

Nigel Smith

Hydrogen exploration: a review of global hydrogen accumulations and implications for prospective areas in NW Europe

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Abstract

From a geological perspective, hydrogen has been neglected. It is not as common as biogenic or thermogenic methane, which are ubiquitous in hydrocarbon basins, or carbon dioxide, which is common in geologically-active areas of the world. Nevertheless, small flows of hydrogen naturally reach the Earth's surface, occur in some metal mines and emerge beneath the oceans in a number of places worldwide. These occurrences of hydrogen are associated with abiogenic and biogenic methane, nitrogen and helium. Five geologic environments are theoretically promising for exploration based on field, palaeofluid and theoretical evidence: ophiolites (Alpine, Variscan and Caledonian in order of decreasing prospectivity), thinned-crust basins (failed-arm rifts, aulacogens), potash-bearing basins, basement in cratonic areas and the Mid Atlantic ridge and its fracture zones. The subsurface areas of these environments are relatively poorly known, compared to hydrocarbon basins.

Hydrogen shows may indicate larger reserves in the subsurface, in a similar way to the beginnings of hydrocarbon exploration in the 19<sup>th</sup> century. The main source of hydrogen is ultramafic rocks which have experienced serpentinization, although other generation processes have been identified, including biogenic production of hydrogen during very early stages of maturation and radiolysis. There are two main tectonic settings where serpentinization has operated. The main accessible onshore areas are where ophiolites are found tectonically emplaced within fold belts. Potentially much larger investigation areas lie in the subsurface of some ophiolites. These areas generally lie outside hydrocarbon provinces. However, where thrusting has emplaced ophiolites over a hydrocarbon-bearing foreland basin, tests involving sub-thrust conventional hydrocarbon exploration plays could also be

## Nigel Smith

employed to search for hydrogen. The other main tectonic setting is in highly extended basins, for example failed rifts or aulacogens, where thick sediments overlie thinned or absent crust above probably serpentinized mantle. These structures occur offshore on continental margins and extend onshore into long-lived rifts which have been reactivated and rejuvenated repeatedly. Conventional seismic reflection data are already available in these areas, but deep subsurface resolution is poor where there are extensive volcanic rocks. Analogues of these occurrences are also found in the deep oceans, along the mid ocean ridges and offsetting transform faults. Here, thin crust and faulting may facilitate serpentinization of the mantle rocks by seawater ingress.

Further research should aim to identify the extent of the hydrogen flux and its probable dominant role in the abiogenic production of hydrocarbons in Precambrian times, a natural process now largely replaced by biogenic participation. A similar industrial process replicates serpentinization, producing hydrogen and ultimately liquid hydrocarbons on a commercial scale in some countries. It remains to be proved whether a contribution from exploration can be made to any future Hydrogen Economy.

### Keywords

Hydrogen, exploration, gas, serpentinites, radiolysis, abiogenic hydrocarbons

In recent years articles and reports have predicted the replacement of hydrocarbon-sourced fuels by hydrogen gas (Eyre *et al.* 2002). Some of these projects and potential sources of hydrogen were reviewed previously (Smith 2002). Articles either incorrectly state that hydrogen does not occur freely in nature, or are unaware of its occurrence and fail to mention any contribution from exploration (e. g. Fisher 2002). What are the prospects of discovering hydrogen? Shows of hydrogen exist at the surface and in mines in some parts of the world (Headlee 1962, Neal & Stanger 1983, Abrajano *et al.* 1988, Lyon *et al.* 1990, Smith 2002), but the key question is how much more might lie in the subsurface and in different places. Only the superdeep (Russian) and Gravberg (Swedish) boreholes could be considered tests, so far, and these were not specifically targeted on hydrogen. In this paper, we review the main areas of hydrogen occurrence and assess the hydrogen prospects of selected equivalent areas in NW Europe. New World examples have been largely excluded here and evidence of hydrogen in these areas will be published elsewhere.

Geological and tectonic control on hydrogen occurrences

Natural processes that lead to hydrogen production and the geological and tectonic environments in which they operate are listed below. The hydrocarbon sources of the following three sections usually lack significant hydrogen shows but are included to show the relationship of a few exceptions.

*Hydrocarbon-bearing basins*

Gases derived from burial of biogenic sediments form widespread natural gas fields and numerous shows in petroliferous and gas-prone sedimentary basins. Methane-dominated thermogenic dry gases (e.g. Fig. 1A) are concentrated in the major (coal-sourced) basins. Wet gases are associated with oilfields in or adjacent to more marine source rocks. Generally hydrogen contents below 0.1% are found in most of these conventional hydrocarbon gases. However in Estonia, on the island of Koksher, gas comprising 79% methane and 20.8% hydrogen was discovered in a glacial formation at 90' (27 m) depth and some wells in the Stavropol gasfield Sarmatian reservoir (Miocene) have elevated hydrogen content (Fig. 1B, Bohdanowicz 1934). The Koksher gas may be related to Baltic Cambrian reservoirs in offshore Swedish fields. Grip & Odman (1944) showed that Cambrian reservoirs on the island of Oland had slightly elevated hydrogen contents (up to 4.9%). Zinger (1962) reported elevated hydrogen content of waters near the oil and gas fields in Visean rocks of the Lower Volga region, Russia and high concentrations of hydrogen in boreholes in the October field at Grozni, Chechnya.

*Young organic-rich sediments*

Biogenic gases, produced by bacteria, include hydrogen. Generation occurs relatively quickly in surface sediments and subsequent burial takes source rocks and gas into the thermogenic field below a depth of about 600 m. Hydrogen is present in the waters of the Caspian Sea (7.3 cm<sup>3</sup> per litre) and in some freshwater lakes (8 cm<sup>3</sup> per litre). Baltic Sea sediments contain 0.2-0.6 cm<sup>3</sup> per kg between 3-8 metres depth (Levshounova 1991).

## Nigel Smith

Numerous biological systems utilise hydrogen as an energy source. In common with landfill sites, hydrogen, from whatever original abiogenic or biogenic source, is lost at a very early stage, a process which continues as shown by the declining hydrogen content relative to increasing source (rock) maturity of coals and their precursors (Fig. 2).

### *Hydrogen content of coals*

UK coals have a range of hydrogen content (1.62% to 5.48%; Fig. 2), but hydrogen is rarely found in the free gases of coalmines. Former Soviet Union coal-derived gases have hydrogen contents ranging from 2.9-40% (Levshounova 1991). According to Molchanov (1981) the hydrogen content is higher in coal gases than in the surrounding gasfields.

Before discovery of North Sea gas, the UK's domestic gas was generated from bituminous coal at gasworks and known as 'town gas', a mixture of producer gas and coal gas which had a composition of about 51% hydrogen, 15% carbon monoxide, 21% methane, 10% carbon dioxide and nitrogen and 3% other alkanes.

### *Decomposition of methane to graphite and hydrogen at temperatures above 600°C*

Graphite is found in crystalline rocks in many places and may result from decomposition of methane ( $\text{CH}_4 = \text{C} + \text{H}_2$ ; Apps & van de Kamp 1993). Graphite-rich veins were found in Windischeschenbach KTB, Germany's superdeep borehole (Walther & Althaus 1993) but the importance of this very deep process is unknown.

### *Radiolysis of water and organic matter by radioactive isotopes of uranium, thorium and potassium*

Radiolysis of water produces hydrogen (see reactions in Apps & van de Kamp 1993). Vovk (1987) also attributed the characteristic of increasing calcium-bearing salinity with depth of the waters of crystalline basement areas to the decay of radioactive potassium isotope  $\text{K}^{40}$  to  $\text{Ar}^{40}$  and  $\text{Ca}^{40}$  (Nesmelova & Travnikova 1973). Metal mines in Canada, Russia and Finland contain these

## Nigel Smith

characteristic waters and emit hydrogen. Radiolytic calcium readily reacts with water to form hydrogen ( $\text{Ca} + 2\text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{H}_2$ ) in crystalline basement and potash-bearing areas (see below).

Levinson (1977) drew attention to the possibility of hydrogen having been the reducing agent in some uranium deposits. This association is supported by palaeofluid evidence (Salvi & Williams-Jones 1997).

### *Cataclasis*

Hydrogen is generated in fault zones by cataclasis of silicates in the presence of water (Apps & van de Kamp 1993). Venting of hydrogen gas has been reported from Japan and California. Many faults e.g. San Andreas are more associated with carbon dioxide springs (Barnes *et al.* 1978), although hydrogen has also been identified here (Sato *et al.* 1985). As far we know there are no active faults in NW Europe where hydrogen has been detected.

### *Extrusive igneous rocks (non-ultramafic)*

Reaction between dissolved gases in the system C-H-O-S, in particularly basaltic magmas, can produce hydrogen (Apps & van de Kamp 1993). Calc-alkaline (subduction-related) volcanoes are prolific sources of gases. The largest proportion of volcanic gases consists of steam and carbon dioxide (Gerlach 1982). Other gases emitted from volcanoes include nitrogen, hydrogen, hydrogen chloride, hydrogen fluoride and hydrogen sulphide (Headlee 1962). Hydrogen content of the gas in volcanoes amounted to 0.5-4%, with Surtsey, Iceland the highest (Gerlach 1982).

### *Alkaline igneous complexes*

There is very little evidence of felsic or mafic intrusive rocks containing hydrogen (Fig. 3). However alkaline intrusions (carbonatite and nephelinite complexes e. g. the Lovozero and Khibina Alkaline Igneous complexes, Kola Peninsula, Russia) comprising olivine-rich rocks from mantle depths, appear



## Nigel Smith

mines and boreholes have similar hydrogen percentages and range of other gases. The Juuka area has serpentinite lenses in mica gneisses and schists, in rocks dated as 1900-2100 Ma but the Pori area is within 1300-1400 Ma sedimentary rocks (Sherwood-Lollar *et al.* 1993). Recent serpentinization or radiolysis (see above) may be responsible for these shows.

### *Potash-bearing strata*

Hydrogen gas is also relatively abundant (up to 20-30% of the total gas) where some of the reservoir or source beds contain anhydrite or gypsum (Knabe 1989, Levshounova 1991). This association is also supported by palaeofluid evidence. Hydrogen has migrated into conventional hydrocarbon reservoirs in some of these cases e.g. Stavropol (Fig. 1B, Bohdanowicz 1934). Hempel (1989) distinguished six different gas emission types by composition in the Permian potash and Kupferschiefer mines of eastern Germany, in which one type consisted of methane and nitrogen with a hydrogen content of more than 30%. Knabe (1989) tabulated emissions from different Permian lithologies and found that the hydrogen content was higher in potash beds.

Nesmelova & Travnikova (1973) studied gas in the Verkhmekamsk, Starobinsk and Stassfurt potash deposits and attributed the high hydrogen contents to radioactive transformation of potassium to argon and calcium. Calcium probably reacted with water to form hydrogen. Zinger (1962) attributed the hydrogen to sulphate-reducing bacteria and reduction of sulphate to hydrogen sulphide.

### *Salt-bearing strata*

Headlee (1962) attributed the occurrence of hydrogen in salt mines to the absence of substances with which hydrogen could react within the salt beds. Mine gases at Leopoldshall Salt Mine (Zechstein, Permian of Stassfurt, Germany) flowed for at least 4.5 years, producing hydrogen at a rate of 128 cubic feet per day (cf, Rogers 1921).

### *Ultramafic rocks*

## Nigel Smith

The main type of igneous rock which contains shows of hydrogen gas is ultramafic in composition, and serpentized rocks contain higher amounts of hydrogen (Fig. 3). The location of ultramafic rocks is controlled by intrusion, volcanism and tectonism. The Earth's mantle is made of ultramafic rocks and such rocks are also produced from melts that formed in the mantle. These melts are intruded into the deeper parts of the crust, in large volumes, as large plutons (e.g. Stillwater, USA and Muskox, Canada) and in small volumes in high level 'volcanic' complexes (e.g. kimberlites and komatiites). Mantle rocks are found nearer the surface and in large volumes beneath the oceans, especially along mid ocean ridges and the mantle wedge above subduction zones. However, ultramafic rocks also occur in the continental crust at the surface, as tectonically-emplaced ophiolites within fold belts (e.g. Styles *et al.* 2000), beneath deep basins lying between mountain chains (e.g. Zonenshain & Le Pichon 1986) and as layered intrusions within rifts and in highly extended basins (in both volcanic and non-volcanic continental margins), where the continental crust is highly stretched (e.g. O'Reilly *et al.* 1996).

Ultramafic rocks (harzburgites and peridotites) originally contain about 70-80% olivine and dunite up to 100% olivine (Coleman 1977). Emplacement at the surface or exposure to water leads to serpentization, which is a process of hydrolysis by ferromagnesian minerals (olivines and pyroxenes). A product of this process is hydrogen gas.

### Surface ophiolites

Ophiolite complexes are large blocks of oceanic crust and mantle that have been tectonically emplaced onto continental margins. They range in outcrop size from a few kilometres lateral extent to thousands of square kilometres and ultramafic rocks can be over 5 km thick. Ophiolites are found in all the Phanerozoic mountain belts and Precambrian greenstone belts. Ophiolites showing evidence of hydrogen or abiogenic methane gas generation are the Semail Ophiolite (Oman and the United Arab Emirates), which is of Cretaceous age (Neal & Stanger 1983), the Ural Mountains, Russia where ophiolites are Variscan in age (Betehtin 1961) and include several discrete ultramafic plutons (Lidin *et al.* 1982) e.g. Kempirsay (Devirts *et al.* 1993) and Nishna-Tagil'sk (Fig. 4B, Bohdanowicz 1934), Poison Bay Fiordland, South Island, New Zealand of Palaeozoic age (Lyon *et al.* 1990) and Zambales Ophiolite of Luzon Island, Philippines of Cretaceous age (Abrajano *et al.* 1988).

Deep marine basins lying within mountain chains and containing thick sediments, which overlie probable ophiolites

Seismic refraction data reveals thick low velocity sediments overlying thinned middle or lower crust, probably ophiolitic in origin, for example beneath the South Caspian Sea and the Black Sea. Their crustal structure and position within chains of fold belts suggest they are either remnant oceanic or back arc basins which have escaped significant tectonism. Recent sedimentation rates are very high because the basins form topographic lows surrounding mountainous uplifts (Zonenshain & Le Pichon 1986). Some of them contain conventional hydrocarbon source rocks. At deeper levels than currently drilled they may be underlain by serpentized peridotites covered by relatively old sediments, into which hydrogen gas may have migrated, although no shows of hydrogen are known to us.

Large layered crustal intrusions

In some continental rift zones, the crust is thinned sufficiently for mantle rocks to be found relatively close to the surface. The large plutonic complexes are found in continental areas and the largest ones include ultramafic rocks that are a few kilometres thick and lateral extent of hundreds of square kilometres. The ultramafic rocks are generally less serpentized than those from ophiolite complexes. Areas where intrusions have evidence of hydrogen gas generation are at Sudbury Mine, Ontario, Canada (Sherwood *et al.* 1988), which produced 96 litres per day of hydrogen (= 3.4 cfd, in normally quoted hydrocarbon test figures) and Juuka Mine, Finland (Sherwood Lollar *et al.* 1993).

Mantle beneath ocean crust

Hydrogen is known to be present along the mid ocean ridges and their transform faults and specifically along the Mid Atlantic Ridge (MAR) at 63° N, Reykjanes Ridge, 36° 14' N (Palmer *et al.* 1995), Rainbow Field Springs off the Azores (Donval *et al.* 1997) and Hengill, SW Iceland where high hydrogen contents coincide with higher than average  $R/R_A$  ratios of about 14, indicating a mantle source (Marty *et al.* 1991). A serpentized peridotite seamount east of Bermuda has evidence of gas

Nigel Smith

venting, with calcite, aragonite and brucite chimneys. This seamount is interpreted as a fault-topped core complex (Cann & Morgan 2002). The emerging fluid is at 45-75°C, highly alkaline (pH 9-9.8), with calcium concentrations and, like onshore serpentinising fluids is rich in hydrogen (249-428 mmol kg<sup>-1</sup>) and methane (136-285 mmol kg<sup>-1</sup>).

Welhan & Craig (1979) estimated that the total flux of hydrogen to the ocean was the equivalent of 125 MMcfd. Holloway & O'Day (2000) estimated that 301 moles of hydrogen per m<sup>3</sup> of MORB dyke are released at the Rainbow site of the MAR. The entire basaltic layer (layer 2) of the oceanic crust may contribute seventeen thousand million moles of hydrogen per day (26.8 MMcfd).

Serpentinite seamounts have been discovered in the forearc basins of convergent margins of the west Pacific Ocean (Ishii 1989). No hydrogen has yet been reported from these seamount areas. Because of the serpentinization and high pH fluids identified there, we expect that hydrogen will be found in this geological environment. There are no analogous present day sites in NW Europe.

#### The relationship between hydrogen and kimberlites (Davidson 1964)

Kimberlite lineaments (relatively narrow zones, with several small intrusions) occur in well-defined geographically restricted provinces. They are confined to cratonic areas not affected by Proterozoic orogenesis. The pipes and dykes of kimberlite breccia were emplaced at high levels in the crust as a cold mush of highly gas-charged rock fragments (Heinrich 1966).

In a kimberlite pipe at Udachnaya-Zapadnaya, Yakutia, Siberia, Russia (Davidson 1964) a borehole recovered gas comprising 50% hydrogen, but an investigation of fluid inclusions (Apps & van de Kamp 1993) found only nitrogen (75-96%), methane (4.4-16%) and carbon dioxide (2.4-9.5%) gases.

#### Serpentinization

Primary igneous ultramafic rocks crystallise from melt at high temperatures, 1200°C or more, and are largely composed of the ferromagnesian minerals olivine [(MgFe)<sub>2</sub>SiO<sub>4</sub>], orthopyroxene



The main phase of serpentinization varies for the different associations of large masses of ultramafic rocks. An early ocean floor phase occurs when the mantle cools below 500 °C (Macdonald and Fyfe 1985). Ophiolite complexes undergo another phase of hydration during the obduction process. This is when the ocean crust and underlying mantle breaks up and is pushed up over the sediments of the continental margin (Coleman 1977). Tectonism involved with obduction fractures the rocks and facilitates the ingress of fluids. This is a process that takes many thousands and possibly as long as a million years. At least three different fluids, of probable meteoric origin, have caused serpentinization within fold belt mountains after emplacement (Neal & Stanger 1983, Barnes *et al.* 1972). The temperature of serpentinization ranges from 30-300°C (Neal & Stanger 1983, Sherwood Lollar *et al.* 1993), probably reflecting the different phases of serpentinization. Laboratory experiments have produced initially hydrogen and subsequently hydrocarbon gases from mixtures of olivine and saltwater (or freshwater) at high temperatures and pressures (Berndt *et al.* 1996).

Fluids rising from below, from deep parts of subduction zones, are probably responsible for serpentinization of the overlying mantle wedge and for causing serpentinite diapirism in forearcs. This will occur from depths of many kilometres up to the seabed (Ishii 1989).

#### *Effects of serpentinization on the physical properties of the rocks*

Mantle rocks normally occur at depths of at least 10 km beneath the oceans (Coleman 1977) and 30 km beneath continental crust (O'Reilly *et al.* 1996). Unaltered mantle rocks have densities of about 3.3 Mg m<sup>-3</sup> and P-wave velocities of 7.8-8.1 km s<sup>-1</sup>, whereas 100% altered serpentinites have densities as low as 2.5 Mg m<sup>-3</sup> and P-wave velocities of about 5 km s<sup>-1</sup> (Fig. 5; Kern & Tubia 1993). This low density, amid generally higher rock densities, makes serpentinites vulnerable to diapirism. Some serpentinites have subsequently experienced metamorphism e.g. the Malenco peridotite of northern Italian Alps, where fluid inclusions revealed that highly reducing fluids containing hydrogen were formed during metamorphism (Peretti *et al.* 1992).

Prospectivity of ophiolitic ultramafic rocks

Gas shows have been observed in many ophiolitic ultramafic rocks (Neal & Stanger 1983, Lyon *et al.* 1990, Abrajano *et al.* 1988). However, hydrogen is not always the main gas present; methane, nitrogen and helium contents are often high but the former two can have biogenic origins and the latter is not necessarily of mantle origin. Where serpentinization is occurring hydrogen content probably depends on whether it has been biogenically consumed after generation. Methane content depends on methanogenic production or subsequent Fischer-Tropsch reactions.

It is important to establish the abiogenic or biogenic origin of the methane, especially if this is the only gas present. Hydrogen abundance versus methane  $\delta^{13}\text{C}_{\text{CH}_4}$  (Fig. 6) helps to discriminate between various origins of methane.  $\delta^{13}\text{C}_{\text{CH}_4}$  (-20 to -55‰) defines most of the world's thermogenic gasfields but the methane from metal mines in basement rocks also occupies this part of the field, although its origin is probably abiogenic (Sherwood Lollar *et al.* 1993).

#### *Potential volumes of hydrogen*

Hydrogen reservoirs of a significant size require generation from a large volume of serpentinite, a cap rock or similar trapping mechanism and a relatively recent date of generation which affords less opportunity for hydrogen loss.

The potential volume of hydrogen produced by the serpentinization process is a function of the amount of olivine and pyroxene altered to serpentine. 10% of the volume of olivine serpentinized is the value normally used (Smith 2002). The Semail ophiolite, the largest in the world, has exposed limits of 500 km x 50 km x 5 km thick, comprising perhaps 50% ultramafic rocks and therefore a volume of ultramafic rocks of circa 62,500 cubic kilometres. If 50% has been serpentinized, around 3,125 cubic kilometres of hydrogen have been produced ( $109 \times 10^{12}$  cubic feet). This figure is 5 times the annual US domestic natural gas production (Howell 1993). A similar calculation for the peridotite rocks outcropping in the Lizard Ophiolite produces 1.73 bcm of gas (Smith 2002). These figures do not include a contribution from rocks forming the subsurface beneath Permo-Triassic strata offshore of the Lizard Peninsula and north of the Semail Ophiolite in the Gulf of Oman, where of course, we do not

know the state of freshness of olivines or the degree of serpentinization. Thayer (1966) also estimated a contribution of hydrogen from pyroxene at volumes of 5% of the total pyroxene serpentinized.

Large bodies of fresh ultramafic rocks near the surface have considerable hydrogen-forming capacity but probably have little potential, as the rates of reaction are very slow due to the low temperature, and hydrogen is likely to leak away rather than be trapped. Large serpentinite bodies near the surface also have little potential as the hydrogen-forming capacity has been used. Exposed ophiolite complexes appear to be a less likely prospect. Ophiolites are emplaced over shelf sequences and are generally found at the top of the nappe pile. Subsurface ophiolites have more potential. Many ophiolites crop out near coasts, some of which are fault-bounded. Post-orogenic faulting and basin formation may lead to burial by a combination of permeable and impermeable rocks (as in hydrocarbon basins). The early-deposited rocks in a basin are often coarse clastics (breccias and conglomerates) and later basin dewatering may allow penetration of fluids into the basement and any produced hydrogen to be trapped by later, overlying impermeable rocks of the subsequent thermal relaxation basin. Overlying sediments of Tethyan ophiolites are carbonates, clastic sediments or thin oceanic sediments. In the Mediterranean subsurface Messinian salt (Miocene) also probably overlies ophiolites.

#### *Flow rates*

Generally low flows emanate from hydrogen seeps, where quantified. Many of these seeps may be long lasting but the evidence is not conclusive. Hydrogen flowed from the Molodezhnaya chromite mine, Kempirsay pluton in the Urals, Russia at a rate of 17.6 cfd, which lasted for three years. Seepage from the entire mine was calculated to be 700 cfd (Devirts *et al.* 1993). At B'lad and Nizwa, in Oman, flows of 10 litres per second were recorded (Neal & Stanger 1983; 36630 cfd each). Gas flows in Kola mines, from alkaline rocks, have lasted up to 6 years but flows are as low as 4.8 litres/day (less than 1 cfd). Initial emission of short-lasting flows reached 13 cfd (Nivin *et al.* 2001).

#### *Reservoirs*

## Nigel Smith

Most of the natural gas seepage is emerging from the ultramafic rocks in the Alpine fold belt (Smith 2002) and the physical properties suggest that it could form a reservoir. In Oman the gas emerges from the contact between ultramafic rocks and overlying mafic rocks comprising the crustal, upper part of the ophiolite sequence (Neal & Stanger 1983). Serpentinized peridotite, serpentinized lherzolite, dunite and peridotite rocks all have very low porosities (0.1-0.8%). Serpentinite is generally more porous (up to 14.5%, Stesky & Brace 1973) and a competent reservoir for about 80 oilfields in the coastal plain of Texas and virtually all of Cuba's fields.

In UK areas Permo-Triassic sandstones overlie both the Lizard and Unst ultramafic rocks. Both Permian (Rotliegend) and Triassic sandstones are good hydrocarbon reservoirs in other parts of the UK.

### *Potential of UK ophiolites*

UK ophiolites are Palaeozoic in age, which suggests that they should be less prospective than the Alpine ophiolites. Only the Lizard and Midland Valley-S Uplands areas are discussed here.

#### Lizard Peninsula, Cornwall, England

This 20 square mile outcrop is part of the Variscan-emplaced ophiolite, lying within the Variscan fold belt. Emplacement was from the south onto a Devonian basin. Recent dating has suggested a more lengthy history between the age of basement rocks and the emplacement of the ophiolite (Cambrian to Devonian, Styles *et al.* 2000). Attempts have been made to trace these rocks into the subsurface (Busby & Smith 2001). Lefort (1973) also modelled magnetic anomalies farther south and attributed them to older ophiolites. In view of the older dates of some Lizard rocks the southern anomalies may be connected at depth. There are no reported shows of gas or significant high pH springs.

#### Midland Valley-S Uplands, Scotland

## Nigel Smith

In the SW of the Midland Valley of Scotland, south of Girvan, serpentinized ultramafics named the Ballantrae Complex (early Palaeozoic in age) occur and are limited southeastwards by the Southern Upland Fault (Stone & Smellie 1988). Ultramafic rocks, also interpreted as an ophiolite, occur within the Highland Boundary Fault Zone on the NW margin of the Midland Valley (Ikin & Harmon 1984). Serpentinities are dominant here and some have been metamorphosed. The age of the series is considered to include the early Arenig.

Similar ultramafic rocks may occur eastwards (to the North Sea) and westwards beneath younger rocks and Tertiary basalts as far as Ireland's west coast, along the southern margin of the Midland Valley. Because ophiolitic rocks occur both on the northern and southern faulted boundary of the Midland Valley a simple and possible model predicts similar rocks to occur in the subsurface between these localities. The gravimetric and aeromagnetic anomalies at Blairgowrie, Bathgate and Stonehaven (K. Rollin pers. comm. 2003) could therefore be interpreted as ophiolitic bodies. There are no reports of gas or high pH springs in any of these areas, indicating prospectivity value. Nevertheless subsurface rocks may have experienced a different history.

Leggett *et al.* (1983) suggested that the main remnant of younger Iapetus oceanic crust (Ordovician to Silurian age) lies between 15-45 km depth, beneath the Southern Uplands Fault. A highly conductive layer, interpreted as Iapetus suture mylonites (Beamish & Smythe 1986), which might include fluid-filled ophiolites, dips north between about 6-30 km, beneath the Solway Firth Basin and Southern Uplands (south of the Leggett *et al.* position). However, Banks *et al.* (1996) regarded the cause of the high conductivity as the presence of graphite rather than fluids.

Prospectivity of ultramafic rocks of rifts (failed arm basins and aulacogens with thin crust)

Failed arm basins are formed at extensional triple plate junctions, on the margins of the present day ocean, and usually make angles of between 90° and 120° with the continental margin. Aulacogens are long-lived, rejuvenated and reactivated rifts, which have avoided orogenesis, yet impinge at high angles on fold belts. The Rockall Trough is orientated parallel with the currently spreading Icelandic Mid Atlantic Ridge, north of the Labrador-Biscay basins (north of the Charlie Gibbs Fracture Zone).

## Nigel Smith

The Labrador-Biscay basins were undergoing rifting during mid Cretaceous times to early Tertiary times (Chalmers & Pulvertaft 2001). The configuration suggests that the trough probably formed as a failed N-S arm (orientated at right angles) when spreading was occurring along the Labrador-Biscay basins.

The Atlantic margin exhibits both volcanic and non-volcanic basins. The Rockall Trough, where the main extension was early Cretaceous, became a volcanic basin connected to the early Tertiary Thulean volcanic province, whereas similar basins south of the Charlie Gibbs Fracture Zone (CGFZ) e.g. the Galician margin are non-volcanic. However the basement of these different margins may be the same. Beneath a relatively sediment-starved cover, serpentinite has been drilled on exposed seamounts off Galicia and the Rockall Trough is also modelled with underlying serpentinite.

### *Rockall Trough*

O'Reilly *et al.* (1996) modelled a Rockall Trough crustal section with thick sediments (age: Tertiary and Cretaceous with possibly early Mesozoic and late Palaeozoic) and thick basalts (Thulean igneous province) overlying thin upper and lower crust. Neither the lower sediments nor the underlying lower crust and mantle rocks have been drilled. The lower crust overlies a mantle characterised by anomalously low velocities ( $7.5\text{-}7.8 \text{ km s}^{-1}$ ), suggesting partial serpentinization has taken place (O'Reilly *et al.* 1996, see Fig. 5).

### Conclusions

Hydrogen is produced by serpentinization and onshore surface shows (mostly outside NW Europe) may indicate that resources lie at depth, in down-dip locations. The Tethyan and Pacific fold belt ophiolites are likely to be more prospective, with their subsurface bodies the preferred initial targets; however virtually no data is available for these areas. Coupled with the environmental benefits of hydrogen, compared to carbon-rich gases, these indications should justify exploration at the best sites. Combined hydrogen-hydrocarbon tests are possible where ophiolites are thrust over sediments.

## Nigel Smith

Rift basins of various kinds have sediments or thin crust overlying probably serpentinized mantle. These prospects are very deep and extensive serpentinization may not have occurred. However more conventional clastic reservoir rocks, in the sequence above, could be targets. Test drilling could be accomplished by deepening hydrocarbon exploration wells. Alkaline intrusions, with their hydrogen shows, are tectonically associated with rift basins, aulacogens and transform boundaries. The rift and ophiolite prospects fall into an unsustainable category, if they exist, because they are fossil accumulations.

Of two tectonic regions in the oceans where serpentinization is known (mid ocean ridges and forearcs) NW Europe has only a section of the Mid Atlantic Ridge, part of which lies onshore in Iceland. The prospects in the oceans are sustainable, as they are being formed today, and capture rather than drilling is probably required.

Hydrogen is also found in other geological situations where it is unlikely to form drillable prospects. However produced hydrogen is quickly transformed to abiogenic hydrocarbons by Fischer-Tropsch-type reactions or consumed by bacteria (e.g. methanogens).

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### References

- Abrajano, T. A., Sturchio, N. C., Bohlke, J. K., Lyon, G. L., Poreda, R. J. & Stevens, C. M. 1988. Methane-hydrogen gas seeps, Zambales Ophiolite, Philippines: deep or shallow origin? *Chemical Geology*, **71**, 211-222.
- Andreeva, T. A. & Molchanov, V. I. 1978. Hydrogen and hydrocarbon gases in the composition of the gaseous inclusions in rocks. *Soviet Geology & Geophysics*, **19**, 10, 24-30.

- Apps, J. A. & van de Kamp, P. C. 1993. Energy gases of abiogenic origin in the Earth's crust. *In*: Howell, D. G. (ed.) 1993. *The future of energy gases*. U.S. Geological Survey Professional Paper, **1570**, 81-132.
- Banks, R. J., Livelybrooks, D., Jones, P. & Longstaff, R. 1996. Causes of high crustal conductivity beneath the Iapetus suture zone in Great Britain. *Geophysical Journal International*, **124**, 433-455.
- Barnes, I., Rapp, J. B., O'Neil, J. R., Sheppard, R. A. & Gude, A. J. 1972. Metamorphic assemblages and the direction of flow of metamorphic fluids in four instances of serpentinization. *Jahrbuch Mineral. And Petrol.* **35**, 263-276.
- Beamish, D. & Smythe, D. K. 1986. Geophysical images of the deep crust: the Iapetus suture. *Journal of the Geological Society, London*, **143**, 489-497.
- Berndt, M. E., Allen, D. E. & Seyfried, W. E. 1996. Reduction of CO<sub>2</sub> during serpentinization of olivine at 300 C and 500 bar. *Geology*, **24**, 351-354.
- Betehtin, A. G. 1961. Mikroskopische untersuchungen an platinernen aus dem Ural. *Neues Jahrbuch Miner. Abh.* **97**, 1-34.
- Bohdanowicz, C. 1934. Natural gas occurrences in Russia (USSR). *Bulletin of the American Association of Petroleum Geologists*, **18**, 750-760.
- Busby, J. P. & Smith, N. J. P. 2001. The nature of the Variscan basement in southeast England: evidence from integrated potential field modelling. *Geological Magazine*, **138**, 6, 669-685.
- Cann, J. R. & Morgan, J. 2002. Secrets of the Lost City. *Geoscientist*, **8**, 11, 4-5.
- Chalmers, J. A. & Pulvertaft, T. C. R. 2001. Development of the continental margins of the Labrador Sea: a review. *In*: Wilson, R. C. L., Whitmarsh, R. B., Taylor, B. & Froitzheim, N (eds) *Non-Volcanic rifting of continental margins: a comparison of evidence from land and sea*. Geological Society Special Publication, **187**, 77-105.
- Chapelle, F. H., O'Neill, K., Bradley, P. M., Methe, B. A., Clufo, S. A., Knobel, L. L. & Lovley, D. R. 2002. A hydrogen-based subsurface microbial community dominated by methanogens. *Nature*, **415**, 312-315.
- Christensen, N. 1978. Ophiolites, seismic velocities and oceanic crustal structure. *Tectonophysics*, **47**, 131-157.
- Coleman, R. G. 1977. *Ophiolites*. Springer-Verlag.

## Nigel Smith

- Dando, P. R., Hughes, J. A., Leahy, Y., Niven, S. J., Taylor, L. J. & Smith, C. 1995. Gas venting rates from submarine hydrothermal areas around the island of Milos, Hellenic Volcanic Arc. *Continental Shelf Research*, **15**, 8, 913-929.
- Davidson, C. F. 1964. The chemical history of the Earth. *In: Advancing frontiers in Geology and Geophysics*. Osmania University, Hyderabad. 191-203.
- Devirts, A. L., Gagaux, F. G., Grinenko, V. A., Lagutina, Y. P., Pereverzov, V. V. & Shukolyukov, Yu. A. 1993. Origin of hydrogen in Kempirsay intrusion ultramafites. *Geochemistry International*, **30**, 2, 139-144.
- Donval, J. P., Charlou, J. L., Douville, E., Knoery, J., Fouquet, Y., Poncevera, E., Jean Baptiste, P., Stievenard, M., German, C. & FLORES scientific party. 1997. High H<sub>2</sub> and CH<sub>4</sub> content in hydrothermal fluids from Rainbow site newly sampled at 36° 14' N on the AMAR segment, Mid Atlantic Ridge (diving FLORES cruise, July 1997). Comparison with other MAR sites. *EOS*, **78**, F832.
- Eyre, N., Fergusson, M. & Mills, R. 2002. Fuelling road transport. Implications for energy policy. Department for Transport.
- Fisher, W. L. 2002. Domestic natural gas: the coming methane economy. *Geotimes*, Nov, 20-22.
- Fitton, J. G. 1987. The Cameroon line, west Africa: a comparison between oceanic and continental alkaline volcanism. *In: Fitton, J. G. & Upton, B. G. J. (eds) Alkaline igneous rocks*. Geological Society Special Publication, **30**, 273-291.
- Fritz, P., Frape, S. K. & Miles, M. 1987. Methane in the crystalline rocks of the Canadian Shield. *In: Fritz, P. & Frape, S. K. (eds) Saline water and gases in crystalline rocks*. Geological Association of Canada Special Paper, **33**, 211-223.
- Früh-Green, G. L., Kelley, D. S., Bernasconi, S. M., Karson, J. A., Ludwig, K. A., Butterfield, D. A., Boschi, C. & Proskurowski, G. 2003. 30,000 years of hydrothermal activity at the Lost City vent field. *Science*, **301**, 495-498.
- Gerlach, T. M. 1982. Interpretation of volcanic gas data from tholeiitic and alkaline mafic lavas. *Bulletin Volcanologique*, **45**, 3, 235-244.
- Greenwell, A. 1907. *Analyses of British coals and coke*. The Chichester Press.
- Grip, E. & Odman, O. H. 1944. On thucholite and natural gas from Boliden. *Sveriges Geologiska Undersökning*, **38**, 6, 3-15.

## Nigel Smith

- Hahn-Weinheimer, P. & Rost, F. 1961. Akzessorische Mineralien und elemente im Serpentin von Leopoldsgrun (Munchberger Gneismasse): ein Beitrag zur Geochemie ultrabasischer Gesteine. *Geochemica Cosmochimica Acta*, **21**, 165-181.
- Headlee, A. J. W. 1962. Hydrogen sulfide, free hydrogen are vital exploration clues. *World Oil*, Nov, 78-83.
- Heinrich, E. W. 1966. *The geology of carbonatites*. Rand McNally & Co. Chicago.
- Hempel, D. 1989. Umfang und Gestaltung des Schlagwetterschutzes im Kali- und Kupferschieferbergbau. *Zeitschifte fur Geologische Wissenschaft*, **17**, 4, 419-429.
- Hoffman, P., Dewey, J. F. & Burke, K. A. C. 1974. Aulacogens and their genetic relation to geosynclines with a Proterozoic example from Great Slave Lake, Canada. In: Dott, R. H. & Shaver, R. H. (eds) *Modern and ancient geosynclinal sedimentation*. Society of Economic Palaeontologists and Mineralogists Special Publication **19**, 38-55.
- Holloway, J. R. & O'Day, P. A. 2000. Production of CO<sub>2</sub> and H<sub>2</sub> by diking-earthquake events at mid ocean ridges; implications for abiotic organic synthesis and global geochemical cycling. *International Geology Review*, **42**, 8, 673-683.
- Howell, D. G. (ed.) 1993. *The future of energy gases*. U.S. Geological Survey Professional Paper, **1570**.
- Ikin, N. P. & Harmon, R. S. 1984. Tectonic history of the ophiolitic rocks of the Highland Border fracture zone, Scotland: stable isotope evidence from rock-fluid interactions during obduction. *Tectonophysics*, **106**, 31-48.
- Ishii, T. 1989. Origin of proto-ophiolites in Izu-Ogasawara-Mariana forearc and their resemblance to the Troodos ophiolite. *Abstracts of the 28<sup>th</sup> International Geological Congress*, **2**, p 99.
- Kern, H. & Tubia, J. M. 1993. Pressure and temperature dependence of P- and S-wave velocities, seismic anisotropy and density of sheared rocks from the Sierra Alpujata massif (Ronda peridotites, southern Spain). *Earth & Planetary Science Letters*, **119**, 191-205.
- Knabe, H-J. 1989. Zur analytischen Bestimmung und geochemischen Verteilung der gesteinsgebundenen Gase im Salinar. *Zeitschrift für Geologische Wissenschaft*, **17**, 4, 353-368.
- Kogarko, L. N. 1987. Alkaline rocks of the eastern part of the Baltic Shield (Kola Peninsula). In: Fitton, J. G. & Upton, B. G. J. (eds) *Alkaline igneous rocks*. Geological Society Special Publication, **30**, 531-544.

- Lefort, J. P. 1977. Possible 'Caledonian' subduction under the Domnanean domain, north Armorican area. *Geology*, **5**, 523-526.
- Leggett, J. K., McKerrow, W. S. & Soper, N. J. 1983. A model for the crustal evolution of Southern Scotland. *Tectonics*, **2**, 2, 187-210.
- Levinson, A. A. 1977. Hydrogen- a reducing agent in some uranium deposits. *Canadian Journal of Earth Science*, **14**, 2679-2681.
- Levshounova, S. P. 1983. Solid solutions of hydrogen in sedimentary rocks. *Doklady Academy of Science, USSR Earth Science section*, **272**, 73-75.
- Levshounova, S. P. 1991. Hydrogen in petroleum geochemistry. *Terra Nova*, **3**, 579-585.
- Lidin, G. D., Matviyenko, N. G., Zimakov, B. M., Gagauz, F. G., Vardoiani, E. Yu. & Pereverzov, V. V. 1982. New data on natural hydrogen gas emanation from ultramafic rocks. *Academy of Science, USSR Earth Science section*, **264**, 204-207.
- Lokhurst, A. (ed) 1998. *The Northwest European Gas Atlas. - Composition and Isotope Ratios of Natural Gases in Northwest European Gasfields*. NITG-TNO, Haarlem. (CD ROM).
- Lyon, G., Giggenbach, W. F. & Lupton, J. F. 1990. Composition and origin of the hydrogen-rich gas seep, Fiordland, New Zealand. *EOS*, V51D-10.
- Macdonald, A. H. & Fyfe, W. S. 1985. Rate of serpentinization in seafloor environments. *Tectonophysics*, **116**, 123-135.
- Mamyrin, B. A. & Tolstikhin, I. N. 1984. *Helium isotopes in nature*. Developments in Geochemistry. Elsevier.
- Marty, B., Gunnlaugsson, E., Jambon, A., Oskarsson, N., Ozima, M., Pineau, F. & Torssander, P. 1991. Gas geochemistry of geothermal fluids, the Hengill area, southwest rift zone of Iceland. *Chemical Geology*, **91**, 207-225.
- Minissale, A., Evans, W. C., Magro, G. & Vaselli, O. 1997. Multiple source components in gas manifestations from north-central Italy. *Chemical Geology*, **142**, 175-192.
- Molchanov, V. I. 1981. *Hydrogen generation in lithogenesis*. Nauka Press, Novosibirsk (In Russian).
- Neal, C. & Stanger, G. 1983. Hydrogen generation from mantle source rocks in Oman. *Earth and Planetary Science Letters*, **66**, 315-320.
- Nesmelova, Z. N. & Travnikova, L. G. 1973. Radiogenic gases in ancient salt deposits. *Geochemistry International*, **10**, 554-559.

- Nivin, V. A., Belov, N. I., Treloar, P. J. & Timofeyev, V. V. 2001. Relationship between gas geochemistry and release rates and the geomechanical state of igneous rock massifs. *Tectonophysics*, **336**, 1-4, 233-244.
- O'Reilly, B. M., Hauser, F., Jacob, A. W. B. & Shannon, P. M. 1996. The lithosphere below the Rockall Trough: wide-angle seismic evidence for extensive serpentinization. *Tectonophysics*, **255**, 1-23.
- Palmer, M. R., Ludford, E. M., German, C. R. & Lilley, M. D. 1995. Dissolved methane and hydrogen in the Steinaholl hydrothermal plume, 63°N, Reykjanes Ridge. In: Parson, L. M., Walker, C. & Dixon, D. (eds) *Hydrothermal vents and processes*. Geological Society Special Publication, **87**, 111-120.
- Peretti, A., Dubessy, J., Mullis, J., Frost, B. R. & Trommsdorff, V. 1992. Highly reducing conditions during Alpine metamorphism of the Malenco peridotite (Sondrio, northern Italy) indicated by mineral paragenesis and H<sub>2</sub> in fluid inclusions. *Contributions to Mineralogy and Petrology*, **112**, 329-340.
- Potter, J. & Konnerup-Madsen, J. 2003. A review of the occurrence and origin of abiogenic hydrocarbons in igneous rocks. In: Petford, N & McCaffrey, K. J. W. (eds) *Hydrocarbons in Crystalline Rocks*. Geological Society London Special Publications, **214**, 151-173.
- Ramdohr, P. 1967. A widespread mineral association connected with serpentinization. *Neues Jahrbuch für Mineralogische Abhandlung*, **107**, 241-265.
- Rogers, G. S. 1921. Helium-bearing natural gas. *US Geological Survey Professional Paper*, **121**.
- Salvi, S. & Williams-Jones, A. E. 1997. Fischer-Tropsch synthesis of hydrocarbons during sub-solidus alteration of the Strange Lake peralkaline granite, Quebec-Labrador, Canada. *Geochimica et Cosmochimica Acta*, **61**, 1, 83-99.
- Sato, M., Sutton, A. J. & McGee, K. A. 1985. Anomalous hydrogen emissions from the San Andreas Fault observed at the Cienega Winery, central California. *Pure and Applied Geophysics*, **122**, 376-391.
- Sherwood, B., Fritz, P., Frapé, S. K., Macko, S. A., Weise, S. M. & Welhan, J. A. 1988. Methane occurrences in the Canadian Shield. *Chemical Geology*, **71**, 223-236.
- Sherwood Lollar, B., Frapé, S. K., Weise, S. M., Fritz, P., Macko, S. A. & Welhan, J. A. 1993. Abiogenic methanogenesis in crystalline rocks. *Geochimica et Cosmochimica Acta*, **57**, 5087-5097.
- Smith, N. J. P. 2002. It's time for explorationists to take hydrogen more seriously. *First Break*, **20**, 246-253.

- Stesky, R. M. & Brace, W. F. 1973. Electrical conductivity of serpentized rocks to 6 kilobars. *Journal of Geophysical Research*, **78**, 32, 7614-7621.
- Stone, P. & Smellie, J. L. 1988. The Ballantrae area. Description of the solid geology of 1:25000 sheets NX08, 18 and 19. *Classical areas of British Geology*, British Geological Survey.
- Styles, M. T., Cook, C. A. & Holdsworth, R. E. 2000. The geology of the Lizard Complex; 100 years of progress. *Proceedings of the Ussher Society*, **10**, 92-98.
- Thayer, T. P. 1966. Serpentinization considered as a constant volume metasomatic process. *The American Mineralogist*, **51**, 685-710.
- Vovk, I. F. 1987. Radiolytic salt enrichment and brines in the crystalline basement of the East European Platform. In: Fritz, P. & Frappe, S. K. (eds) *Saline water and gases in crystalline rocks*. Geological Association of Canada Special Paper, **33**, 197-210.
- Walther, J. & Althaus, E. 1993. Graphite deposition in tectonically mobilized fault planes of the KTB pilot drill hole. *KTB Report*, **93-2**, 493-498.
- Welhan, J. A. & Craig, H. 1979. Methane and hydrogen in East Pacific Rise hydrothermal fluids. *Geophysical Research Letters*, **6**, 11, 829-831.
- Zinger, A. S. 1962. Molecular hydrogen in gas dissolved in waters of oil-gas fields, Lower Volga region. *Geochemistry*, **10**, 1015-1023.
- Zonenshain, L. P. & Le Pichon, X. 1986. Deep basins of the Black Sea and Caspian Sea as remnants of Mesozoic back-arc basins. *Tectonophysics*, **123**, 181-211.

Figure captions

- Fig. 1A.** Conventional gas composition (Leman Gasfield, Southern North Sea, Rotliegend reservoir) typical of NW European Carboniferous source and hydrocarbon basin gas (data from Lokhurst 1998),
- 1B** Conventional clastic reservoir (Miocene Sarmatian of Stavropol, Russia) but with elevated hydrogen content (Bohdanowicz 1934),
- Fig. 2.** Loss of hydrogen accompanying bituminous coalification (data from Greenwell 1907). The coalification scale, representing (hydrocarbon) source rock maturity could be vitrinite reflectance values of less than 0.2% for wood and above 2.5% for anthracites. The dashed line is the probable

cannel coalification trend which shows that cannel coals probably have higher hydrogen contents at any given degree of coalification. The solid line represents the loss of hydrogen in bituminous coals.

**Fig. 3.** Hydrogen content of different rock types.

Serpentinite and magnetite-bearing mudstones (mdst) have the highest yields of hydrogen per unit mass of rock. Hydrogen is the dominant gas extracted from magnetite-bearing rocks. Leopoldsgrun data derive from the Munchberger Gneismasse, Germany (Hahn-Weinheimer & Rost 1961). MORB data derive from the Mid Atlantic Ridge basalts (Pineau *et al.* 1976). Tatar borehole data, Russia derive from Vovk (1987). Sopolyakskaya borehole data derive from Levshounova (1983). The magnetite content of this sample was 4.5%. Higher amounts of magnetite gave even higher yields of hydrogen. Various Russian rocks derive from Andreeva & Molchanov (1978) and show that Precambrian rocks, volcanic rocks and granites yield low values of hydrogen. Magnetite-bearing oolitic limestones from Krasnoyarsk also gave relatively high yields.

**Fig. 4** Hydrogen-bearing gas from alkaline and ultramafic igneous rocks

**A** Foyaite reservoir (Lovozero Alkaline Massif, Kola, Russia): a representative gas composition with methane and relatively high hydrogen content (analysis 24 of table 2 in Potter & Konnerup-Madsen 2003). **B** Dunite reservoir (Nishna-Tagil'sk, Urals, Russia). At 600m depth in a borehole gas containing elevated hydrogen and nitrogen was found (Bohdanowicz 1934).

**Fig. 5.** Decrease in velocity and density with serpentinization.

100% serpentinization produces a rock which has a density as low as  $2.5 \text{ Mg m}^{-3}$  and a velocity of about  $4.8 \text{ km s}^{-1}$ . These are very low values for basement-type rocks, which facilitates diapirism and leads to an increase in porosity (Stesky & Brace 1973). This transforms an unpromising mantle rock into one with possible reservoir characteristics. The Ronda, Spain values are from Kern & Tubia (1993) and the west USA values from Christensen (1978).

**Fig. 6.** Contrast between  $\delta^{13} \text{C}_{\text{CH}_4}$  in hydrocarbon gases and in hydrogen-bearing gases (modified after Smith 2002).

Abiogenic gas field possibly extends to about -20‰ (heavy line) and includes Zambales gas seep (Abrajano *et al.* 1988), gas from East Pacific Rise at 21° N (Welhan & Craig 1979) and Tatar borehole gas (Vovk 1987). Thermogenic gas is dominated by high methane and very low hydrogen typical of hydrocarbon gasfields (e.g. Southern North Sea fields, Groningen and Kinsale, Lokurst 1998) extends to -55‰ (heavy line). However, gases from representative crystalline basement mines in Canada and

Nigel Smith

Finland (Sudbury and Juuka; Sherwood Lollar *et al.* 1993) have similar values to hydrocarbon gases.

Biogenic gases (not shown) are also present in these mines. Sherwood Lollar *et al.* (1993) preferred an abiogenic origin for the hydrogen-bearing gases in the mines.

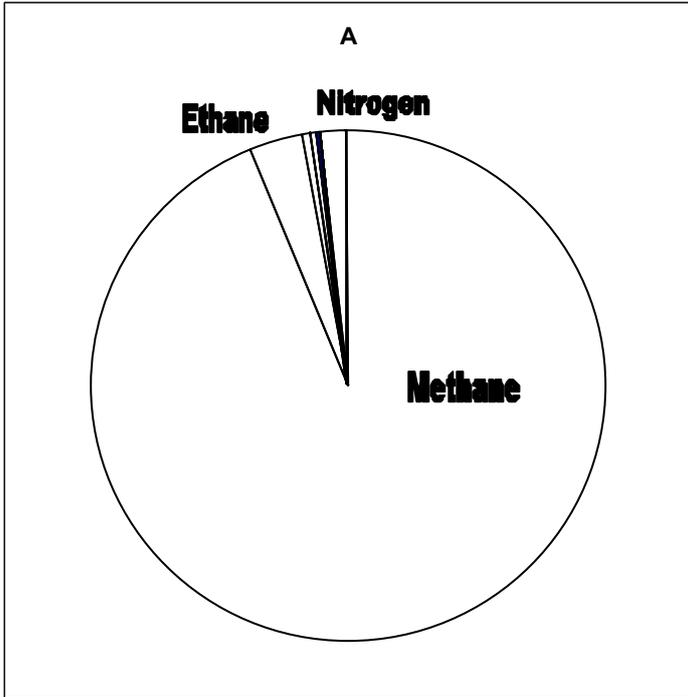


Fig 1A Lemans

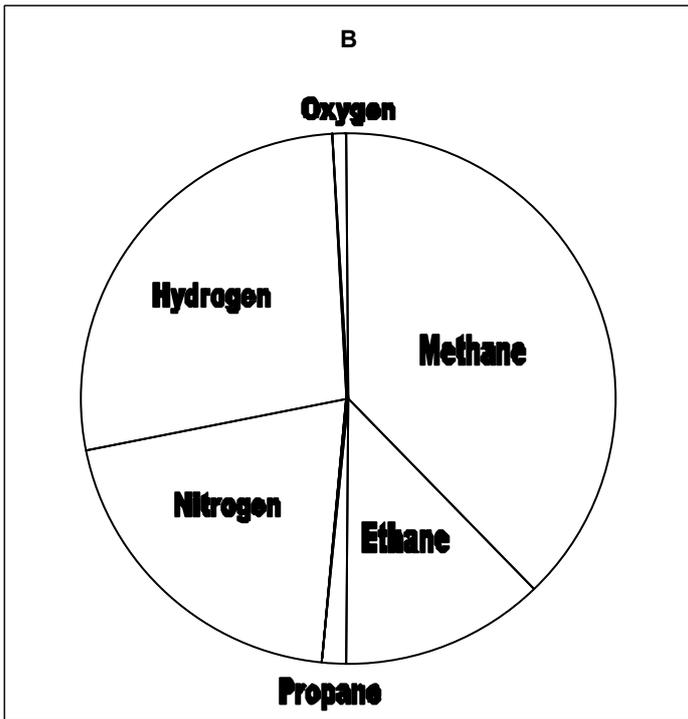


Fig 1B Stavropol

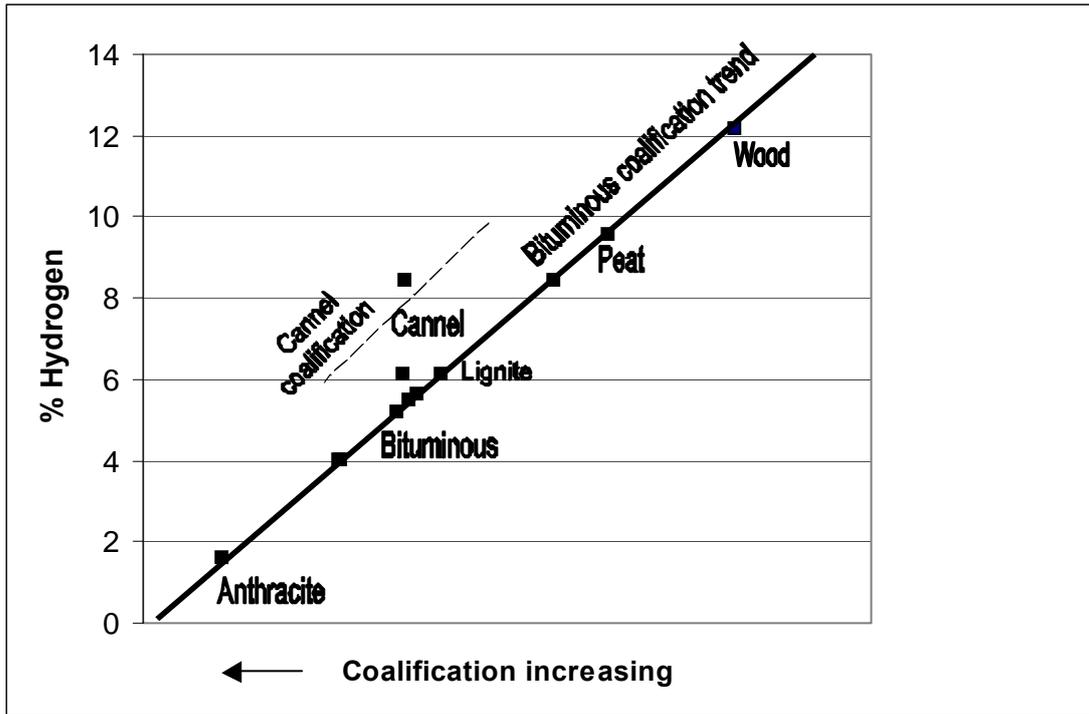


Fig 2 h2 and coals

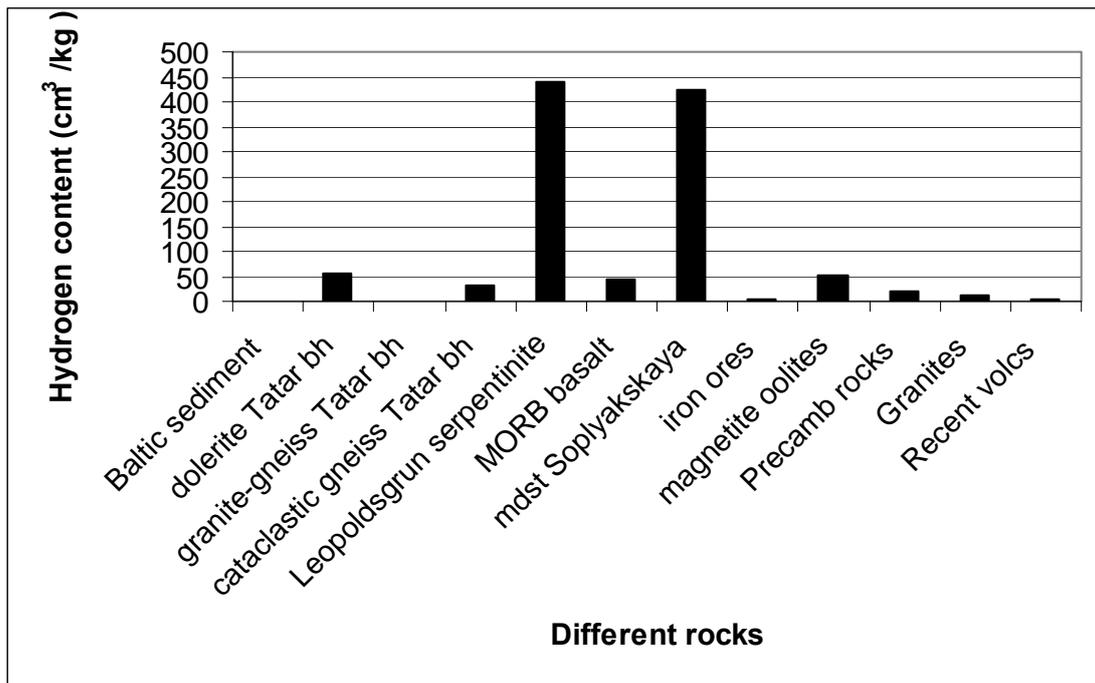


Fig. 3 h2 and rocks

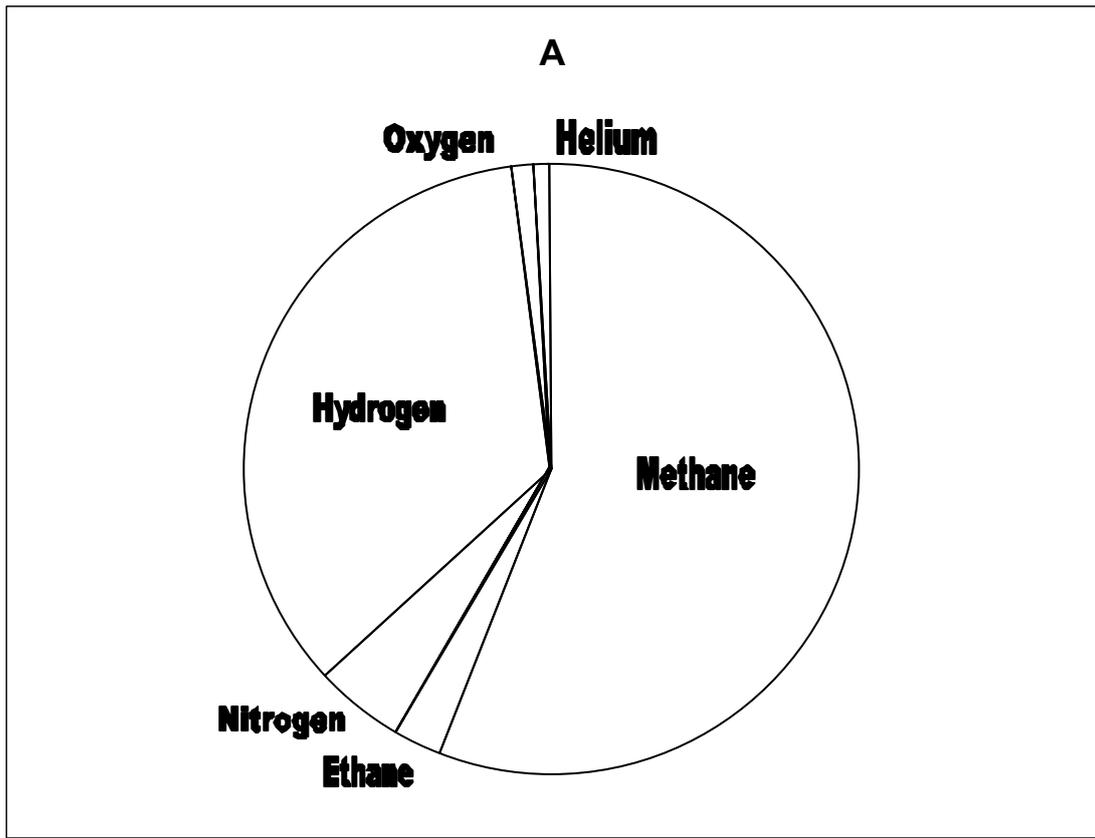


Fig. 4A Lovozero

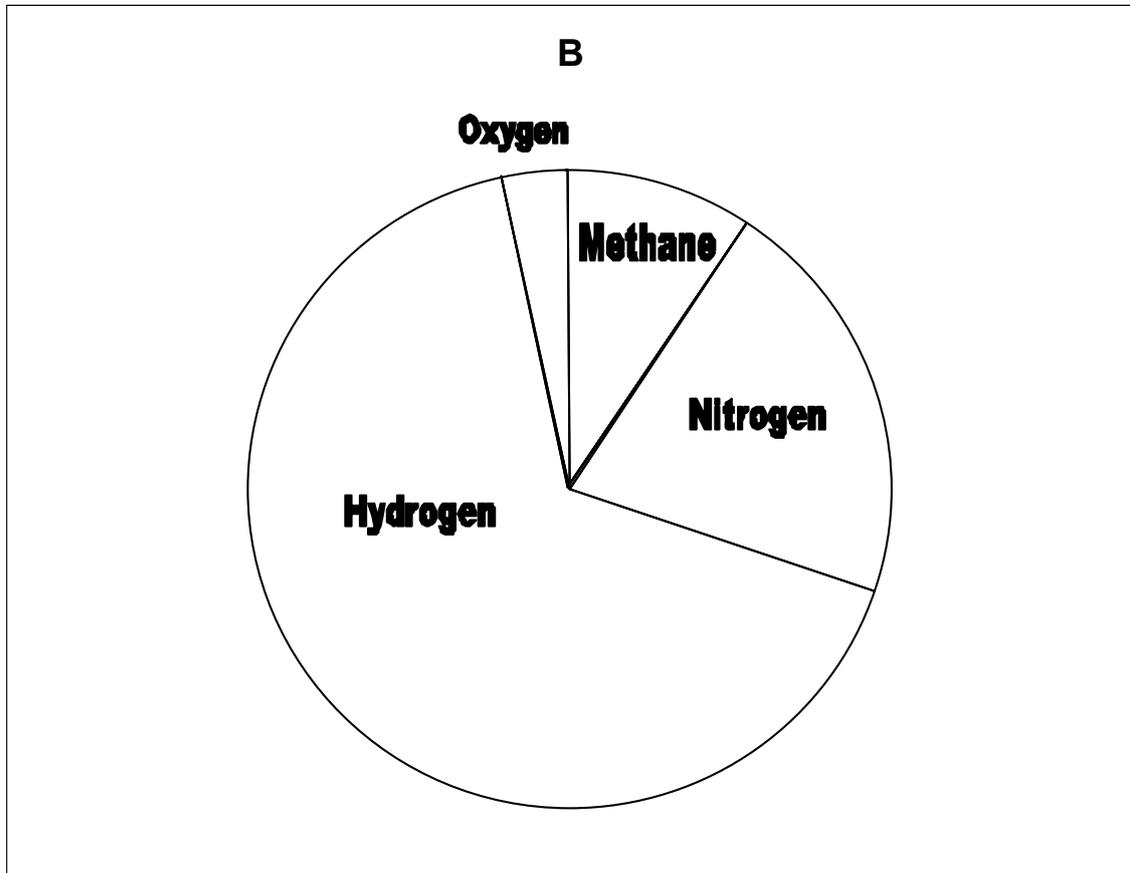


Fig. 4B Nishna

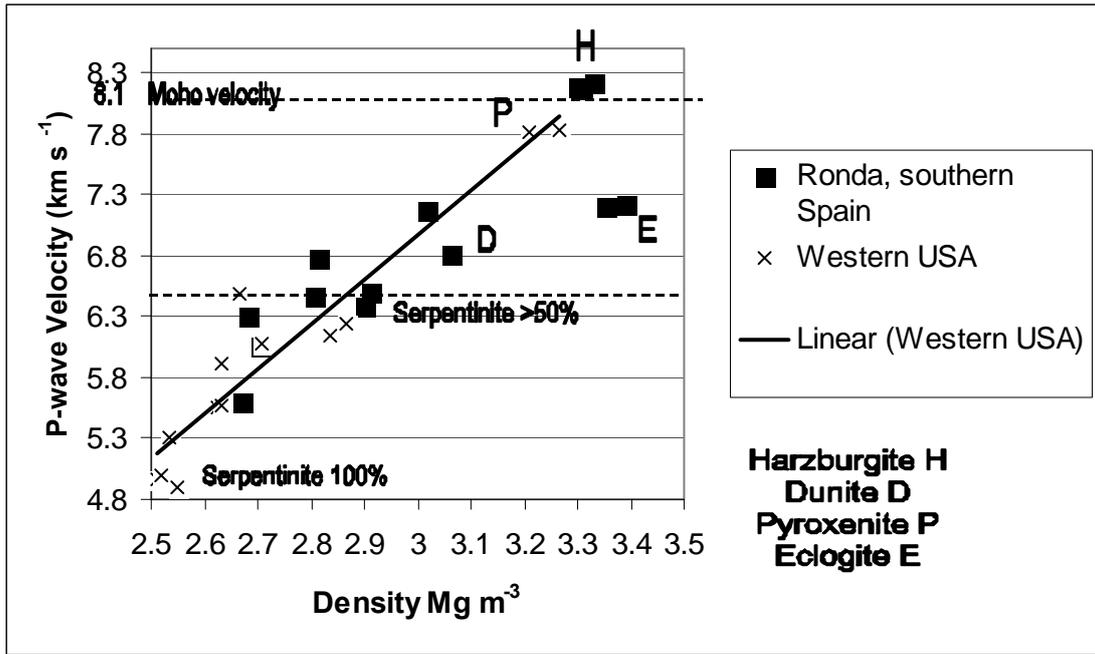


Fig. 5 Density-vel serps

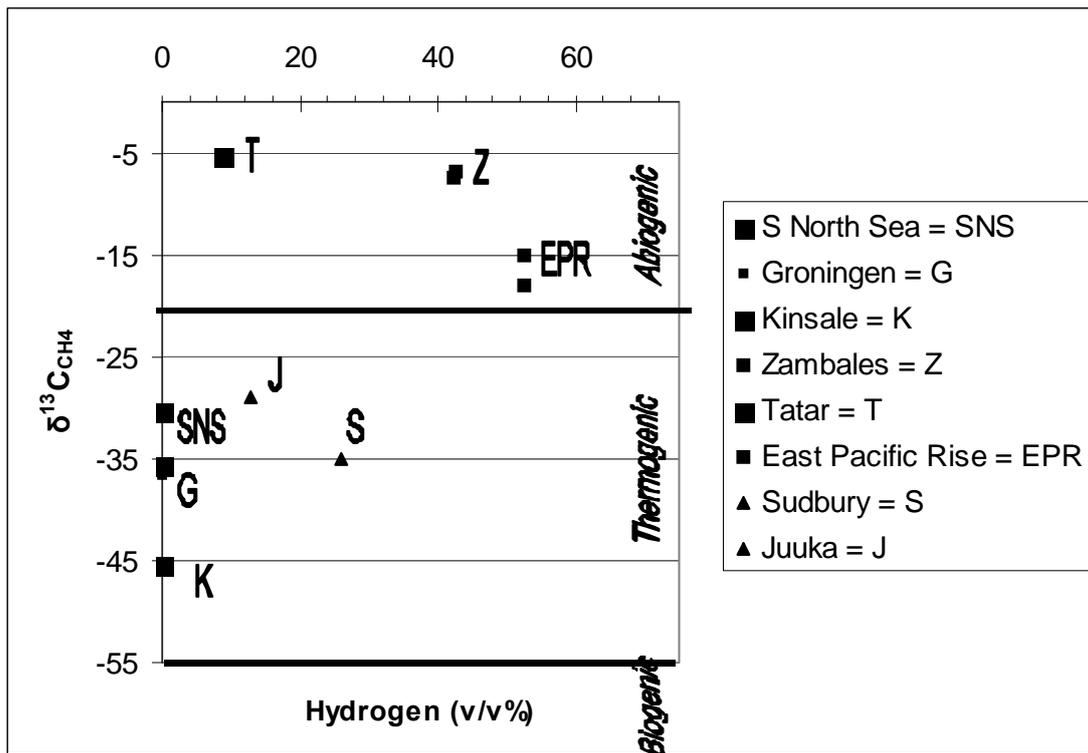


Fig. 6 carbon isotope of CH<sub>4</sub>