Natural hydrogen in the Monzon-1 well, Ebro basin, northern Spain

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Introduction

Sixty years ago, Spain was amid an energy crisis. Totally reliant upon imported oil and with limited in-country alternatives an aggressive campaign of hydrocarbon exploration drilling was initiated throughout the country. Between 1954 and 1964 the finances of its national oil company were bolstered; state of the art drilling equipment was purchased and together with several international partners multiple wells were drilled. One of the prospective areas chosen for exploration drilling was the Ebro Basin and the associated South Pyrenean foothills located in the northern part of the province of Aragón. It was here on March 7th, 1963, that Empresa Nacional de Petróleos de Aragón ("ENPASA") spudded the Monzón-1 exploration well. The well drilled to a total depth ("TD") of 3715 metres below ground level ("mBGL") and encountered shows of methane in fractured Infra-Liassic carbonates which upon drill-stem testing failed to flow at commercial rates. Consequently, the well was plugged and abandoned as an exploration dry hole. Importantly, the well also encountered shows of hydrogen at two levels. The deeper of the two, within the Triassic Bunter Sandstones, was significant enough to be specifically highlighted in the final well report. In 1963 hydrogen was of no interest but fast forward to today and this "dry hole" in Aragón could be a key component in the largest energy transition the world has ever seen.

Location, geological and structural setting

The Monzón-1 well was drilled just a few kilometres southeast of the town of Monzón in Huesca province, Aragón, Spain (Fig. 1). Geologically, it is located at the juxtaposition of the Southern Pyrenean Thrust Belt and the Ebro Basin, to the south of the Pyrenean Mountains (Fig. 1 and Munoz (1992)). It lies immediately south of a salt-cored «triangular» zone of deformation known as the Barbastro Anticline (Fig. 1). The southernmost thrust sheets of the South Pyrenean deformation belt lie a few kilometres to the northeast of the well along the northern flank of the Barbastro Anticline (Fig. 1). The well penetra-

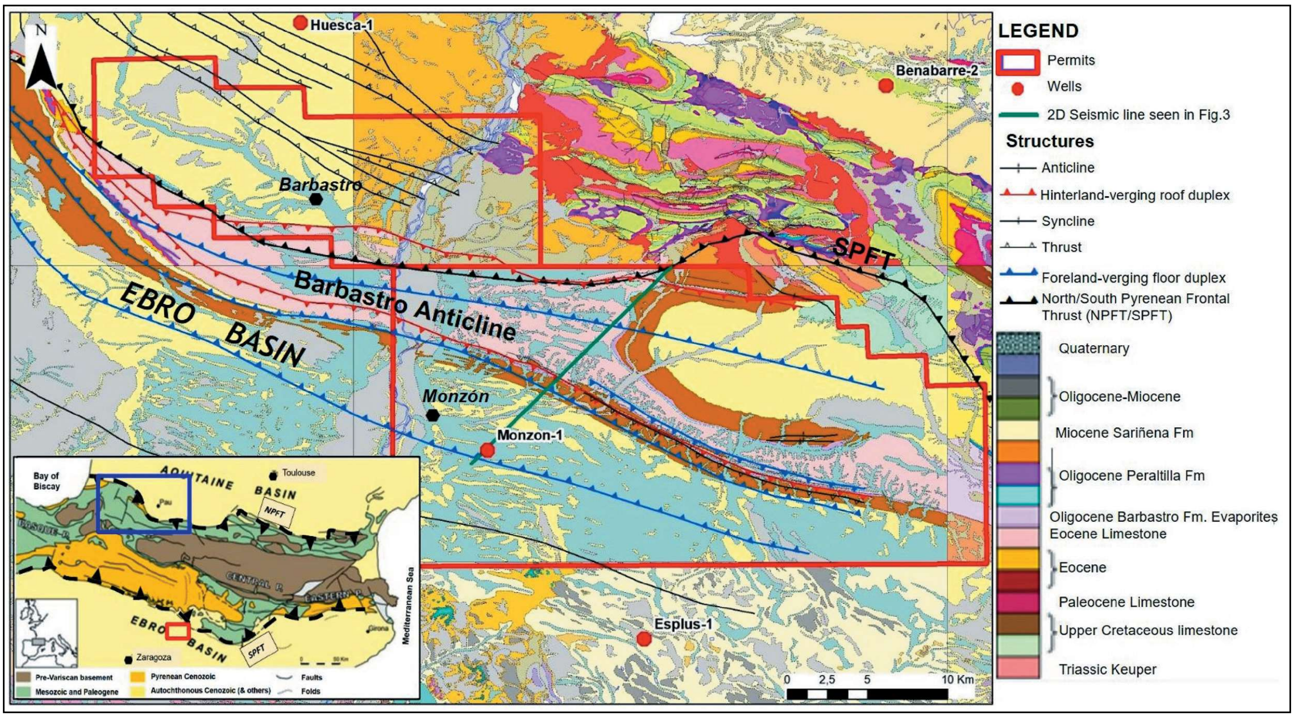

Figure 1. Location and geological setting of Helios Aragon Exploración S.L. permits (red polygon) and the Monzón-1 well. Blue box on insert figure denotes location of area of natural hydrogen emanations studied in the North Pyrenees by Lefeuvre et al., 2021.

1. Helios Aragon Pte Limited, Singapore/Helios Aragón Exploración S.L., Madrid, Spain.

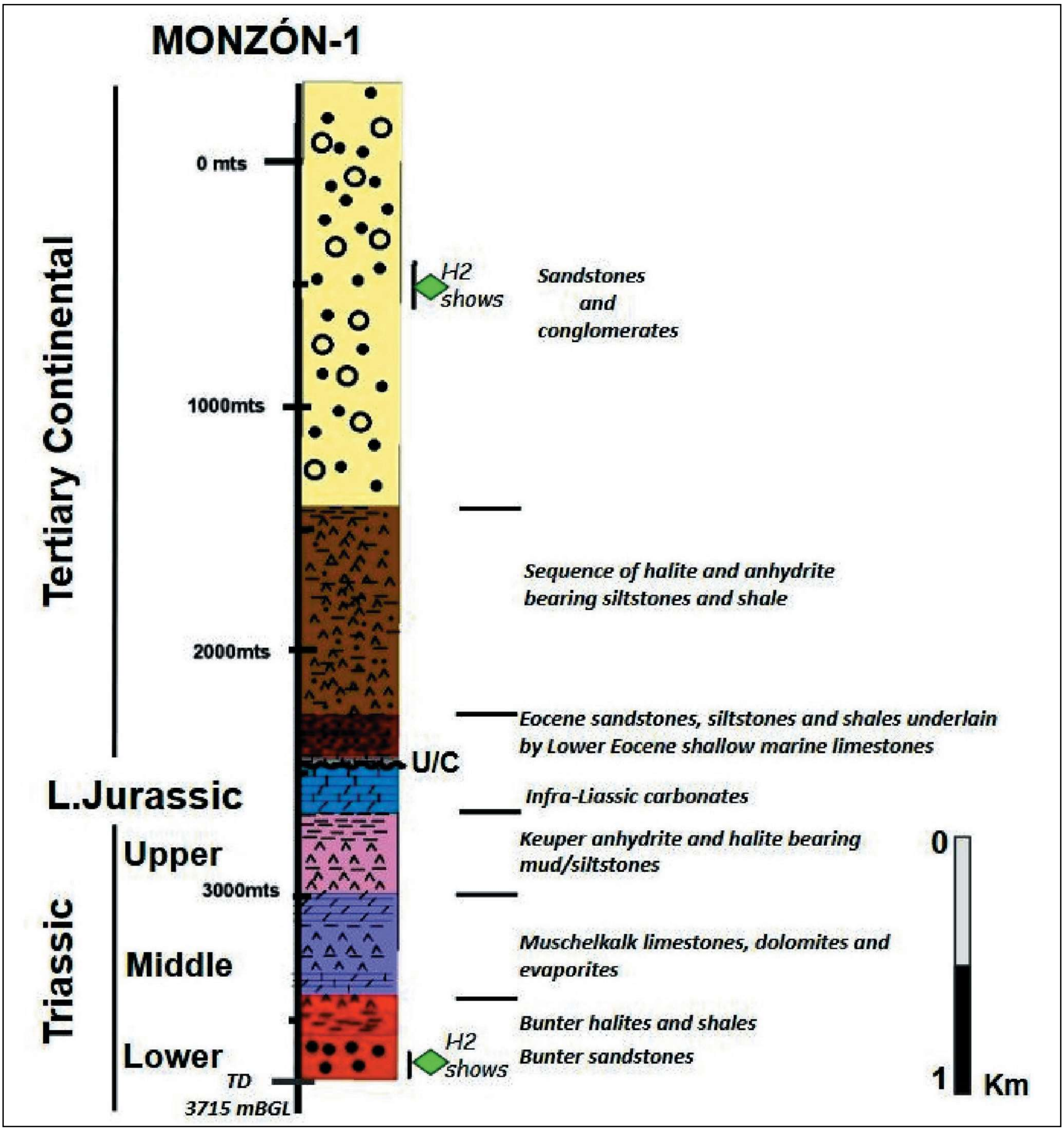

Figure 2. Summarised subsurface geology intersected by the Monzón-1 well with presence of hydrogen shows denoted by green diamonds. From XXX.

ted an autochthonous sequence of Mesozoic to Tertiary deposits resting on basement which is typical for the Ebro Basin succession in this area (Fig. 2).

The Monzón-1 is drilled on a large basement-cored anticline and was defined using 2D seismic and gravity data interpretation at the northern limit of the Ebro basin (Fig.1). The well drilled through a very thick post-orogenic sequence of sandstones and conglomerates (molasse) down to 1402 mBGL, below which a thick interbedded sequence of halite, anhydrite siltstone and shale of Oligo-Miocene age was encountered (Fig. 2). A relatively thin, condensed interval of continental Eocene sandstones, siltstones and shales (the "Red Marls" or "Margosa Roja") was penetrated below 2268mBGL. A highly-condensed interval of Lower Eocene shallow marine limestone was present between 2429 and 2446mBGL. The Eocene limes-

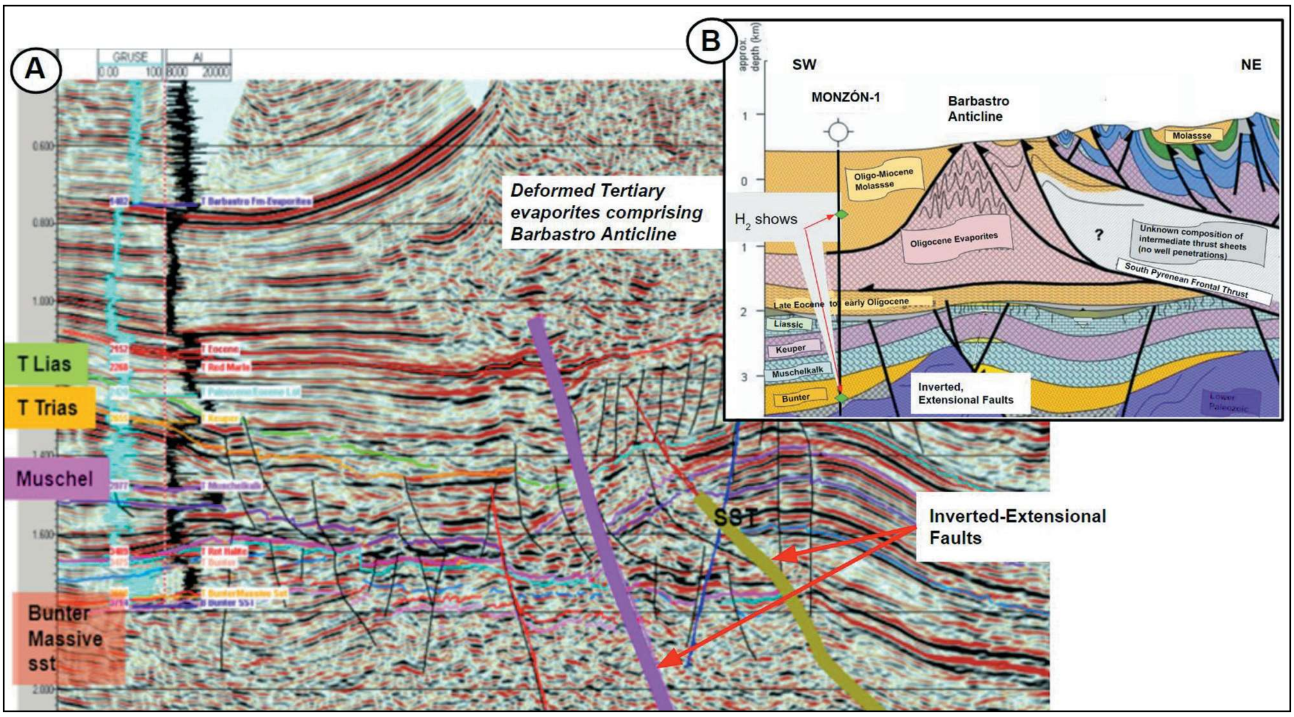

Figure 3. Subsurface structural setting of the Monzón-1 well as interpreted from the 2D seismic line shown on Fig. 1. (A) Extract from seismic line showing Monzón-1 well tie, nearby shallow Barbastro Anticline and deep-seated, basement inversion faults (purple and green). (B) Simplified representation of geological interpretation derived from the seismic data. Green diamonds indicate location of hydrogen shows seen in Monzón-1 well. Figure 3B re-drawn from Prichard (2011).

tone rests unconformably upon Lower Jurassic (Infra-Liassic) carbonates. The entire Middle Jurassic to Palaeocene section was missing due to non-deposition and/or erosion along this unconformity. Below 2655mBGL, the well passed into Triassic strata, with Upper Triassic ("Keuper") anhydritic and halitic mudstones present from 2655 to 2977mBGL, Middle Triassic ("Muschelkalk") limestones, dolomites and evaporites between 2977 and 3415mBGL, and Lower Triassic ("Bunter") halites/anhydrites, shales and porous sandstones below 3415mBGL (Fig. 2). The well TD is at 3715mBGL within Bunter Sandstone conglomerates although the well to seismic tie confirms pre-Mesozoic basement is just a few tens of metres below that depth.

Figure 3 illustrates the location of the well on a modern reprocessed? vintage northeast-southwest oriented 2D seismic line. Note the presence below the Barbastro Anticline of a major, deep-seated basement inversion fault system which bounds the Monzón structure to the north.

Hydrogen in Monzón-1 well

The post well geological and drilling reports of ENPASA reveal shows of "pure" hydrogen were recorded at two levels in the Monzón-1 well (ENPASA, 1963 and Fig. 4). The first is a modest 0.4-1.2% Total Gas (TG) show encountered between 400-600mBGL within coarse sandstones and microconglomerates of Tertiary age. The second, and much more significant, is a 25% TG show encountered between 3683-3714.6mBGL within the Triassic Bunter Sandstones (Fig. 4). This significant gas show is even more surprising given that ENPASA drilled the interval at significant overbalanced pressures with consequential mud loss into the formation (mud weight of 1.40 kilogram/litre equivalent to 11.63 pounds per gallon - figure 4). Unfortunately, no actual drilling mud-log or detailed mud-log reports have survived in the archive for the Monzón-1 well.

By 1963 most global exploration wells would have been drilled with some form of gas monitoring equipment which would have used a gas chromatogram equipped with either a Flame Ionisation Detector (FID) or a Thermal Conductivity Detector (TCD). In the case of an FID system ditch gas during drilling would have been carried through the chromatogram using an "inert" carrier gas. TG measured by FID is the total amount of flammable gas seen in the mud and it is usually accompanied by some form of compositional analysis. The most common carrier gases used for FID are helium or hydrogen. Helium carrier gas is not recorded by an FID. However, hydrogen carrier gas has an obvious and almost immediate FID response and this peak is therefore normally ignored or overridden by hydrocarbon gases. In 1963 most FID chromatographs would have made no separation between methane and hydrogen. Hydrogen is the carrier gas of choice as it is cheaper than helium and it can be made at the rig-site via electrolysis. Therefore, both in the TG and compositional analysis it is usually the hydrocarbon responses that are recorded, thus allowing the routine measurement of methane, ethane, etc. These are the normal components of interest in an oil and gas exploration well.

In order to record the presence of hydrogen in the Monzón-1 well, it is likely that mud gas monitoring was achieved using a TCD system. This system would have probably used helium as the carrier gas and it would have measured all of the combustible gas in the mud including hydrogen. Unfortunately, we do not know which system was used at Monzón-1 and all the well summary log denotes is that the hydrogen shows are associated with measurement via a "Prakla" device (Fig. 4). Research to date regarding what a Prakla device is has proved inconclusive. Importantly, the TCD will also measure any other gases present such as nitrogen, carbon dioxide, etc. but at the Bunter level in the Monzón well only "H_2" (hydrogen) is recorded.

Any TG show of 25% as seen in Monzón-1 is a very impressive gas show and warrants closer scrutiny. Interestingly, an analogous mud-log response to that observed in Monzón-1 and which was also interpreted as pure hydro-

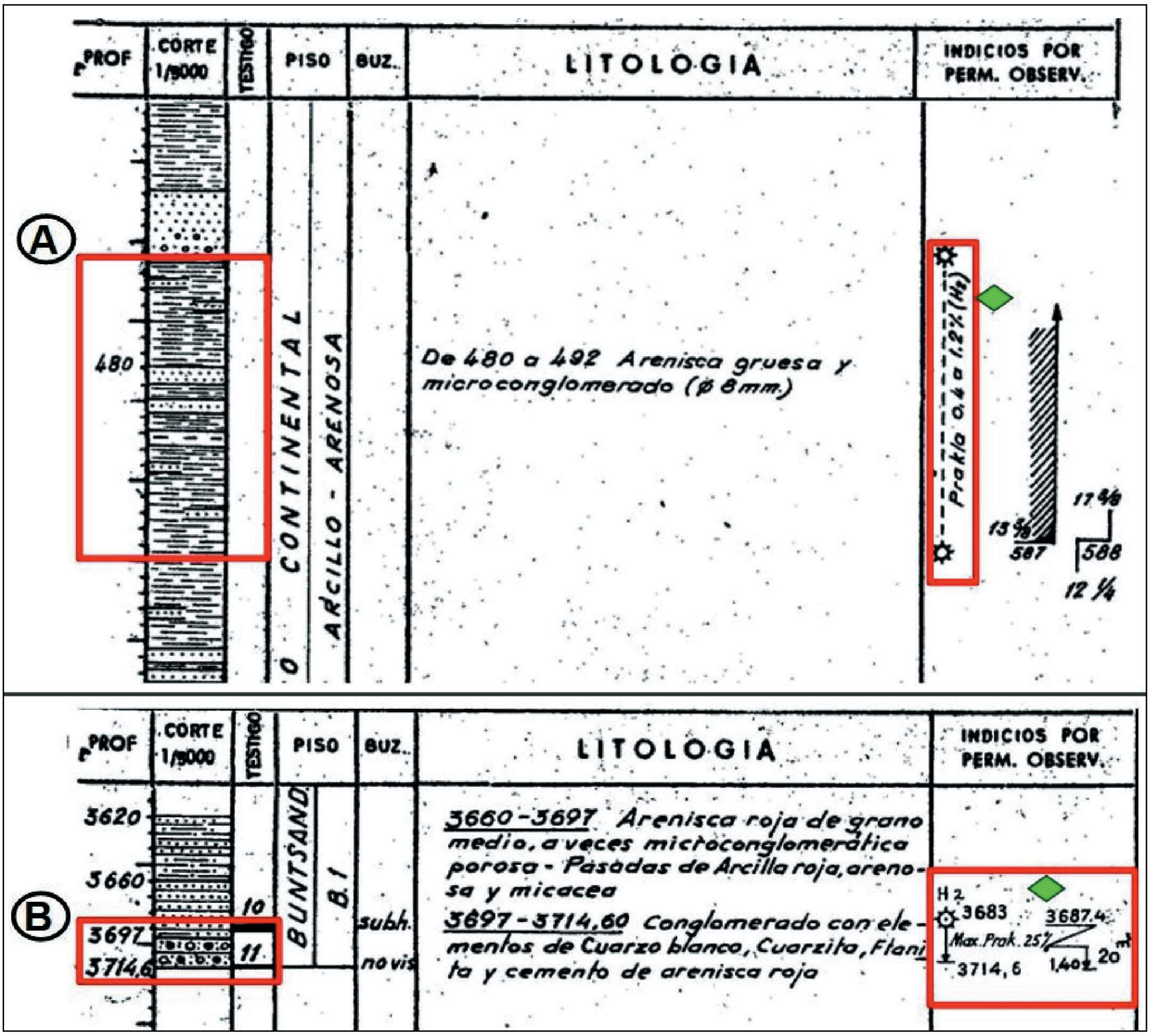

Figure 4. Detail from Monzón-1 post well summary log illustrating depth of hydrogen shows (green diamonds) recorded in the well at the Tertiary (A) and deeper Bunter Sandstone (B) levels. From ENPASA, 1963.

gen has been observed by the authors in another exploration well (Fig. 5).

This well drilled in 1980 has a detailed mud-log and was interpreted by the Exploration Logging ("EXLOG") crew as intersecting significant shows of hydrogen between 3230-3600 feet with a maximum of 200 gas units recorded at 3480 feet (Fig. 5). At this level both the Petroleum Vapour (PV) reading (gas which burns at a lower temperature) and the TG reading were the same. This evidence together with the chromatograph response strongly suggested to EXLOG that the gas being recorded was hydrogen. This was further collaborated by the blender gas which was very similar to that being recorded from the mud flow line. Both the Operator and the EXLOG crew concluded that the mud logging equipment was functioning correctly (checked frequently via carbide tests) and that the flammable gas being recorded was without doubt pure hydrogen. As was most likely the case at Monzón-1 the presence of hydrogen in the mud caused controversy at the well site and EXLOG provided the following commentary with regards the effect of hydrogen on gas detectors:

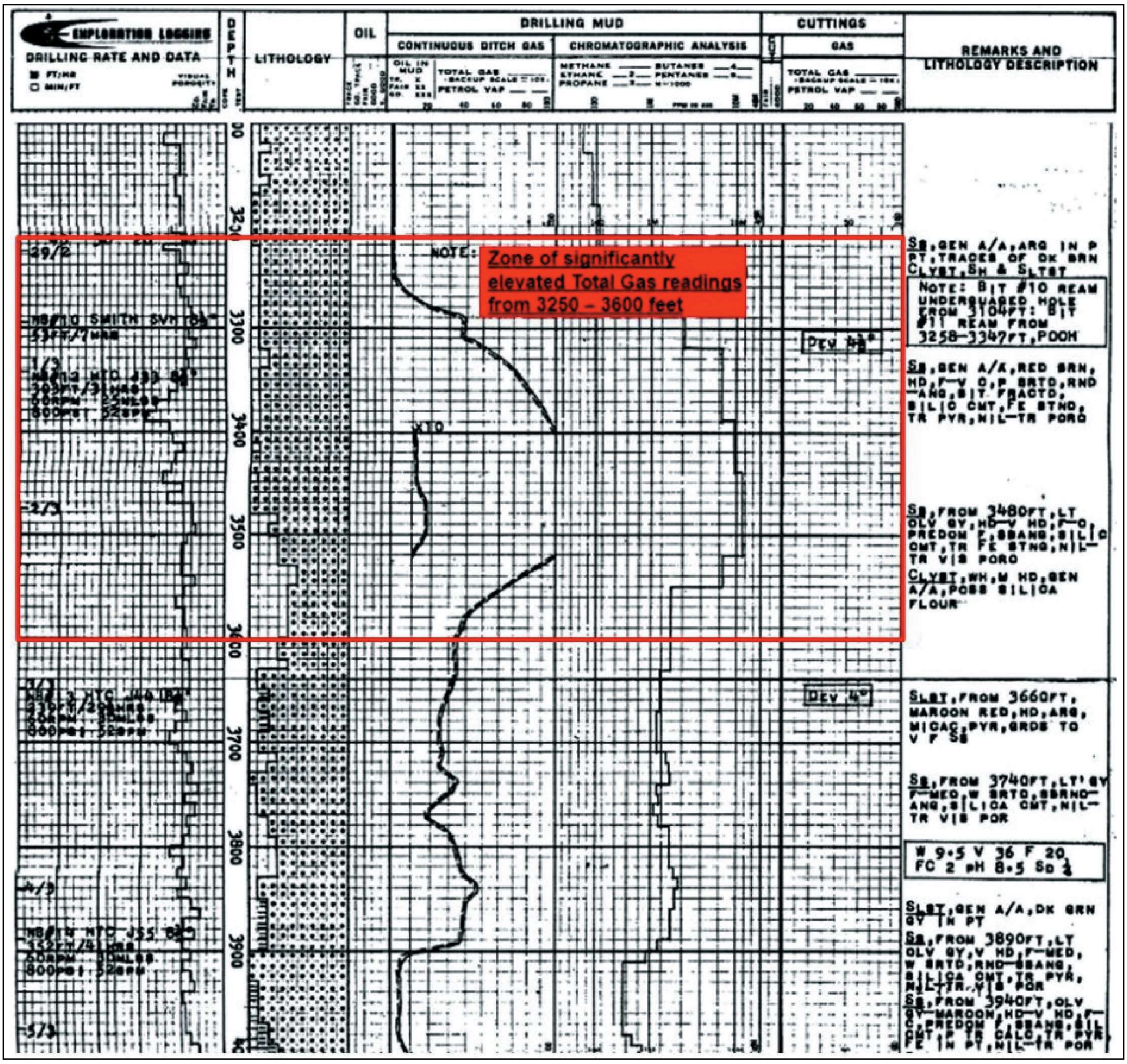

Figure 5. Mud-log extract from an exploration well drilled in 1980 interpreted to have intersected shows of natural hydrogen over the interval 3230 to 3600 feet. Note significant peak and overlap of Total Gas and Petroleum Vapour readings recorded in the drilling mud over this interval. It is assumed a similar response was most likely recorded at the Monzón-1 well. From XXX?

- Ditch gas and Microgas detectors give equal readings of TG and PV. Methane only registers on TG.
- Using a detector voltage of 0.5 volts D.C. hydrogen will give a reading of approximately 25% of the TG (2.8 volts D.C.) or PV (1.5 volts D.C.) readings.
- There is no separation in the readout of the standard EXLOG chromatograph between methane and hydrogen. Hydrogen gives approximately half the response compared to the TG reading as does methane: i.e. 1 unit of TG = 200ppm methane, 1 unit of TG = 100ppm of hydrogen using methane calibration figure. It is this difference which allows methane to be determined above a hydrogen background if present.

In other words, if only hydrogen were present, 1 TG unit of hydrogen gas would result in a TG detector voltage of ~0.35 volts and a hot wire PV reading of ~0.375 volts, i.e. very close. Thus, if only hydrogen is present then the TG and PV readings with be more or less the same, which is what was observed. This fact, coupled with the absence of other gas components supports pure hydrogen presence which is what appears to have been the situation at Monzón-1.

It should be stated that in addition to a purely natural origin, it is feasible the hydrogen in Monzón-1 could have been generated artificially during the drilling process by a combination of drill-bit metamorphosis and/or mud motor failure (Keller and Rowe, 2017). While there is no way of categorically ruling out artificial generation the detailed drilling report for the well makes no mention of abnormal drill-bit wear nor mud motor failure during drilling of the Bunter interval despite there being mud losses into the formation (Fig. 4). For info: nowadays, H2 measurements are routinely used by drillers to help assess drill bit wear status downhole. It is concluded therefore that the hydrogen encountered in the well is natural in origin.

Potential source of hydrogen

Assuming the hydrogen is natural then where would be its likely source? The most obvious answer is it has originated from the deep crust as is the case with the impressive hydrogen emanations recorded on the northern side of the Pyrenees where they are concentrated between the North Pyrenean Fault and the Frontal North Pyrenean Thrust Front (Fig. 1 and Lefeuvre *et al.*, 2021). Assuming a similar deep crustal source for Monzón then the most obvious conduit would be the basement inversion fault system which lies a few kilometres to the northeast of the well (Fig. 3). Interestingly, given the strongly asymmetrical nature? (Fig. 6) of the Pyrenees then the location of Monzón-1 in the South Pyrenees is almost identical geologically to that where the hydrogen emanations are recorded in the North Pyrenees (Fig. 6). In both cases hydrogen is seen in association with crustal scale faults and at the termination of later Tertiary aged compressional thrusting. The big difference between the sou-

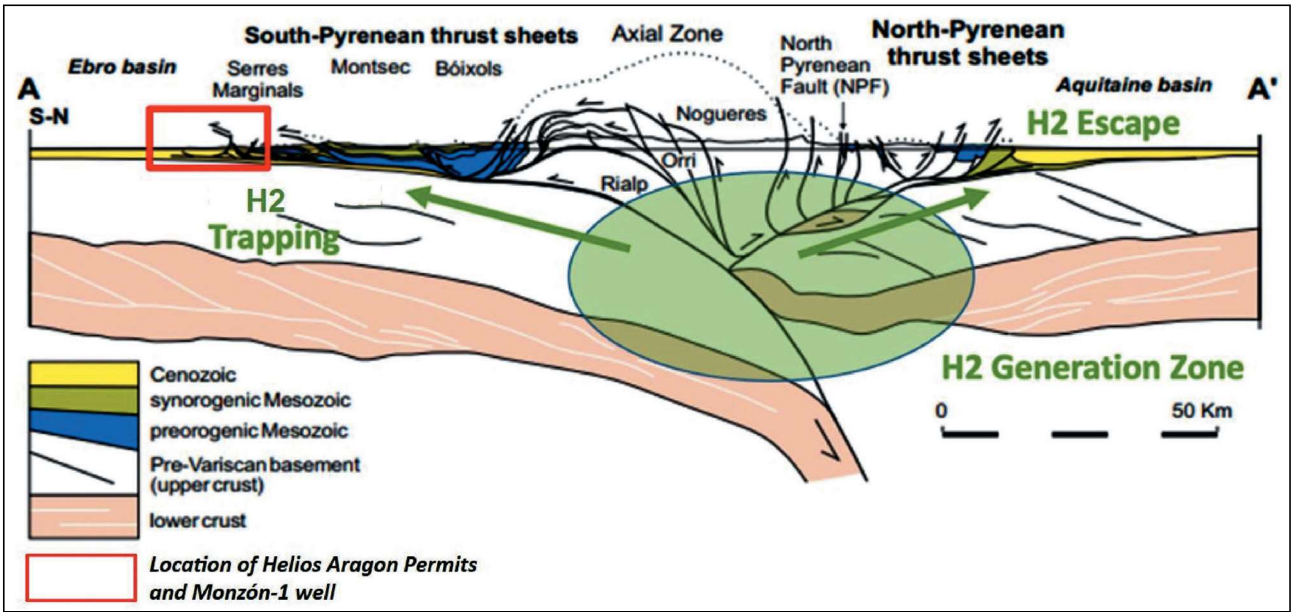

Figure 6. Geological cross-section through the Pyrenean mountain belt illustrating the largely asymmetrical nature? of crustal deformation. Assuming a deep crust/mantle source of hydrogen generation in the central core of the belt the shallower crustal geology in the south with increased presence of Mesozoic and Cenozoic cover deposits may tend to favour trapping of hydrogen in the sub-surface. Modified after Muñoz (1992, 2002).

thern side of the Pyrenees and the north is that there is much more cover of the basement geology in the south by later Mesozoic and Tertiary rocks. Importantly, as observed in the Monzón-1 well, these cover rocks contain many excellent seals such as the halite/anhydrite bearing Bunter shales, Muschelkalk carbonates, Keuper shales, Infra-Liassic evaporites and the thick, halite and evaporitic shales of Tertiary age comprising the core of the Barbastro Anticline (Fig. 2). In total the combined thickness of pure evaporites measured vertically above the Bunter Sandstone in the Monzón-1 well reaches in excess of 1000 metres.

Towards an exploration strategy for natural or "gold" hydrogen

The presence of natural molecular hydrogen found as a gas in the subsurface has been documented in many locations throughout the world (Zgonnik, 2021). In deference to man-made "green" hydrogen produced via zero-emission electrolysis of water naturally occurring hydrogen gas in the sub-surface has been termed either "white" or "gold" hydrogen (Gluyas, 2021; Ball and Czado, 2022). Given the extremely lightweight and highly reactive nature of hydrogen, its occurrence as a free molecule in nature is rare and requires specific subsurface conditions to be met:

- a source of natural hydrogen generation (biogenic, chemical, or radioactive),
- a reservoir rock,
- an impermeable "cap rock or seal" to prevent hydrogen leakage via diffusion,
- the absence of oxygen as this will react with the hydrogen creating water and leaving no trace hydrogen gas was ever present.

The gold hydrogen recorded at the Bunter Sandstone level in the Monzón-1 well conforms perfectly to all the above criteria. The major inversion fault setting up the northern bounding limb of the Monzón structure provides a perfect conduit for deep crustal generated hydrogen gas to migrate upwards into the basement defined structure. Here the hydrogen accumulates in the porous Bunter Sandstone reservoir which is sealed effectively and trapped by a thick sequence (>200 metres) of evaporitic Bunter shales. The depth of the Monzón Bunter reservoir at over 3,500 metres is well below the reach of aerobic processes limiting any oxidation reactions which could consume the free hydrogen molecules.

Conclusion

Significant hydrogen gas shows were documented in 1963 from the Triassic Bunter Sandstone interval in the Monzón-1 exploration well. The Bunter Sandstone lies on a well-defined basement closure and is sealed by a thick sequence of evaporite bearing Bunter shales at a depth greater than 3500 mBGL. The geology documented in the Monzón-1 well perfectly matches the sub-surface conditions thought to be required for the entrapment and concentration of natural gold hydrogen. The well was not tested at the Bunter level the time of drilling leaving the intriguing conclusion that an accumulation of gold hydrogen awaits re-discovery.

Acknowledgements

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