘mud volcanoes’ (**Fig. 5**). These occur when gas



**Fig. 4.** The etching forming the heading of Alessandro Volta’s *First Letter* to padre Carlo Giuseppe Campi, depicting the sampling of inflammable native marsh air (methane) carried out on 3 November 1776 on the shore of Lake Maggiore near Angera.



**Fig. 5.** Mud volcano at Guturdag (Baku area, Azerbaijan). The mudflow just erupted can be observed (Eni).

migration, as a rule guided by cleavage or fault planes, takes place in unconsolidated, water-saturated shaley/silty sediments. Mud outbursts create cone-like shapes and there are frequent violent episodes of an explosive character, in which strong gaseous emissions cause powerful flames. The cones usually measure just a few metres in height, such as those in the Emilian Apennines, well-described since the 18th century by naturalists such as Antonio Vallisneri and Lazzaro Spallanzani, but some, such as those in the Baku area in Azerbaijan, reach heights of several tens of metres. The Baku area, with its mud volcanoes and all the accompanying phenomena (oil fountains, explosions and ignitions of methane gas) is the most famous petroleum locality in history and has been visited the most and described in detail by travellers, naturalists and petroleum geologists. Suffice it to recall the ancient Temple of Zoroaster (the temple of everlasting fire), the references to 'oil fountains' in Marco Polo's *Milione* (second half of the 13th century), the old hand-dug oil wells (documented already in the 16th century), and the first modern oil well (drilled close to Baku in 1848, 11 years before the more celebrated well of Colonel Drake in Pennsylvania).

For oils/bitumens, in the absence of alternatives such as biodegradation, a more precise characterization of the source rock can often be reconstructed, as opposed to gases, for which analyses as a rule offer only indications on the type of generative aspect (biogenetic or thermogenetic) and the degree thereof. Samples of bitumens/asphalts must be selected among those least altered, care being taken to preserve them either in glass containers or wrapped in aluminium film. By means of gas-chromatographic, isotopic and mass spectrometric analyses, it is possible to infer the lithofacies, the depositional environment, the type of organic matter and the approximate age of the source rock.

By correctly framing the various types of oils/bitumens, their areal distribution, and the frequency and amount of shows, it is possible to deduce the importance of a given naphthogenic event. By analysing the free hydrocarbons extractable from potential naphthogenic levels, it is then possible to obtain an exhaustive oil/source-rock correlation.

Surface occurrences of oils and asphalts have aroused man's curiosity since antiquity and it is needless to recall their countless uses here. The first exploitations took place simply to make use of the product that emerged naturally, or with the technique of large-diameter hand-dug wells. Industrial exploitation with small-diameter drilled wells, in the various parts of the world, has always started from areas that had rich natural shows at the surface.



**Fig. 6.** Water, oil and gas spring at Tramutola (Val d'Agri, Basilicata). In the stream immediately below the spring there are clear slicks of dense oil, while at the side an asphalt concretion is visible (Eni).

Occurrences are very often the expression of oil dismigrations from generally small, shallow oil deposits. These lead, in a given petroleum area, to a first cycle of exploration, often limited in time and in quantities of oil that are recovered. It is only with the perfecting of new prospecting approaches that an area can be continuously reassessed, perhaps in the long run leading to further cycles of exploration.

The historical water and oil spring at Tramutola in Val d'Agri, Basilicata (**Fig. 6**), for example, originated from seeping of oil and gas at the surface from a modest, shallow accumulation exploited in the '30s of the last century, due to the fact that seal was inadequate. This accumulation was, in turn, the result of a dismigration from a deeper accumulation. A second cycle of exploration, which began in the '80s aimed at the underlying reservoir, that was better sealed, led to the discovery of the largest onshore oil deposit in western Europe. The oil appearing at the surface was thus an indication of a naphthogenic process identifying an active petroleum system of primary importance.

In the course of the last ten years, methodologies have been developed to detect and interpret the leanest traces of hydrocarbons reaching the surface from even a very deep accumulation. Through geochemical analysis of these traces of hydrocarbons, it is possible to plot positive anomalies on the basis of comparisons with structural maps of deep horizons. Sampling is carried out by collecting cores of the soil (or seabed sediments) or with the direct capture (only on land) of hydrocarbons by means of adsorbent modules left embedded in the

ground for a few days. This methodology can best be applied in areas with known deposits. A calibration can, in fact, be made of the characteristics of the traces of hydrocarbons detectable at the surface on the vertical of hydrocarbon-bearing wells (oil-like signal), and one on the vertical of barren wells, to also obtain a background signal or value determined by the mixture of signals extraneous to the type of the oil in the deposits. Subsequently, through appropriate statistical treatment of the data, a value can be attributed to each sampling point in areas not explored by wells, indicating the likelihood of belonging to the oil-like category (signalling a possible deep accumulation) or to the background, barren category.

An indirect method of exploration, hyperspectrometry, uses a spectrometer mounted in an aeroplane. The spectrometer analyses a large number of bands of the electromagnetic spectrum, and the study is based on the analysis of the chemical/biological changes induced in the soils and in the vegetation by hydrocarbons. This methodology is applied primarily to identify oil-polluted areas, facilitating environmental restoration operations. In the experimental phase it is applied in frontier exploration areas, for which only limited, hard to access geological data are usually available to pinpoint possible natural occurrences of hydrocarbons on land, indicative of a possible active petroleum system in that sedimentary basin.

Offshore, the presence of hydrocarbon occurrences can be identified by using remote-sensing instruments (e.g., satellite radar or airborne laser). Comparative studies of images carried out at successive times enable any anomalies generated by pollution (e.g., oil spills from tankers) to be distinguished from those originating from natural hydrocarbon shows.

### **Source rocks: a component of petroleum systems**

Petroleum systems studies are undertaken in order to understand where oil and gas may be found and produced. The term petroleum in this context is used to refer to oil and gas generated from source rocks. The basic theory behind petroleum system studies is that only when all the components and processes are present and complementarily timed will commercial amounts of hydrocarbons be discovered. The components include: source rock, migration pathway, trap, seal, and overburden. The processes include generation, expulsion, migration, oil cracking, alteration, and mixing of different oils.

In addition, various processes must occur in a complementary time frame for a petroleum trap to be charged with hydrocarbons, e.g., a trap must be present during hydrocarbon generation and expulsion, as otherwise the hydrocarbons will be lost or non-commercially stored.

If rock samples are available from well samples or outcrops, they are a good starting point for determination of potential source rocks. However, oil samples are also an excellent starting point for inference of source rock types using geochemical inversion (Bissada *et al.*, 1993). Geochemical inversion is a technique whereby oil geochemistry is used to make inferences about the source of the oil, e.g., its thermal maturity, lithofacies, and depositional environment. This directs the exploration geologist or geochemist to begin a search for source rocks of a particular lithofacies and perhaps even suggests the age of the source rock. In addition, oil asphaltene provide an excellent analogue for source rock organic matter and can be used both to assess what products are formed at various levels of thermal maturity, and generation rates.

In searching for effective source rocks in a basin, there are often many avenues of information ranging from published data, available well samples and sample repositories. In general the search for a source rock of particular oil leads to an investigation of all prospective source rock intervals. This may range from evaluation of outcrop samples or well samples to inferences based on the lithofacies and geological age derived from oil geochemistry. Thus, a prospective source rock refers to a rock unit that has not been fully characterized by geochemical means and may or may not be a source depending on the results of detailed analyses and correlation to known oil or gas pools. On the other hand, once there is correlation of a source rock to known oil or gas pools, it is called an *effective* source rock (Magoon and Dow, 1994). Finally, if a source rock is analysed, but is immature, i.e., has not been sufficiently converted to commercial quantities of hydrocarbons, it is referred to as a *potential* source rock (Magoon and Dow, 1994). Whether a potential source rock is an effective source rock depends on whether it is buried to greater depths or exposed to higher temperatures elsewhere in a basin or area and then proved by correlation to oils to be an effective source. Certain geochemical characteristics of oils or the geological model corresponding to the depositional history can be used to hypothesize what the source rock may be.

The objectives of identifying and characterizing a source rock are: *a)* to identify the source of oil and

gas; *b*) to determine its capacity to generate and expel hydrocarbons; *c*) to identify the type of products generated; *d*) to identify thermal maturity for determination of oil and gas fairways; and *e*) to determine its rate of decomposition (kinetics) to accurately assess the timing of hydrocarbon generation. Source rock data is then used to determine the likelihood of hydrocarbon charge in a given prospect or region. The ultimate goal of source rock appraisal is to high-grade prospects for drilling and production. One point is certain: if any of the elements or processes of the petroleum system are missing or not properly timed, there will be no commercial hydrocarbon charge in a trap.

### Analytical program to evaluate source rocks

#### Sampling

Well-site cuttings samples are generally taken at 3 to 10 m intervals and good sample identification including lag correction are very important as cores are seldom taken of shales particularly for source rock evaluation. Samples should not be high-graded in any way at this point in the sampling process. Generally, gray to black shales or other darker rock chips are often prospective source rock samples. Approximately 30 g of sample are recommended, although a quantity equivalent to about 160 g is preferred. In some cases as little as 1-5 g of rock is all that is needed for screening analyses, but there is a dependency on carbon yields and the type and number of analyses.

For optimal detection of Light Hydrocarbons (LHs), samples must be either frozen or kept wet, and, if wet, lightly dried. Espitalie *et al.* (1985) found optimum LHs yields when fresh cuttings samples were dried for 20 minutes. Light hydrocarbons can be detected using thermal extraction high resolution gas chromatography (Jarvie and Walker, 1998; Odden *et al.*, 1998) or using a special light hydrocarbon extraction technique (Jarvie, unpublished data). Collection of samples in gas impermeable headspace jars or Iso-Jars (Coleman *et al.*, 2004) is highly recommended. Such a collection technique provides a well-preserved and protected sample of sufficient quantity for any analysis that may ultimately be needed. In any case, a bactericide should be added to the headspace container to prevent bacterial activity on hydrocarbons.

#### Total Organic Carbon

The initial analysis for source rock evaluation is the determination of its Total Organic Carbon (TOC).

TOC provides an indication of the quantity of carbon available to form oil and gas.

Minimum values for TOC that could result in a commercial accumulation are often discussed in the literature. Organic richness can be stated in terms of averages such as Baker (1962) where:

- Values lower than 1.00% are below average; they are less likely to correspond to hydrocarbon source rock interval.
- Values greater than 1.00% are above average: they are more likely to correspond to hydrocarbon source rock interval.

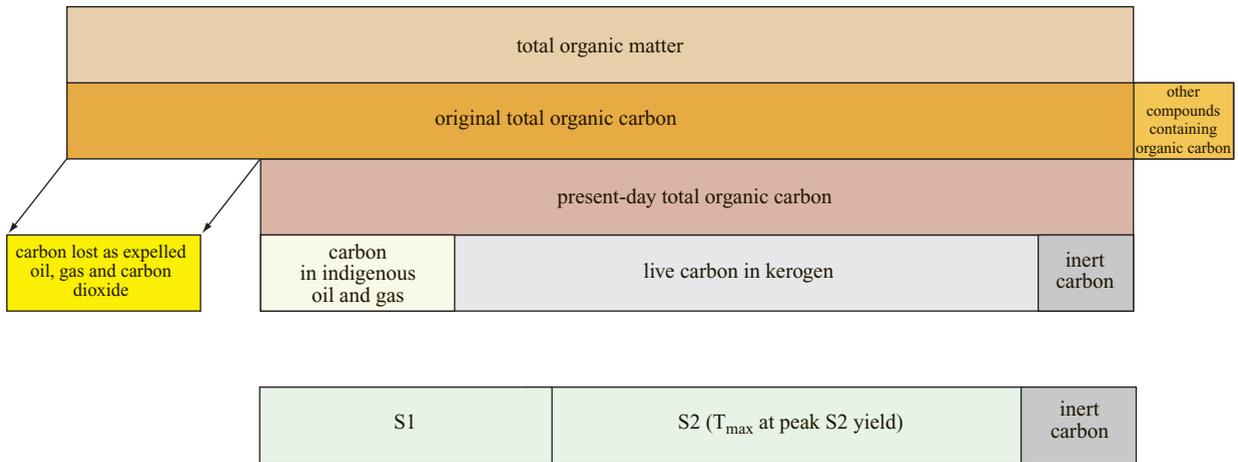
Others use more quantitative terms (Peters, 1986), or define richness in terms of whether a source rock is a shale or a carbonate containing organic matter (Tissot and Welte, 1984). Jones (1984) showed that shale and carbonate source essentially must have the same minimum amount of organic matter to yield commercial amounts of hydrocarbons. In addition, when cuttings are analysed TOC values are often lower than on core samples, due to dilution depending on the extent of mixing with organic lean horizons overlying the source rock.

However, it must be noted that not all carbon contained in a source rock can be converted to hydrocarbons due to lack of hydrogen. Highly oil-prone kerogens have atomic hydrogen-to-carbon (H/C) ratios of about 1.5. As organic matter matures, oil and gas are generated and the reactive carbon content decreases with a concomitant increase in inert carbon due to hydrogen depletion (**Fig. 7**), resulting in a condensed, hydrogen-poor carbon structure. This material has no commercial hydrocarbon potential due to its low hydrogen content. When the generated hydrocarbons are expelled from the source rock, TOC decreases due to the loss of carbon associated with expelled hydrocarbons (see again Fig. 7).

Estimation of original TOC values in mature source rocks is important for predicting the amount of oil or gas that could be generated from a source rock. At high thermal maturities, the TOC value of Type II kerogens (oil prone, marine algal) will be reduced by 30-50%. Type I kerogens (oil prone, lacustrine algal) will have a 30-80% reduction in TOC, whereas Type III kerogens (gas prone, terrestrial) will have a reduction of less than 30%. This means that typically less than half of the TOC content of an immature source rock is converted to hydrocarbons at high maturity, so minimum TOC values for 'commercial' source rocks is likely closer to 2.00%.

#### Rock-Eval analysis

TOC is complemented by bulk thermal extraction and pyrolysis data (often referred to as Rock-Eval,



**Fig. 7.** Model of total organic matter in a sediment sample.

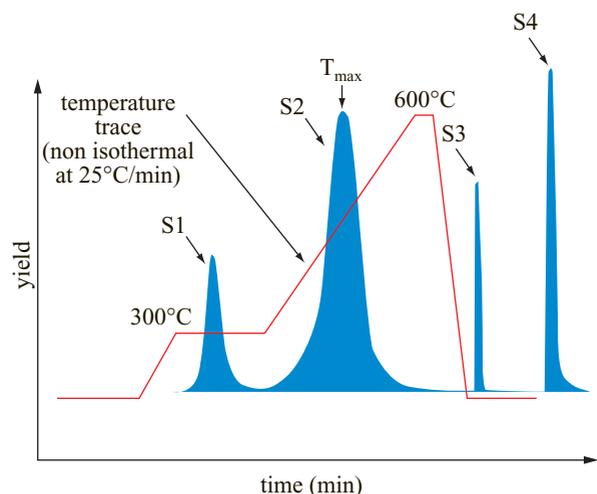
Espitalie *et al.*, 1977) or SR Analyser (Jarvie *et al.*, 1996) data. In this type of analysis a small aliquot (25-100 mg) of rock sample is heated to sub-pyrolysis temperatures (<350°C) distilling volatile hydrocarbons followed by pyrolysis (cracking) of organic matter by programmed heating to high temperature (550-900°C) (**Fig. 8**). Detection is accomplished by a flame ionization detector (FID), which provides a response corresponding to the carbon content. This provides an indication of the free oil content (S1) and the remaining generation potential (S2). The temperature ( $T_{max}$ ) at which the maximum evolution of pyrolysis hydrocarbons occurs is recorded and is related to the thermal maturity of the sample (if only kerogen is present). Some instruments also record the yield of carbon dioxide, which by definition is organic, at temperatures below carbonate decomposition. However, inorganic carbon dioxide will contaminate this yield particularly from surface weathering or oxidation.

Combined TOC and Rock-Eval/SR Analyser data provide an indication of: *a*) the total quantity of organic carbon available for the formation of hydrocarbons (wt.% TOC); *b*) the present-day petroleum potential of a source rock (remaining potential hydrocarbon yield, S2 yield in mg hydrocarbon/g rock); *c*) the present-day kerogen type (oil or gas proneness, Hydrogen Index or S2/TOC·100); *d*) the thermal maturity of the source rock ( $T_{max}$  in °C); and *e*) oil shows and potential reservoir intervals (normalized oil content in mg S1/TOC·100).

These data are referred to as present-day since all parameters are affected by thermal maturation. Thus, interpretive schemes must use these values in the context of the maturity of the source rock.

One of the most useful chemical parameters for an initial assessment of kerogen type is the Hydrogen Index (HI). Jones (1984) provided guidelines for interpretation of HI data in terms of depositional environment and likely product type (**Table 1**). It should be noted that kerogen typing by HI values is not infallible. For example, HI is often used to type kerogens as lacustrine (HI values >700), but this is not strictly true as many lacustrine rocks can have HI values less than 700, e.g., various units in the Green River oil shale, or in the Cacheuta Formation (Argentina).

HI is only an indication of the present-day potential in mature source rocks. Its original potential will have been reduced depending on the level of thermal maturation. Computation of original HI values is also important in volumetric calculations and once the original TOC value is calculated, the



**Fig. 8.** Rock-Eval pyrogram.

**Table 1.** Table for assessing source rocks by HI values (Jones, 1984)

KEROGEN TYPE	HYDROGEN INDEX	OXYGEN INDEX	H/C RATIO	ORGANIC MATTER	DEPOSITIONAL ENVIRONMENT	INTERNAL STRUCTURE	PRINCIPAL PRODUCTS
I	700-1,000+	10-40	1.4	Algal; Amorphous; Rare terrestrial	Anoxic (saline); Lacustrine; Rare marine	Finely laminated	Oil
II	350-700	20-60	1.2-1.4	Algal; Amorphous; Common terrestrial	Anoxic; Marine	Laminated; Well bedded	Oil
II/III	200-350	40-80	1-1.2	Mixed marine; Terrestrial	Variable; Deltaic	Poorly bedded	Mixed oil/gas
III	50-200	50-150	0.7-1.0	Terrestrial; Mostly vitrinite; Fegraded algal	Mildly oxic; Shelves/Slope; Coals	Poorly bedded; Bioturbated	Gas
IV	<50	20-200	0.4-0.7	Highly oxidized; Reworked	Highly oxic; Anywhere	Massive; Bioturbated	Dry gas

original HI value is determined or approximated as follows:

$$HI_o = \frac{TOC_o - TOC_p + S2_p}{0.083 \cdot TOC_o \cdot 100}$$

where *o* = original and *p* = present-day.

Original HI values are useful in computation of the extent of transformation of kerogen to hydrocarbons. One formula for computed kerogen Transformation Ratios (TR) is (Espitalie *et al.*, 1985):

$$TR = \frac{HI_o - HI_p}{HI_o}$$

or a modified version of the above provided by Pelet (1985):

$$TR = \frac{1,200(HI_o - HI_p)}{HI_o(1,200 - HI_p)}$$

$T_{max}$  is a chemical indication of thermal maturity, and as such, will vary with kerogen type. It is generally not a reliable maturity indicator for lacustrine or other kerogens having a uniform composition.  $T_{max}$  can be related to vitrinite reflectance for Type III and some Type II kerogens by a simple equation (Jarvie *et al.*, 2001):

$$R_o = 0.0180(T_{max}) - 7.16$$

where  $R_o$  is the percent vitrinite reflectance in oil.

This formula can be used only when the source rock maturity is not particularly high, and keeps within the early to late oil maturity range, corresponding to

$T_{max}$  between 430 and 459°C. At high thermal maturities,  $T_{max}$  can become erratic due to the low kerogen yields where a distinct pyrolysis peak is often not readily discernable. In addition, care must also be exercised as some oil prone kerogens will often have suppressed  $T_{max}$  values due to impregnation of solid hydrocarbons in the rock matrix.

**Amounts of oil and gas generated**

A common question in petroleum exploration is the likelihood of hydrocarbon charge from a given source rock in a reservoir. One of the assessments of a source rock must include the volume of oil or gas that it could generate. A volumetric assessment methodology was developed by Schmoker (1994) that allows computation of the mass of oil and gas generated from a source rock if the original TOC, original HI, present-day HI, rock density, and source rock thickness and areal extent are known or can be estimated. Schmoker's methodology yields very high volumes of oil and gas. However, modifications to his approach can provide more realistic answers. For example, the TOC value must only be the reactive organic carbon content, not the entire TOC. The extent of conversion to gas must also account for insufficient hydrogen to hydrogenate all carbon even in the reactive carbon. Further, some oil and gas are often expelled from the source rock into other reservoirs. Also not all oil and gas can be recovered. With these limitations in mind, the Schmoker approach provides a relative comparison of the volumetric yields that can be obtained from various source rocks.

### Vitrinite reflectance, Thermal Alteration Index, and visual kerogen assessments

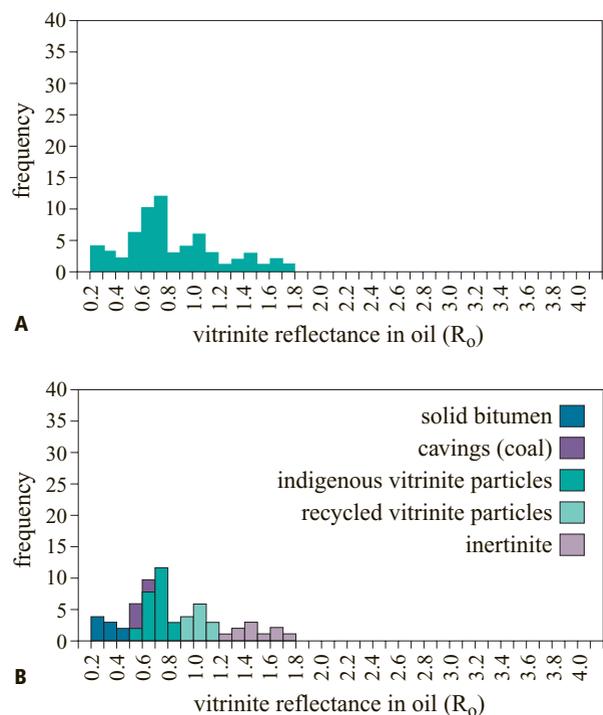
Percent vitrinite reflectance in oil ( $R_o$ ) is another indication of the maximum temperature exposure of a rock, i.e., its thermal maturity. It is derived from a visual examination of either isolated organic matter (kerogen) or whole rock sample, mounted in a non-fluorescing medium. Its utilization is derived from the seminal work of Rogers (1860), who first recognized that coal was a geothermometer. White (1915) rediscovered the work of Rogers and related coalification processes to the occurrence of oil and gas in the Appalachian Basin (USA). An excellent historical account of this is provided in Burgess (1977). Vitrinite reflectance measurements rely on the expertise of the microscopist to accurately identify vitrinite particles derived from woody biomass that are indigenous to the rock. Sometimes due to the presence of bitumen, solid hydrocarbons, recycled OM (Organic Matter), and inertinitic particles, identification of indigenous populations of vitrinite is not obvious and certainly can be subjective (Fig. 9).

The microscopist will also use the color of palynomorphs or spores – techniques referred to as Thermal Alteration (TAI) or Spore Coloration Indices (SCI) – to aid the assessment of thermal maturity. These techniques help guide the selection of indigenous vitrinite in isolated kerogen as do chemical measurements (e.g.,  $T_{max}$ ) when available. It is somewhat easier to discern indigenous vitrinite in whole rock mounts as they are identified by their bedding planes within the rock matrix. In a whole rock mount, the number of actual vitrinite reflectance measurements will typically number 20 or fewer readings, whereas kerogen isolates may give upwards of 50 readings. It is essential to note that the number of readings is less important than the accuracy of determining the indigenous population of vitrinite particles, although a minimum of 10-20 readings is desirable.

Source rock samples are seldom the best samples for vitrinite reflectance measurements as oil-prone source rocks often only have limited amounts of vitrinite and are often suppressed. It is often useful to obtain samples of overlying and underlying horizons (especially any coaly intervals) and project maturity through the source interval. This also allows calculation of paleo-geothermal

gradients in a well. Often, maturation profiles will show a linear profile through non-source and coaly intervals, and then have lower readings in source rocks. This is referred to as suppression. Suppression of reflectance is caused by the presence of or the mis-identification of hydrocarbons closely associated with kerogen. Lo (1993) devised a means of correcting suppressed source rock reflectance values based on hydrogen indices. Landis and Castaño (1995) also published a calibration curve and regression for correcting the reflectance of solid bitumen, thereby rendering those readings useful in source rock maturation assessments.

Visual kerogen assessments also aid kerogen type assessments based on the distribution of various organic macerals that are either oil or gas-prone. Typical descriptions will include amorphous, herbaceous, vitrinite, and inertinite populations, but depending on the microscopist, percentages of specific macerals will be included such as liptinite, alginite, cutinite, sporinite, etc. These petrographic data are invaluable in aiding both the assessment of kerogen type and selected chemical parameters such as HI and  $T_{max}$ . For example, the presence of primarily inertinitic macerals will often yield a very high  $T_{max}$  value (500°C and higher).



**Fig. 9.** Vitrinite reflectance histograms: A, total population of readings; B, determination of the indigenous population.

**Solvent extraction**

The ultimate test of an effective source rock is correlation to an oil sample. Correlation of source rocks to oils is initiated by solvent extraction of the rocks removing free oil and bitumen from the rock matrix. Source rock samples in the oil generation window are needed for correlation to oils as immature rocks do not have similar characteristics as crude oils and overmature samples will only yield biomarker depleted extracts due to extensive cracking of these compounds. For further analytical procedures for preparation of source rock extracts, see below.

**Pyrolysis-Gas Chromatography**

A simple technique to evaluate source rocks for their oil or gas potential is Pyrolysis-Gas Chromatography (Py-GC). Extracted rock samples or kerogens are pyrolyzed and the pyrolysis effluent flows through a gas chromatograph. Detection of the separated compounds yields a distribution of doublets consisting of alkenes and alkanes as well as intermediate peaks of various chemical classes (aromatics, thiophenes, phenols, etc.). Using the ratio of total gas yield (sum of C<sub>1</sub>-C<sub>4</sub> hydrocarbons) to total gas plus oil yield provides an indication of the oil or gas proneness of the organic matter. Various gas to oil ratios have been utilized and are referred to by a variety of names, such as GOGI (Gas Oil Generation Index, BP; see **Table 2**).

Other interpretive schemes have used ternary distributions of C<sub>1</sub>-C<sub>5</sub>, C<sub>6</sub>-C<sub>14</sub>, and C<sub>15</sub><sup>+</sup> hydrocarbons (Horsfield, 1990) as well as other compounds (Larter, 1990), and multivariate approaches using specific compounds identified by Principal Component Analysis (PCA; John Zumberge, *personal communication*).

**MicroScale Sealed Vessel pyrolysis**

A technique used to generate hydrocarbons in a laboratory setting is the MicroScale Sealed Vessel (MSSV) approach (Horsfield *et al.*, 1989). This approach employs micro-sized pyrex or quartz tubes (40 µl) that are sealed after adding small amounts of isolated source rock organic matter (1-2 mg) or oil asphaltene and filling the dead space with quartz beads. Subsequently, the MSSV tubes are heated under either isothermal or nonisothermal conditions and yield a Gas Chromatographic (GC) fingerprint of the generated compounds that is comparable to a crude oil generated by natural maturation under geological conditions. This fingerprint

**Table 2.** Gas-Oil Generation Index

GOGI VALUE	INTERPRETATION
<0.35	Oil prone
0.35-0.50	Mixed oil-gas
>0.50	Gas prone

and associated data provides an invaluable means of analysing a source rock at different levels of maturation and determining the changes in the yield and distribution of products. It is used on biodegraded oils or seeps to obtain a reasonable fingerprint of the original generated oil. Data analysis ranges from assessment of the gas and oil generation yields to pristane-to-phytane ratios and paraffin yield and distribution profiles.

**Rate of organic matter decomposition (kinetics)**

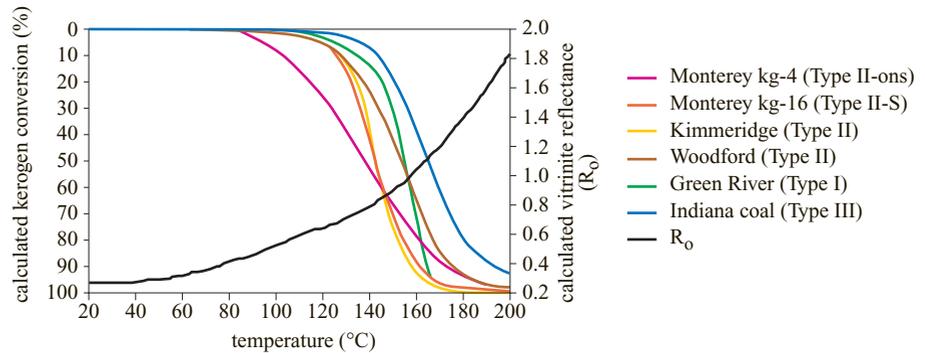
Kinetic parameters describe the rate at which organic matter decomposes into hydrocarbons under a given thermal history. As organic matter decomposes, the most labile bonds break first, followed by more refractory bonds. A variety of reactions occur during kerogen formation processes (diagenesis) and hydrocarbon generation (catagenesis). Decomposition reactions are influenced by the chemical composition and structure of organic matter (Claxton *et al.*, 1994). The rates of decomposition of various source rocks are shown as calculated transformation ratios versus temperature in **Fig. 10** (Jarvie *et al.*, 1996). This illustrates that the position of the oil window is variable, i.e., at the same level of vitrinite reflectance or thermal maturity, source rocks may be converted to hydrocarbons at different rates. The position of the gas window is also highly variable depending on the source rock and the primary products formed during decomposition of its organic matter.

Compositional kinetic schemes describe more than the rate of kerogen to hydrocarbon reaction rates, as they describe the formation of specific hydrocarbons such as methane, ethane, propane, and higher molecular weight hydrocarbons and non-hydrocarbons (Espitalie *et al.*, 1988; Jarvie *et al.*, 1998). Source rock samples as well as oil/seep asphaltenes can be used for kinetic measurements.

**Additional source rock evaluation techniques**

Source rocks may be characterized by a variety of other useful techniques. Elemental analysis was

**Fig. 10.** Rates of organic matter decomposition determined on a variety of source rocks.



commonly performed in the past (van Krevelen, 1961), but this has largely been replaced by HI and Oxygen Index (OI) values typically plotted in modified van Krevelen plots (Espitalie *et al.*, 1977). Elemental analysis of isolated kerogens, however, provides a more accurate assessment of kerogen type and maturation pathways. This technique is in disfavour due to kerogen isolation procedures that are often chemically and environmentally problematic and the cost of analysis.

Mud Gas Isotopic Logging (MGIL; Ellis *et al.*, 2003) and desorbed (headspace) gas are also techniques that can be used to evaluate potential source rocks as a source or even reservoir of gas. For example, if a source rock is penetrated during drilling, its gas composition and carbon isotopic values can be related to test or production gases.

Fluid Inclusion Stratigraphy (FIS) is a more recent tool that examines paleo-fluids trapped in the rock matrix. This analysis requires a thoroughly cleaned rock sample to avoid any contamination from indigenous or non-indigenous oil. The FIS technique is fast and inexpensive and provides an abundant amount of molecular information on both hydrocarbons and non-hydrocarbons. These data have been used to delineate and characterize pay zones (Hadley *et al.*, 1997; Hall *et al.*, 1997).

Hydrous Pyrolysis (HP) is a laboratory maturation technique that has been widely used to generate oils from source rocks (e.g., Lewan, 1985). It is also used for kinetic determinations (Hunt *et al.*, 1991; Lewan and Ruble, 2002; Lewan and Jarvie, 2003).

## Oil-to-oil and oil-to-source rock correlations

### Background

The correlation of crude oils to one another and to source rock extracts provides invaluable information on the petroleum systems that are functional in a field or basin. Exploration geologists use this information to rank prospects for hydrocarbon charge, identify potential fairways for oil and gas production, including the likelihood of extending existing producing trends or identifying new ones. In addition, development geologists and engineers use detailed oil fingerprinting analyses to assess reservoir continuity, the extent of commingling of production, enhanced oil recovery, and even well plumbing. This latter work can be completed without shutting in a well and losing production.

One of the most important functions of organic geochemistry is to identify the specific source rock of an oil to aid in identifying additional prospects for oil and gas. This requires correlation of oil to source rock extracts. However, the source rock is not always available for analysis and, in this case, the source rock must be hypothesized or inferred from oil geochemistry.

Correlation techniques include bulk properties and detailed geochemical analyses. Bulk properties include physico-chemical properties such as API (American Petroleum Institute) gravity (specific gravity) and chemical measurements such as sulphur and acid contents. Detailed geochemical assessments provide molecular level details essential to distinguish oils that may be similar based on bulk properties. In addition, geochemical inversion can be used to infer the characteristics of the likely source rock for the oil (Bissada *et al.*, 1993).

Bulk oil properties and analyses are useful for the initial typing of oils. For example, the U.S. Bureau of Mines typed Permian Basin oils using strictly atomic ratios of sulphur, nitrogen, and carbon (Jones and Smith, 1965). Bulk chemical and physical properties

include also sulphur content (wt. %), nickel and vanadium contents and LC (Liquid Chromatography) fractionation yields.

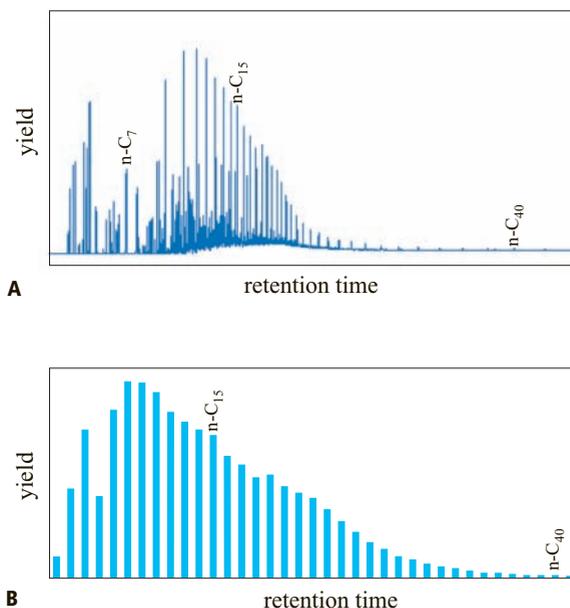
**Molecular properties**

Gas Chromatography (GC) is a technique used to fingerprint oils. A GC fingerprint is basically a histogram of the yield and distribution of compounds that are separated and detected by the GC/detector system. A fingerprint of a crude oil is shown in **Fig. 11 A** with a histogram of the normal paraffin yield and distribution in **Fig. 11 B**.

One of the simplest and widely used correlation parameters is the ratio of two isoprenoid biomarkers, pristane and phytane (Illich, 1983). A high phytane content is indicative of highly reducing (anoxic) depositional environment typical of carbonate source rocks. High pristane content indicates increasing oxidicity or relatively lower hydrogen concentration in the depositional environment. Interpretative guidelines are shown for pristane-to-phytane (Pr/Ph) ratio (Hughes *et al.*, 1995) in **Table 3**. These ratios should be used with caution at high levels of thermal maturation as phytane decomposes before pristane and the Pr/Ph ratio will be higher as a result of phytane depletion. The ratio of these isoprenoids to n-alkanes is also utilized as they provide information on maturation and biodegradation of an oil as well as the source rock (Connan and Cassou, 1980). A plot of Pr/n-C<sub>17</sub> versus Ph/n-C<sub>18</sub> is commonly used to group oils and rock extracts both by type and extent of maturation.

Other parameters from GC analysis used for correlation purposes are the overall paraffin envelope, which varies by source type and maturity, the ratio of n-C<sub>17</sub> to n-C<sub>27</sub>, which is used as an indicator of waxiness (i.e., source material related), and the Carbon Preference Index (CPI), which is used as a very general assessment of source lithofacies and thermal maturity. At low maturity there is often odd carbon preference; in carbonates there is often an even carbon preference. These data are used as a complementary interpretive tool to pristane/phytane ratios and with biomarker and carbon isotope results.

The Light Hydrocarbons (LHs) are increasingly being used for oil-oil and oil-source rock correlation. Benchmark studies (Thompson, 1983; Mango, 1990, 1992; Mango *et al.*, 1994; Bement *et al.*, 1994; Halpern, 1995; Ten Haven, 1996; Jarvie, 2001) have shown that LHs carry useful information regarding genetic associations, alteration, and thermal maturity of oils. Inclusion of LH data is essential for petroleum systems studies, otherwise mixing and alteration of oils can easily be overlooked. LHs constitute the



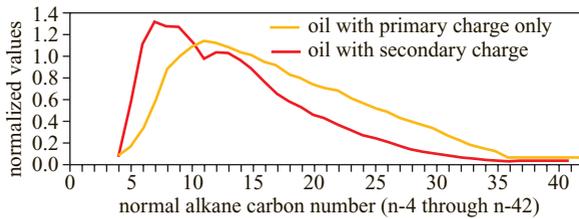
**Fig. 11.** A GC fingerprint: A, binary output from the GC itself; B, histogram showing the yield and distribution of normal paraffins.

primary compounds in condensates generated from source rocks during late catagenesis. This becomes an important correlation parameter during this generation stage as sterane and terpane biomarkers are depleted or absent due to cracking. Halpern (1995) devised polar plots that used C<sub>7</sub> LHs for both oil correlation and oil transformation. Moreover, it has been shown that analyses of light hydrocarbons have application in oil-to-source rock correlation studies because the lighter (C<sub>5</sub>-C<sub>8</sub>) fraction of source rocks often can be evaluated through thermal extraction (Jarvie and Walker, 1998; Odden *et al.*, 1998) or special extraction techniques. It has further been shown that lithofacies predictions may be possible from light hydrocarbon data.

Normalized paraffin distributions and slope factors are especially useful to assess GC fingerprints for

**Table 3.** Pristane-to-phytane (Pr/Ph) ratio interpretation

Pr/Ph	DESCRIPTION
<1.00	highly reducing, carbonate to marl lithofacies, some lacustrine
1.00-3.00	moderately reducing, marl to shale lithofacies some lacustrine
>3.00	moderately oxidizing, fluvial-deltaic lithofacies, coals



**Fig. 12.** Normalized paraffin profiles in unaltered oil, and an oil with a secondary charges of light hydrocarbons in an oil from Lybia.

alteration or mixing. The lightest paraffins will always be reduced in 'dead' oil samples (atmospheric oil samples that have lost most of their solution gas) and this will result in a decline in the paraffin profile below about  $C_6$ . However, secondary charges of light oil will alter this profile and a marked change in the profile will be evident in the lightest hydrocarbons (**Fig. 12**).

### Correlation using biomarker ratios

Biological markers (biomarkers) are molecular fossils that link oils to their original biological progenitor. For oils that are not severely biodegraded a large number of biomarker compounds or their diagnostic fragment ions are available for correlating oils or rock extracts. One of the simplest approaches is pattern recognition between different sets of ion chromatograms. For example, it is easy to distinguish the differences between terpane 191  $m/z$  ion chromatograms (GC-MS, Gas Chromatography-Mass Spectrometry) in carbonate versus shale source rocks (**Fig. 13**). One of the strengths of biomarkers is their resistance to biodegradation. A scale for ranking levels of biodegradation was developed by Peters and Moldowan (1993) ranging from 1 (light biodegradation) to 10 (severe biodegradation). When reporting biodegradation of crude oils, these scales are generally referred to based on the extent of depletion as determined from the measured data.

Various compounds and compound classes as well as a multitude of ratios are used to characterize oil and source rock extracts (Peters and Moldowan, 1993; Peters *et al.*, 2005).

### Carbon isotopes

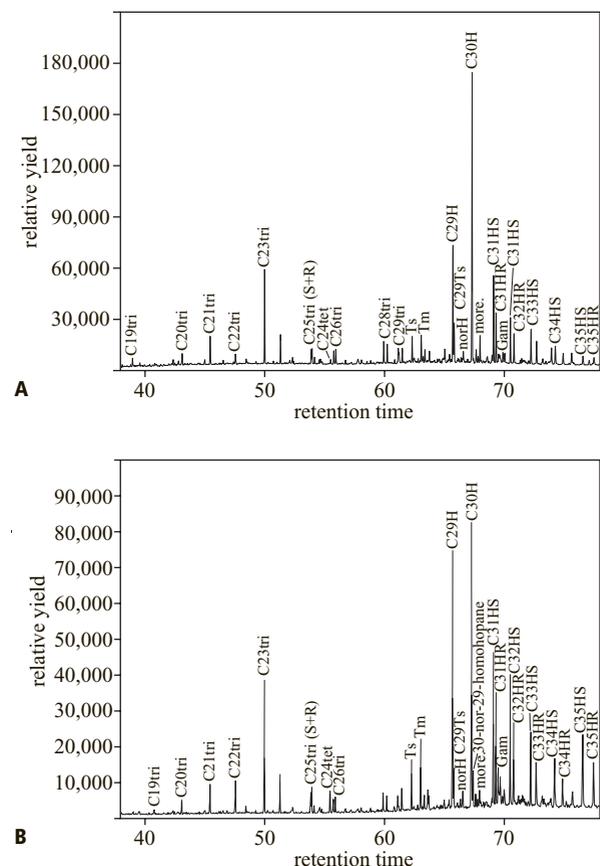
Carbon isotopes are generally measured on the whole oil or fractions of the oil such as the saturate and aromatic fractions. The ratio of carbon-13 to carbon-12 ( $^{13}C/^{12}C$ , relative to a standard) can be used to differentiate certain oils. For example, Sofer (1984)

demonstrated that terrestrially sourced oils can be distinguished from marine sourced oils by cross plotting saturate vs. aromatic hydrocarbons. More recently high resolution geochemical techniques have been utilized to measure carbon isotopic ratios of individual hydrocarbons including biomarker compounds such as terpanes and steranes (Mello *et al.*, 2003; Moldowan *et al.*, 2004).

### Carbon isotopic values of biomarkers

A technique for measuring the carbon isotopic values of specific alkanes, isoprenoids, hopanes (also called terpanes), and steranes enables typing oils that have very similar source contributions based on standard geochemical techniques. For example, Late Cretaceous and Upper Jurassic oils from the Middle East and the Gulf of Mexico have been clearly distinguished by this approach (Moldowan *et al.*, 2004).

For detailed information on analytical techniques and instruments the reader is referred to Peters and Moldowan, 1993 and Peters *et al.*, 2005.



**Fig. 13.** Terpene ion GC-MS chromatogram (191  $m/z$ ) of oils from the Permian Basin, USA: A, a carbonate-sourced oil; B, a shale-sourced oil.

## Maturity assessment of oils

Biomarker ratios are commonly used for assessment of the maturity of oil samples. Common ratios include Ts/Tm (where Ts is C<sub>27</sub> 18 $\alpha$ -trisorhopane and Tm is C<sub>27</sub> 17 $\alpha$ -trisorhopane), ratios between R and S stereoisomers in hopanes or steranes, and TAS (triaromatic sterane) ratios. Methylphenanthrenes have also been used for oil maturity assessments and have been quite precise with some petroleum systems particularly terrestrially sourced oils.

In addition LHs, can be used to predict thermal maturity as shown by Schaeffer and Littke (1988) who demonstrated a change in the concentration of dimethylcyclopentanes relative to vitrinite reflectance.

A calculated temperature of expulsion (CTemp, in °C) was derived from the work of Frank D. Mango and others at Shell's Bellaire Research Center (Bement *et al.*, 1994; Mango, 1997) and is computed as:

$$\text{CTemp (}^\circ\text{C)} = 140 + 15 \left( \ln \frac{2.4 - \text{DMP}}{2.3 - \text{DMP}} \right)$$

where DMP is dimethylpentane.

Since the LHs increase with increasing thermal maturation, they can be used to predict Gas-to-Oil Ratios (GOR<sub>s</sub>) on pristine (unaltered) oil samples such as US Williston Basin (Mango and Jarvie, 2001). Their equation utilizes C<sub>6</sub> and C<sub>7</sub> isoalkanes such that:

$$\ln \text{GOR} = (1.33 \ln 2\text{MP}) - (2.81 \ln 3\text{MP}) + (3.19 \ln 2\text{MH}) - (0.875 \ln 3\text{MH}) + 7.2$$

where MP is methylpentane and MH is methylhexane.

Specific field and basin calibration may be required, however.

## Alteration of crude oils

Petroleum source rocks and reservoir oils are in a dynamic environment that is constantly changing through time. For example, an initial charge of low maturity oil can be supplemented by secondary charges of higher maturity oil from the same source or from other source rocks that have reached the oil expulsion stage. Thus, a single oil reservoir can have multiple inputs, although this has often gone unrecognized.

Further, alteration processes complicate the assessment of oils. These processes may include: a) mixing; b) biodegradation; c) evaporative fractionation; d) gas washing; e) water washing;

f) deasphalting; g) thermal chemical sulfate reduction (TSR); h) oil cracking, or any combination of these processes.

## Water washing and biodegradation

Water washing is the emplacement of water through a hydrocarbon pool. Water washing has two potential impacts on crude oils: it will selectively dissolve more water-soluble, light aromatic hydrocarbons. If fresh water, bacteria may be introduced to the petroleum pool and biodegradation could occur. A case study of water washing in Nevada crude oils was shown by Palmer (1984).

Biodegradation is a process whereby certain bacteria metabolize crude oil in a systematic fashion. Biodegradation proceeds by consumption of the simplest and lightest molecules to the more complex and heavier molecules. Thus, biodegradation decreases the API gravity and increases the viscosity of oils in a systematic fashion.

Oils may be biodegraded to varying extents.

Various levels of biodegradation were summarized by Peters and Moldovan (1993) in a scale ranging from 1 (least degraded) to 10 (severely degraded).

Generally, biodegradation is slowed and eliminated when a reservoir is above temperatures of about 80°C. However, changes in the burial history of sediment can often bring a deeper, once hotter reservoir into a cooler zone where bacteria become active, prior to subsequent reburial, and vice versa.

## Evaporative fractionation

Any fractionation process involves a change in the composition of gas and oil. The lightest hydrocarbon, methane, has the highest fugacity, which describes its ability to expand and migrate through sediments. However, when gas exsolves from a liquid hydrocarbon pool, light alkanes are selectively dissolved in the gas and the residual oil is enriched in light aromatic hydrocarbons. This process was described and experimentally detailed by Thompson. Thompson's aromaticity/paraffinicity plot is an integral part of any crude oil assessment (Fig. 14). Evaporative fractionation also means that there are two pools of hydrocarbons often suggesting a deeper oil pool.

## Deasphalting

When crude oils have a secondary charge of non-hydrocarbon gas, hydrocarbon gases, or condensate, it is possible that the asphaltene will precipitate out of the oil forming a tar mat. This process has been shown to occur in the Western Canada Basin by Milner *et al.* (1977) and is a common occurrence in petroleum systems where various episodes of vertical migration have occurred.

### Thermochemical sulphate reduction

High concentrations of hydrogen sulphide ( $H_2S$ ) gas in reservoir gases are derived from Thermochemical Sulphate Reduction (TSR; Orr, 1974). In TSR,  $H_2S$  is essentially formed by the reduction of sulphate, leading to elemental sulphur. Sulphur subsequently reacts with hydrocarbons to form  $H_2S$  and  $CO_2$  resulting in low quality oil accumulations. As a consequence of this reaction, the  $\delta^{13}C$  (isotopic fraction of  $^{13}C$ ) of  $CO_2$  is comparable to that of the oil, whereas the  $\delta^{34}S$  of  $H_2S$  is comparable to that of the sulphate.

Carbonate-evaporite reservoir sequences tend to have high  $H_2S$  concentrations (Le Tran, 1972). Such reservoirs have  $H_2S$  concentrations ranging from 6 to 98% of the total gas deposits. In these sequences there is the possibility of high sulphate concentrations from the evaporites and low concentration of iron in the carbonates that would otherwise bind  $H_2S$  as pyrite as would occur in shales.

### Oil cracking

Oils will decompose much like kerogen into less complex and lighter hydrocarbons, while also forming a refractory carbonaceous residue at higher temperatures. Cracking of resins and asphaltene fractions of crude oils will occur between 100-150°C comparable to temperatures required for kerogen decomposition to hydrocarbons. However, a temperature exceeding 145°C is required for the onset of paraffinic fractions of oil cracking to gas. This latter decomposition can be modeled with the kinetic parameters of Waples (2000).

Diamondoid analysis has been shown to be an effective approach for assessing oil cracking (Mello *et al.*, 2003; Moldowan *et al.*, 2004). While extended hopanes and steranes are cracked to lighter hydrocarbons at higher temperatures, diamondoids are very stable. Thus, a ratio of less stable to more stable compounds will provide an indication of oil cracking. This technique is important since biomarker maturity parameters cease to be useful above about 0.90% vitrinite reflectance.

### Mixing of oils

Pristine crude oils in reservoirs may be mixed with lighter hydrocarbons derived from the same source rock at higher thermal maturity or from oil or gas from other source rocks. Mixing has proven to be a difficult process to discern except in the most obvious cases such as a condensate charge emplaced into a biodegraded oil. Typical oil correlations have relied primarily on the middle to high molecular weight hydrocarbons derived from GC and GC-MS analyses and carbon isotopes of fractions of oils. A full range of

analyses may be required, but mixes can often be discerned by detailed interpretation of LHs especially slope factors (i.e., parameters which take into account the n-alkane distribution slope in the chromatogram), plus middle range hydrocarbons, and biomarkers. Thus all oil studies should include an assessment of the possibility of oil mixing.

### Interpretation of geochemical parameters

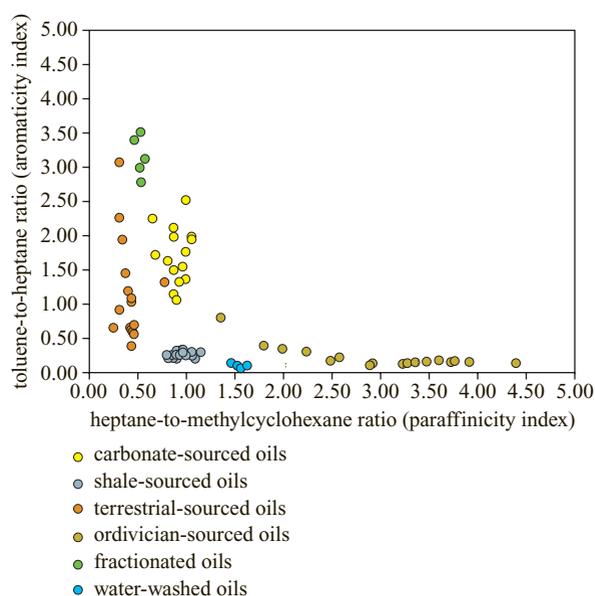
Basic guidelines for interpretation of geochemical parameters discussed in this paper are detailed in **Table 4**.

### Geochemical characterization of natural gas

Natural gas is the gaseous part of petroleum and consists of a mixture of gaseous hydrocarbons such as methane, ethane, propane, butanes and pentanes.

Gaseous hydrocarbons can be formed through different generation mechanisms. Among the main genetic processes are biogenic formation (by methanogenic bacteria, at a low temperature) and thermogenic formation. By means of geochemical analysis it is possible to determine the origin of gaseous accumulations or surface gaseous occurrences, and to obtain information on the presence of an effective petroleum system (Mattavelli *et al.*, 1983; Schoell, 1983, 1988; Faber, 1987; Rice, 1993).

Thanks to recent technological developments, it is today possible to geochemically characterize even minute quantities of gas found dissolved in drilling

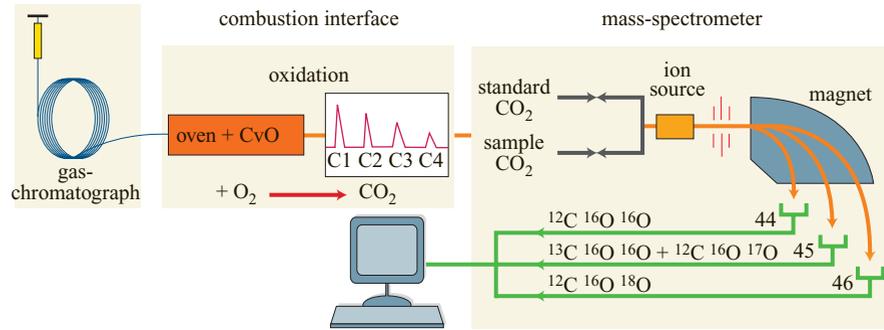


**Fig. 14.** Thompson's aromaticity vs. paraffinicity plot.

**Table 4.** Guidelines for interpretation of TOC, Rock-Eval, vitrinite reflectance data and gas, oil and condensate

DESCRIPTION	VALUES	INTERPRETATION	REFERENCES
<b>I. ROCK ANALYSES</b>			
TOC (wt. %)	<1.00 >1.00	Below average Above average	Baker, 1962
Hydrogen Index (HI) (mg HC/g TOC)	0-50 50-200 200-350 350-700 700-1,000	Type IV dry gas prone Type III gas prone (usu. terrestrial) Mixed Type II/III mixed oil/gas Type II oil prone (usu. marine) Type I oil prone (usu. lacustrine)	Espitalie <i>et al.</i> , 1977
$T_{max}$ (°C)	<430 430-439 440-450 451-459 460-475 >475	Immature Early oil window Peak oil window Late oil window Wet gas window Dry gas window	Espitalie <i>et al.</i> , 1985
$T_{max} R_o$ Vitrinite Reflectance in oil ( $R_o$ )	$R_o = 0.0180(T_{max}) - 7.16$ 0.20-0.55 0.55-0.74 0.75-0.94 0.95-1.09 1.10-1.39 >1.40	Immature Early oil window Peak oil window Late oil window Wet gas window Dry gas window	Dow e O'Connor, 1982
<b>II. GAS, CONDENSATE AND OIL INTERPRETATIVE GUIDELINES</b>			
<b>A. Gases</b>			
Carbon isotopes	ca. -60 -55 to -60 <-55	Biogenic gas Mixed gas Thermogenic gas	Schoell, 1983
<b>B. Condensates and oils</b>			
<b>Organofacies and lithofacies indicators</b>			
<i>Carbonate lithofacies indicators</i>			
Pristane / Phytane	<1.00 >1.00		Didyk <i>et al.</i> , 1978 Hughes <i>et al.</i> , 1995
Dibenzothiophene / Phenanthrene			
C <sub>35</sub> homohopanes	High abundance		
Diasteranes vs. steranes	Diasteranes low		
C <sub>24</sub> tetracyclic / C <sub>26</sub> tricyclic terpanes	>1.00		
<i>Marine shales</i>			
Pristane / Phytane	1.00-3.00		
C <sub>29</sub> / C <sub>30</sub> hopanes	C <sub>29</sub> << C <sub>30</sub>		
C <sub>35</sub> / C <sub>34</sub> hopanes	<1.00		
Diasteranes vs. regular steranes	Diasteranes abundant		
<i>Terrestrial / Coaly Source</i>			
Pristane / Phytane	>3.00		
Presence of oleananes and lupanes			
C <sub>19</sub> and C <sub>20</sub> dominant in tricyclic terpanes			
High abundance of wax			
Diasteranes	High		
C <sub>27</sub> C <sub>28</sub> and C <sub>29</sub> steranes	C <sub>29</sub> >> C <sub>27</sub> , C <sub>28</sub>		
C <sub>31</sub> hopanes	Very high		
C <sub>24</sub> tetracyclic / C <sub>26</sub> tricyclic terpanes	>1.00		
<i>Lacustrine source</i>			
4-methylsteranes	Abundant		
Diasteranes vs. regular steranes	High diasteranes		
<b>Thermal Maturity</b>			
<i>Light hydrocarbon analyses</i>			
CTemp = 140 + 15[ln(2.4 - DMP/2.3 - DMP)]	95-150 °C		Mango, 1997
<i>Biomarker analysis</i>			
C <sub>29</sub> aaa sterane 20S/(20S+20R)	0.00 to 0.55		Seifert and Moldowan, 1986
Extended hopanes C <sub>32</sub> 22S/(22S+22R)	0.00 to 0.62		Ensminger <i>et al.</i> , 1977
C <sub>27</sub> hopanes Ts/(Ts+Tm)	0 to 1.00		Seifert and Moldowan, 1978
C <sub>20</sub> - C <sub>21</sub> / (C <sub>26</sub> - C <sub>29</sub> ) triaromatic steranes	Relative		
C <sub>28</sub> TA / (C <sub>29</sub> Ma + C <sub>28</sub> TA) (tri- and mono-aromatic steroids)	0 to 1.00		
MPI = 1.5(3MP+2MP)/(P+9MP+1MP)	0.6-1.5	Oil window	

**Fig. 15.** Geochemical characterization of natural gas by means of chemical and isotopic analysis.



muds during the drilling of a well (headspace sampling).

The analytical methodologies used are gas-chromatography (to determine the chemical composition of the gases) and analysis of stable isotopes. Isotopes are atoms containing the same number of protons but a different number of neutrons. Isotopes are divided into two categories: radioactive and stable. Radioactive isotopes disintegrate spontaneously to form atoms of other elements with the emission of radiations which, in some cases, may be dangerous. Stable isotopes, on the other hand, have a stable nucleus and therefore do not pose any radiogenic risks (see schematic diagram of the analytical set-up in **Fig. 15**). The isotopic characterization of hydrocarbons is carried out by the analysis of the stable isotopes of carbon and hydrogen (although the latter is used only in special cases). As stated above, natural gas is formed through two main mechanisms: the biogenic process and the thermogenic process. In actual fact all hydrocarbon accumulations are of biogenic origin as they derive from the decomposition of organic matter, but in this context the term biogenic is used to indicate a particular mechanism of natural gas formation at low temperature. An alternative term to biogenic gas is bacterial gas.

### Biogenic gas

Biogenic gas as a natural energy resource represents, on a worldwide scale, about 20% of the available hydrocarbon resources (Rice, 1993). The mechanism of generating gas by bacteria takes place at great depths, under anoxic conditions (absence of oxygen) and at relatively low temperatures (lower than 70°C) on immature organic matter. For the formation of commercial accumulations of biogenic gas, however, particular geological conditions are required, favouring the preservation of these accumulations (early entrapment systems, formation of efficient cover and high rates of sedimentation).

The majority of biogenic gas accumulations are contained in depositional sequences of alternating

sand and clay: continental type organic matter (type III kerogen, derived from terrestrial organic matter, upper plants and wood fragments) is degraded, under anoxic conditions, by methanogenic bacteria and the gas thus formed is almost always lost due to the lack of any effective seal. Where favourable conditions exist (contribution of continental organic matter, high rate of sedimentation and formation of adequate cover) gas accumulations may be formed that can also be commercially interesting.

The elements characterizing biogenic gas are:

- Chemical composition: biogenic gas is chemically very dry (i.e., almost exclusively methane with traces of ethane or in any case with a content of upper homologues of less than 0.1% apart from minute quantities of CO<sub>2</sub> and N<sub>2</sub>); thermogenic gas (which under particular conditions can also be dry) can instead contain appreciable concentrations of upper homologous compounds (ethane, propane, butane, pentane, etc.), namely condensable compounds. Hence the term wet and the parameter *Gas Wetness*, defined as a ratio and expressed as a percentage. It is the sum of the hydrocarbons (excluding methane) divided by the sum of all the hydrocarbons comprising the gas:

$$\left[ \frac{\sum(C_2 + C_3 + iC_4 \dots + C_n)}{\sum(C_1 + C_2 + C_3 + iC_4 \dots + C_n)} \right] \cdot 100$$

- The isotopic content of carbon (isotopic ratio <sup>13</sup>C/<sup>12</sup>C): biogenic gas is isotopically well characterized, having carbon isotopic value (δ<sup>13</sup>C) of between -110 and -60‰. During the transformation of the organic matter into gas, bacteria tend to prefer using light carbon (<sup>12</sup>C) rather than heavy carbon (<sup>13</sup>C), so that the methane formed has a negative carbon isotopic ratio (δ<sup>13</sup>C) (in this regard it should be observed that the isotopic values of the carbon in hydrocarbons, both gaseous and liquid, are always negative).
- The isotopic composition of hydrogen (isotopic ratio between deuterium and hydrogen or D/H) reflects exactly the same scheme so that biogenic gases are always leaner in deuterium compared

with thermogenic gases (isotopic range  $\delta D$  between  $-250$  and  $-170$  ‰).

In Italy, a good example of biogenic gas accumulations is provided by the numerous reservoirs located at relatively shallow depth (below 2,000 m) onshore in the Po Valley, and also by the deposits in the nearby Ravenna offshore (formations constituted by alternating Pliocene sand and clay, Mattavelli *et al.*, 1983). The biogenic gas of the Po Valley, with very negative  $\delta^{13}C$  values (usually between  $-70$  and  $-76$ ‰), is found in reservoirs located both at shallow and very great depths (one offshore well has produced biogenic gas at a depth of approximately 4,500 m and is the deepest occurrence of biogenic gas mentioned in literature).

The isotopic trend with depth in gas wells in the Po Valley shows that it is possible to find both types of gas (biogenic and thermogenic as well as the two mixed, or mixed gas). Mixed gas is usually found in reservoirs of Messinian age whereas Mesozoic reservoirs contain only thermogenic gases. Particular geological conditions can, however, favour the migration of deep thermogenic gases into shallower reservoirs without there being any modifications in the isotopic signal of the gas.

### Thermogenic gas

Thermogenic gas is formed from kerogen or from oil and, as a result of heating during deposition, can be generated by the thermal cracking of the organic matter (kerogen) into both gaseous and liquid hydrocarbons (primary thermogenic gas or oil-associated gas) and by the thermal cracking of an oil at a high temperature into gas (secondary thermogenic gas).

Thermogenic gas, which is generated at higher temperatures ( $80$ - $150^\circ C$ ), is generally much richer in the higher homologues compared to biogenic gas. The isotopic value of methane carbon ( $\delta^{13}C$ ) is related to the level of maturity of the sediments that have generated it, and falls between  $-60$  and  $-20$ ‰, while the isotopic values of hydrogen varies between  $-200$  and  $-80$ ‰.

To distinguish a primary thermogenic gas from a secondary thermogenic gas (ultramature, i.e., formed at higher temperatures,  $150$ - $200^\circ C$  and more), the quantity of higher homologues is taken into consideration. Generally a primary thermogenic gas is characterized by high percentages of higher homologues (*Gas Wetness* up to  $50$ - $60\%$ , e.g., in the Val d'Agri wells in Basilicata), whereas a secondary thermogenic gas has a very low *Gas Wetness* parameter (even less than  $0.2\%$ ).

These characteristics can be attributed to the thermal cracking of liquid compounds: heavy,

complex molecules (e.g.,  $C_6$  and higher) crack when subjected to high temperatures and form simpler molecules. The ultimate consequence of this mechanism of thermal degradation is the formation of a gas consisting mainly of methane. This gas is chemically similar to biogenic gas but can easily be distinguished from by its higher content of  $^{13}C$  ( $\delta^{13}C$  methane between  $-30$  and  $-27$ ‰) and deuterium.

In the presence of low maturity organic matter, thermogenic gas could be mistaken for a biogenic gas (low  $^{13}C/^{12}C$  ratio and minor presence of higher homologues). However isotopic analysis of ethane and propane can be used to determine the genetic origin of the gas.

### Characterization of non-hydrocarbon compounds

Non-hydrocarbon gases that can be associated with natural gas are commonly carbon dioxide, nitrogen and hydrogen sulphide. The presence of these compounds is a negative element in the economic assessment of the find as it reduces their commercial value (the energy content of the gas being lower). Their presence requires investments in plants and equipment needed to remove and dispose of these gases. They also poses technical (corrosion of materials) and safety problems.

*Carbon dioxide ( $CO_2$ )*. Discovery of  $CO_2$  is not very frequent, but its presence can seriously affect the economics of a find. Examples of  $CO_2$  accumulations are provided by the Pannonico Basin, by the Cooper-Eromanga Basin (Australia), by the South China Sea field, and by the Palino-Candela field (southern Italy).

According to statistics drawn up by Thrasher and Fleet (1995) the likelihood of finding  $CO_2$  greater than  $20\%$  is  $1:100$ , but, when encountered, the average of these finds have a  $CO_2$  content close to  $50\%$ . This indicates that the likelihood of finding carbon dioxide is not very great, but that when it does occur, the  $CO_2$  levels are so high that they make the discovery of the accumulation an uneconomic proposition unless the resource in question can be exploited on the site, with appropriate strategies (electrical power stations operating on *lean-gas*).

Among the various mechanisms of  $CO_2$  formation, the most important ones are: *a*)  $CO_2$  derived organically (one mechanism is the breakdown of organic matter during diagenesis and catagenesis); *b*) bacterial breakdown of oil ( $T < 70^\circ C$ ); *c*)  $CO_2$  produced by volcanic activity and by intrusive magmatic bodies; *d*) as the product of the thermochemical reduction of sulphates (TSR) with hydrocarbons.

*Nitrogen ( $N_2$ )*. At present little is known about the isotopic chemistry of nitrogen in oil basins and this could be due to the fact that accumulations are often the result of a mixing of gases formed through various

genetic mechanisms. By studying particular cases in which the origin of the nitrogen was due to a single mechanism, it has been possible to establish with sufficient accuracy the fields of variation of the isotopic datum of nitrogen according to the mechanisms responsible for its formation. Large accumulations of nitrogen have been discovered in many oil basins, such as Great Valley, California (Jenden *et al.*, 1988), the Volga-Ural Basin, the Mid-European Basin (Jenden *et al.*, 1988; Kroos *et al.*, 1995), and the Yinggehai Basin, just to mention a few.

*Hydrogen sulphide (H<sub>2</sub>S)*. H<sub>2</sub>S because of its dangerous nature poses many problems from the standpoint of safety (it can be detected by scent at levels of a few parts per million, but beyond 30 ppm the nerve centres of the olfactory system can no longer perceive it and it is at this level that the danger exists). Bringing oil discoveries into production when H<sub>2</sub>S is present involves far higher costs due to the problems associated with the corrosion of the materials used in production facilities and with its disposal. In nature, H<sub>2</sub>S accumulations occur that can be as high as 98% of the total gas yield.

The hydrogen sulphide (H<sub>2</sub>S) can be originated bacterially or inorganically. In its bacterial origin, the sulphate dissolved in the waters is reduced to H<sub>2</sub>S. However, this mechanism cannot yield levels of H<sub>2</sub>S greater than 5%. Another limit to bacterial formation of H<sub>2</sub>S is temperature, which must be lower than 80°C.

With regard to its inorganic origin, two mechanisms can be distinguished:

- Thermal decomposition of kerogen: H<sub>2</sub>S is formed during the various phases of the diagenesis of the organic matter. This mechanism is usually present in carbonate rocks, whereas in clays the presence of iron acts as a natural limiting factor (precipitation of pyrite, FeS<sub>2</sub>).
- Thermochemical reduction of the sulphate (TSR): this is a thermochemical reaction that occurs at temperatures of at least 120°C between hydrocarbons and evaporites. This mechanism is the one that accounts for the highest concentrations of H<sub>2</sub>S.

## Conclusion

Source rock evaluation proceeds along a pathway whereby a sequence of analytical tests is implemented to determine the source potential and possible correlation to known oil or gas pools. The analytical scheme must provide means to determine the potential of the rock for hydrocarbons, what type of hydrocarbons would be formed (gas vs. oil), its thermal maturity (immature, oil, or gas zone), and its rate of decomposition (kinetics). These data are used to map organofacies, generation potentials, maturity

zones, and transformation ratios to assess the best prospects for oil or gas. Mature source rock extracts provide samples for correlation to oil samples to determine whether it is an effective source rock, i.e., the source of oil or gas. Multiple samples of a single source rock are needed in this evaluation as slight variations in organofacies will often alter biomarker characteristics.

Oil correlations and oil-to-source rock correlations rely on bulk and detailed chemical analyses. Bulk techniques include sulphur, nickel, vanadium, elemental compositions, and fractionation yields as well as API gravity of crude oils. Detailed chemical analyses include GC fingerprinting, biomarkers, and carbon isotopes as well as new techniques such as carbon isotopic values of biomarker compounds and diamondoid ratios to assess oil cracking.

Oil analysis must include an assessment of oil alteration, whether from secondary charges (mixing), biodegradation, evaporative fractionation, water washing, thermochemical sulfate reduction, or deasphalting. The geological setting and chemistry of oils can be very dynamic and changes due to various processes must be accounted for in crude oil assessments.

The ultimate goal of any petroleum systems study is to aid the identification of the best prospects for future oil and gas production including those that may have been overlooked in the past. This may include assessments that aid the understanding of oil quality as well as reservoir compartmentalization.

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