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The origin and nature of hydraulic fractures and veins within The Burren, County Clare, Ireland.

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Abstract

Carboniferous (Mississippian) limestones of The Burren are cross-cut by sub-vertical veins, from 1μm up to 50cm thick, defining a strongly clustered and scale-independent system in which predominantly N-S veins are transected by longer NNE-trending veins. Vein infills mainly comprise of calcite, but with subordinate amounts of quartz, sulphide (mainly galena and sphalerite) and fluorite also occurring, particularly in the south-central part of the area. Thinner and shorter veins are planar and discontinuous in plan view, sometimes forming en-echelon arrays, with thicker veins forming better connected and more complex structures which extend for several kilometres across the Burren region. Veins with 'exotic' infills are generally both longer and thicker, and they appear to be spatially associated with, or up to 5km to the north of, a 5km wide zone of ENE-trending Variscan monoclinal folding. Individual veins are vertically persistent, and the same structures are seen throughout the exposed ca 1200m thick Carboniferous sequence, from Tournaisian limestones through to Serpukhovian-Bashkirian siliciclastics. The veins are mainly extensional, sometimes with a component of sinistral displacement particularly on NNE-trending veins, displaying fibrous growth through to hydraulic fracturing and brecciation. Their formation is attributed to the valving of overpressured fluids within Mississippian basins during N-S Variscan compression. Pb isotope analysis supports a model in which sulphide infills are scavenged from underlying basement rocks or hydrothermal Zn-Pb mineralisation during the tectonic inversion of post-rift sequences overlying Lower Carboniferous normal faults.

Introduction

Analysis of the geological structure of Carboniferous sequences in Ireland is often hampered by the paucity of inland exposure. This shortcoming mainly arises from the widespread cover of rocks of this age by younger Quaternary drift deposits and the susceptibility of limestone-dominated bedrock to erosion and karstification. The Burren region in western Ireland provides exceptional exposure of thick sequences of Mississippian platform limestones, which are generally relatively undeformed apart from gentle folding and the development of fracture systems which are Variscan in age, or younger (Fig. 1).

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In many respects the Mississippian limestones of the Burren are similar to those which are very poorly exposed across much of Ireland. The Burren region thus provides a basis for defining the geometrical characteristics and processes associated with structures which are most likely developed in Carboniferous rocks elsewhere, but which have not previously been analysed or even identified. Building upon earlier work (e.g. Coller 1984; Gillespie *et al.* 2001; Moore and Walsh 2013), this study reviews the basic structure of the Burren and investigates the nature and origin of an array of N-S extensional veins within the region. These veins are calcite-dominated, but also contain more exotic mineral infills, such as fluorite, quartz and occasional sulphides. They are attributed to hydraulic fracturing during the Variscan orogeny (Figs. 1 & 2; Gillespie *et al*. 2001), with their calcite infill derived from the broad range of underlying Carboniferous carbonate lithologies, and their quartz and sulphide content sourced from underlying early Carboniferous mineralisation and cherts, or perhaps even deeper stratigraphic levels.

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Geological Background and Setting

The karst terrain of the Burren region in northwest County Clare is developed in a thick sequence of Mississippian limestones (Fig. 1). Limestone pavements on the upper parts of hills and along the coast provide superb exposures of relatively undeformed Viséan limestones (Asbian to Brigantian regional substages; Gallagher *et al*. 2006; see Figs. 1 and 2), comprising c.400m of mostly platform carbonates deposited within a post-rift sequence associated with Mississippian N-S crustal extension. The late Asbian Aillwee Member of the Burren Limestone Formation forms the well-developed terraces on the upper parts of several hills in the Burren (Figs. 1, 2B). The Aillwee Member consists of cyclic units of algal packstones/grainstones, 2-20m thick. Each of these units is topped by a palaeokarst surface and they are separated by thin clay layers, termed ‘clay wayboards’ (Walkden 1972; see Fig. 2), which are usually less than 20cm thick. The clay wayboards are rarely seen at outcrop because they are either preferentially weathered out or covered by vegetation. The tiered topography of the Burren due in large part to glacial stripping of the limestone bedrock along the more easily erodible clay wayboards. The overlying Brigantian Slievenaglasha Limestone Formation crops out on the hills in the southern part of the Burren and comprises 3-20m thick cyclic units of crinoidal grainstones with coral thickets and cherty limestones (Fig. 2a). These younger cycles lack palaeokarst surfaces and are not separated by clay wayboards.

Underlying this lithostratigraphic sequence in the Burren is c.500m of Tournaisian to mid-Viséan (Holkerian) limestones, with relatively subordinate shales, which unconformably overlie Old Red Sandstone facies (Fig. 1). The upper part of this older sequence, which includes the Tubber Limestone Formation (c.300m of calcarenitic limestones with rare shale and chert interbeds) and the underlying Waulsortian Limestone Formation (up to 70m thick, comprising of carbonate mudbank facies) was deposited during a regional phase of Tournasiain (upper Ivorian) to early Viséan (Arundian) rifting. Further to the south, these relatively shallow water limestones are replaced by the deep-water sequences of the E-W trending Shannon Basin which extends to the south of the Shannon estuary. Syn-rift sediments to the east of the Gort Lowlands are affected by normal faults which sometimes control the formation of broadly contemporaneous Zn-Pb mineral deposits. These are commonly hosted by Waulsortian mudbank limestones and they include the Kilbricken, Silvermines and Tynagh deposits, all of which are located within 40km along strike of the overlying post-rift sequence of the Burren and Slievenaglasha formations. Lateral thinning and the disappearance of Waulsortian facies towards the west would suggest that any equivalent Mississippian Zn-Pb deposits underlying the Burren must be hosted within other basinal units (e.g. the Ballysteen Limestone Formation or Lower Limestone Shales; Fig. 1) or in the Caledonian basement. Unconformably overlying the Tournaisian and Viséan limestones of the Burren is a c.1km thick Serpukhovian to Bashkirian (formerly Namurian) sequence of deep-marine to deltaic siliciclastics (Fig. 1). This post-rift basinal sequence was deposited within the E-W trending Clare Basin, the Pennsylvanian equivalent of the Shannon Basin, and it thins and becomes more shale rich towards Galway Bay in the north.

The Burren is generally marked by an absence of structural complexity compared to other regions in the south of Ireland, circumstances which partly explain why previous geological studies have concentrated on other topics, such as hydrogeology, karst geology and sedimentology/stratigraphy (e.g. Drew 1990; Gallagher *et al*. 2006; Simms 2000, 2003, 2006; Barham et al. 2015). Coller (1984) outlined the relatively undeformed nature of associated sequences, with relatively subdued bed dips (< 10^0) which give way southwards to a series of widely spaced E-W to ENE-trending monoclinal folds. Folding was attributed to approximately N-S Variscan compression, with the formation of associated smaller-scale structures, including conjugate sets of en-echelon vertical vein arrays and minor shear fractures believed to post-date folding. The widespread development of approximately N-S veins was supported by later studies (Fig. 3), with Gillespie *et al*. (2001) providing an analysis of the vein geometries and their scaling, as well as suggesting a Variscan origin arising from hydraulic fracturing and the valving of underlying overpressured fluids during N-S compression. Detailed geological mapping by Conor MacDermot of the Geological Survey of Ireland highlighted the presence of associated veins which sometimes contain relatively discontinuous developments of quartz and sulphides along their length (field sheets are available at secure.dcenr.gov.ie/goldmine/index.html).

In this paper we consider a selection of issues relating to the structural geology of the Burren, which provide a rationale for the nature and origin of the main vein system, including their more exotic infills such as quartz and sulphides.

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General geological structure of the Burren region

The relatively simple structure of the Burren compared to adjacent areas, and indeed much of Ireland, is the backdrop to the formation of the N-S vein systems developed in the area. Similar vein systems have been described elsewhere (e.g. Dolan 1984; Sanderson 1984), but nowhere are they better developed and observed than in the Burren region. In this study we suggest that the structural simplicity of the Burren mainly arises from the stratigraphic age of the sequence and from its location, issues which are highlighted by examination of the geological map of the region and adjacent areas (Fig. 1).

Even on the scale of the Clare-Galway area, previous work has highlighted the marked differences in Carboniferous structure either side of a c.10km wide NNE-trending zone centred approximately along the contact between the Burren and Tubber formations in the Gort Lowlands of NE Clare and SE Galway (Fig. 1):

- To the west, the rocks of the 'Clare Block' are characterised by E-W to ENE-WSW trending folds, which are open and monoclinal in the north and become tighter and closer towards the south, with the development of an associated near axial planar cleavage (Coller 1984, Cooper *et al*. 1986). Relatively modest amounts of Variscan shortening (<7.4%; Bresser & Walter 1999; Tanner *et al*. 2011) have been recorded within the Pennsylvanian sequence for over 50km along the Clare coast, with a decline in the northern half of the county extending into south Galway to values of < c.2%. This block has been referred to by Cooper *et al*. (1986) as 'Zone 2b' on the Variscan deformation map of Ireland developed by Gill (1962).
- To the east, the 'Central Ireland Zone' or 'Zone 2a', has been described as containing folds and steep ductile-brittle shear zones, strongly influenced by Caledonian (i.e. Lower Paleozoic) basement rocks, with deformation again declining northwards but with cleavage and minor folding developed within 'shear zones' as far north as the Tynagh Zn-Pb deposit (35 km due east of the south-east coast of Galway Bay).

Whilst it is not clear if there are marked differences in the amount of strain within these zones, mainly because quantitative strain measures have not been performed in the east, a change from more localised basement controlled Variscan deformation in the east to the more distributed deformation in the west is accepted by previous work (Coller 1984; Cooper *et al.* 1986).

The E-W change in structure across the Gort Lowlands has been attributed to one of two basic models:

(i) The presence of a steep NNE-trending shear zone of Variscan age, which is referred to as the Fergus Shear Zone (Coller 1984).

(ii) A difference in the elevation of the main detachment associated with Variscan thrusting, from within basement rocks to the east ramping up into the base of the Clare Shale Formation (Serpukhovian-Bashkirian) overlying the Burren Viséan limestone sequence in the west (Cooper *et al*. 1986), leading to the sub-division of Zone 2 on the structural zonation map of the Irish Variscan (Gill 1962).

Supporting evidence for either of these models is, however, generally either sparse or indirect. No regional decollement has been identified in either area and whilst there are structures within the Gort Lowlands, the most distinctive feature of the area is that the structural grain, both within the Carboniferous and underlying Lower Paleozoic basement, changes from closer to NE-oriented in the east to approaching E-W in the west. This characteristic is typical of much of the west of Ireland with, for example, Caledonian and Carboniferous structures showing a similar strike swing in east Galway and Mayo (Worthington and Walsh 2011). As Coller (1984) suggests, this swing implies that structures in the Burren more directly reflect N-S oriented Variscan compression, with areas to the east potentially accommodating a component of sinistral shear. The fundamental difference of structure between east and west is not, however, marked by either very high strains or by the generation of a well-defined NNW-trending shear zone within the Gort Lowlands and further to the south. As a consequence, instead of invoking the presence of a major regional zone, we suggest that the associated structural change is a temporal rather than a spatial effect.

Cursory examination of the north Clare geological map shows that the early Carboniferous normal faults of the east appear to die out westwards within the Gort Lowlands (Fig. 1). This spatial interpretation is, however, apparent, because the faults disappear into the syn-rift Tubber Limestone Formation and are, perhaps with one exception, never seen developed within the post-rift Burren sequence. The westward disappearance of the normal faults is therefore attributed to the younger and, ultimately, post-rift nature of the exposed sequences, with an associated upward decrease in fault displacement on syn-rift horizons towards unfaulted overlying post-rift horizons. This interpretation also provides a rationale for differences in structural complexity, with the presence of normal faults, with displacements of up to several hundreds of metres (as in Tynagh), having a strong localising effect on Variscan inversion-related folding, partly arising from the buttressing (i.e. compression) of hanging-wall sequences against basement rocks. The influence of pre-existing structure on later folding in the Burren region is, nevertheless, suggested by the development of Variscan monoclines which appear to be spatially coincident with the westward continuation of early Carboniferous normal faults observed in the eastern inliers (Fig. 1). The northernmost of these normal faults, which is the strike equivalent of the Tynagh fault, continues through Gort, giving way laterally and upwards to a series of southward verging monoclines, with limb dips of up to c.35^0 to the south, which are not seen in the northern part of the Burren region where beds generally dip south at less than c.5^0. It is tempting to suggest, therefore, a genetic link between the predominantly northward dipping normal faults transecting the inliers and the southward-verging nature of the monoclines, to provide a deformation geometry which is consistent with the inversion of normal faults into overlying post-rift sequences (Reilly *et al*. 2017). Whilst this and many other aspects of the associated folding should be the subject of more detailed studies, the available constraints provide strong grounds for the lateral extension of early Carboniferous normal faults under the Burren, a suggestion which has important implications for development of vein systems in the area.

Vein system – outcrop studies

The Burren is transected by an array of vertical veins, which usually strike c.N-S or 10-15^0 east of North. The veins are predominantly extensional in nature, but with some, particularly those which strike at 10-15^0, displaying a subordinate component of sinistral shear (see below; Moore & Walsh 2013). This geometrical configuration is consistent with previous interpretations attributing these structures to approximately N-S compression (Coller 1984; Gillespie *et al*. 2001; Moore & Walsh 2013). The veins have thicknesses varying from μm-scale up to c.50cm, and form systems which are strongly clustered on a range of scales (Fig. 3). Veins are easily observed from aerial photographs as dissolution of the adjacent limestones has produced cm-wide grykes which faithfully follow and widen sub-vertical fractures. As a consequence, vein clusters can be observed on km-scale aerial photographs (Fig. 4) and on the c.300m high hill scarps of the southern shores of Galway Bay (Fig. 2; Gillespie *et al*. 2001). Here we first consider the basic scaling characteristics of the vein system, followed by a description of the nature and content of their fill.

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Scaling characteristics

The veins shown on the regional map of the Burren (Fig. 1) are the most persistent and best-defined structures on aerial photographs. At this scale the main vein geometries are oriented 10-15^0 east of North with ubiquitous intervening veins which are closer to N-S oriented. On larger scales, what appear to be individual continuous veins in map view can, on closer examination, be seen to comprise clusters of highly segmented and sometimes en-echelon vein arrays, which are, in turn, separated by even thinner and shorter veins (Fig. 4). This strongly clustered system, which on higher-resolution maps reveals progressively smaller scale details of broadly similar structures, is typical of scale independent geometries (Odling *et al*. 1999). In this section we describe the geometry of the Burren Vein system in map and then cross-sectional view, followed by a summary of their principal scaling characteristics.

Outcrop examination of veins and vein clusters indicates, as expected, that the longer more continuous veins and vein clusters are typically thicker (> 10cm), than the shorter and more isolated veins (<1mm). Whilst calcite is by far the dominant vein infill, some veins, and particularly the longer and thinner veins, are quartz-, sulphide- and fluorite-bearing. Whatever their size, individual veins and vein segments are relatively planar in map view (Figs. 3 & 4), with very rare sigmoidal or splaying veins. Typically, however, thicker veins are characterised by breached bridges between segmented veins and the presence of a more continuous, better linked, vein which is irregular on m- to dm-scale. This is highlighted at the Cullaun Two cave, which is localised along a very persistent cluster of veins extending more than 7km laterally towards Ballyvaughan and through a 350m stratigraphic sequence from the top of the Slievenaglasha Formation in the south towards the base of the underlying Burren Formation in the north (Figs. 1 & 5). This cluster provides an aggregate vein thickness of c.40cm and whilst it appears relatively simple and planar on large scales, it is more complex on m-scale, comprising an array of interconnected veins together with the development of breccias (Fig. 5; see below).

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Previous work on smaller scale veins (< 60m long) from well exposed terraces and wave cut platforms in the Burren suggests an average length:thickness ratio of c.5000 and a maximum value of c.30,000 (Bech *et al*. 2001). Lower ratios can occur, but are always associated with multi-segment vein clusters in which veins represent interacting segments which together form a single larger structure (Vermilye and Scholz 1995; Gillespie *et al*. 1999). For multi-segment veins, vein widening and an associated increase in vein thickness provides lower length:thickness ratios (< 1000) for individual segments, leading to the linkage (or bridging) of segments and the emergence of a through-going thicker vein. Those veins which can be mapped on large-scale aerial photos, includingthe Cullaun Two vein (Figs 1 & 4) can have very high length:thickness ratios, well in excess of 5000, a characteristic which is consistent with a suggested non-linear relationship between vein length and thickness (Vermilye and Scholz 1995). The origin of this relationship is beyond the scope of this paper, but is believed to arise from the non-linear relationship between fracture length and stress intensity at fracture ends and differing degrees of interaction on different scales.

Given the nature of bedrock exposure in the Burren and their large areal extent, vein geometries in map view are easier to define than those developed in cross-section profile. The vertical persistence of veins is, however, supported by vein distributions on hill scarps and smaller scale outcrops (Figs. 2 & 3), and by the manner in which veins transect bed-related terraces as they extend across the Burren (Fig. 4). This is best demonstrated on the north facing hillside of Black Head, where most of the veins visible on 0.5km scale views appear to transect the 0.5m thick shale between the Maumcaha Member and Terraced Member of the Burren Limestone Formation. This persistence is also matched by quantitative measurements of the persistence ratio of thin veins (< 2mm) observed on metre-scale outcrops (Fig. 3), representing the fraction of veins extending from one bed to another. High vertical persistence ratios, generally ranging from 0.63 to 1.0 (Gillespie *et al*. 2001), are consistent with the observed through-going nature of individual veins and with the apparently scale-independent nature of the vein system. For example, the quartz-calcite veins of Poll Gonzo cave, which together have an approximate thickness of c.50cm, transect a 25cm thick clay layer and are part of a single mappable structure which extends 20km across the Burren and intersects the entire stratigraphic sequence (Fig.6). In that sense, the veins are very different from conventional uplift-related (i.e. exhumation) joints which are often contained within individual beds, and are stratabound, often showing scale-bound and relatively regular spatial distributions (Gillespie *et al*. 2001). In The Burren these joints have much more variable strike orientations and are not vertically persistent, reflecting the influence of nearer-surface stress conditions rather than a well-defined tectonic stress field (personal observation JP Moore). Scale independence of structure is reflected in a variety of associated scaling properties. In areas where grykes are not developed and the thicknesses of veins are preserved, such as along the coast close to Gleninagh Castle (Fig. 3B-C), the veins display power-law scaling both in terms of vein thickness and vein spacing, where spacing is the strike-perpendicular distance between adjacent veins (Gillespie *et al*. 2001). Power-law scaling, in which a parameter defines a straight-line curve on a log-log plot of parameter size (e.g. thickness or spacing) against the numbers of veins greater than a given size, is typical of scale-independent systems (Gillespie *et al*. 1999, 2001).

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The Burren vein system is not just restricted to the Viséan limestone sequence, but is also widely developed within the overlying Serpukhovian-Bashkirian sandstones and shales, and the underlying shallow water to mudbank limestones deposited during Tournaisian basin development. For example, N-S calcite veins and vein clusters are developed within both the Moymore and Liscannor Flagstone Quarries (adjacent to Ennistymon and Milltown Malbay, respectively), which are within the Central Clare Group and about 155m and c.275m, respectively, stratigraphically above the uppermost limestones in the Burren (Fig. 1). Since an equivalent array of N-S oriented quartz or calcite veins have not been documented within the Lower Paleozoic basement rocks, the available evidence suggests that this vein system may be restricted to the Carboniferous basinal sequences, an issue we return to later.

The internal structure and content of veins and vein clusters

Veins in the Burren are dominated by calcite infills with a relative paucity of non-carbonate infills. In all cases, the non-carbonate content is usually very subordinate to calcite and varies considerably along the length of individual veins. Here we briefly describe the internal structure and, in particular, content of different vein infills defined from field studies, with the minerology and geochemistry considered in the next section.

Calcite veins

Smaller calcite veins are characterised by simple extensional offsets with no, or very limited, shear sense and are therefore Mode I extension fractures (Bons *et al.* 2012). Vein-perpendicular calcite fibres and field observations of cross-cutting relationships, best seen on coastal outcrops, support this predominantly extensional nature, but also highlight the presence of subordinate sinistral shear, most often associated with NNE-trending veins. The fibrous nature of small vein infills (<1cm) are syntaxial, with minerals growing outwards from the wall rock, and indicate the operation of small incremental extensional events, on mm- or smaller scales, during vein growth, with the internal structure of individual veins characterised by multiple events marked by cross-cutting veins and crack-seal increments (Ramsay 1980). Larger and thicker (cm-scale) veins often comprise dense clusters of veins, but an increase in vein thickness is also generally marked by interconnected vein arrays, with vein bridging and linkage, and by breccias (Fig. 5). The latter vary in character from jigsaw and crackle breccias, in which clasts can be restored to their pre-fracturing configuration, to chaotic breccias, in which clasts are rotated and/or further travelled. In Cullaun Two cave, breccia development is characterised by limestone breccia fragments floating within a crystalline calcite matrix (Fig. 5C). This matrix does not show the simple fibrous infill of thinner veins and instead comprises coarser calcite crystals more typical of larger extensional events and hydraulic brecciation.

Siliceous veins

The importance of hydraulic brecciation processes is supported by evidence from some of the veins with non-carbonate infills, the most common of which are quartz -bearing. These siliceous veins are relatively resistant to erosion and when present often show evidence of both fracture networks and breccia develpment (Fig. 7). The significance of these veins across the Burren region was not appreciated until the late Conor MacDermot of the Geological Survey of Ireland mapped them during the 1970s and 1980s. His 6” field sheets (i.e. 1:10560) show the full extent of siliceous and other mineralised veins (GSI online digital archive [GOLDMINE]: secure.dcenr.gov.ie/goldmine/index.html). Within the central part of The Burren (around Carron – Slievecarran hill area; Fig. 8) MacDermot recorded at least 27 quartz-bearing veins on bedrock field sheet maps for the Burren area and subsequent mapping by one of the authors (CB) has shown numerous examples of siliceous (i.e. quartz-bearing) veins outcropping on the surface (Fig. 8), even when quartz represents rather limited and patchy distributions within individual calcite veins. Siliceous veins are, therefore, considered to be components of the Burren vein system, representing the localised ingress of silica rich fluid pulses along the thicker and more extensive veins in particular.

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Quartz-bearing veins comprise fibrous through to vuggy crystal infills within clusters of up to cm-scale quartz veins, which form parallel to complex networks within zones up to 65cm across (Fig. 9). The relative quartz to calcite content of individual veins is often difficult to estimate because of lack of exposure and karstification. The quartz-calcite vein on Turlough Hill (Fig. 4B) is, however, very well exposed and comprises approximately 50% quartz relative to calcite infill in a zone which is c.40cm wide (Fig. 9A). In some cases, breccias are developed containing limestone clasts (up to 10cm) within a quartz or quartz/calcite matrix (Fig. 7A). Breccia clasts are generally angular, but sometimes appear to have more rounded edges, a feature which might suggest hydraulic streaming or perhaps clast dissolution. Clasts can be surrounded by fibrous quartz which sometimes forms drusy cavity infills, perhaps because of dissolution of later calcite infills. The importance of later karst-related dissolution gives the quartz vein networks a very porous, or spongiform, appearance at outcrop scale, resulting in rough and sharp exposures.

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Whilst the vast majority of veins in the Burren are carbonate filled and form elongate karstified grikes, or depressions, across the landscape, quartz veins form (positive relief) outcrop ridges (Fig. 10). Compared to their pure calcite counterparts, siliceous veins appear to be more often sulphide- and fluorite-bearing (see below) though this may partly be a preservational issue. MacDermot's bedrock 6" field sheet maps highlight their relatively localised distribution which is mainly restricted to a N-S trending c.7km wide zone in the central part of the Burren (see red lines on Fig. 8). This broad zone extends southwards from 1-2km south of the Galway Bay coastline for c.15km into the main series of NE-oriented monoclines, but not further to the south, where the vein system comprises only calcite veins. As with the main calcite vein system, individual veins are most often N-S oriented, apart from the two main NNE-oriented siliceous veins extending through the central part of the area (i.e. MacDermot's fault and Poll Gonzo vein). The map expression of individual quartz veins on MacDermot's field sheets are relatively discontinuous (Fig. 11) and this is supported by the along-strike variability in the widths of ridges at smaller outcrop scales (Fig. 10), with width gradients of as high as 1 (e.g. 25cm change in width over a distance of 25cm). These rapid changes in width are consistent with a component of strike-slip displacement along these veins and with multiple increments of vein growth arising from finite and discontinuous veining events.

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Sulphide and fluorite-bearing veins

More exotic minerals contained within the Burren veins include a variety of sulphides, carbonates and fluorite. These, together with quartz, appear to be preferentially contained within some of the larger veins/vein clusters transecting the region. The main sulphide minerals are galena, sphalerite and chalcopyrite, though secondary alteration products include smithsonite, malachite and azurite (see below and Cole 1922), and earlier records of silver most likely refer to argentiferous galena (Cole 1922). Sulphide-bearing veins are apparently restricted to within and no more than about 5km north of the series of NE-trending monoclines and are generally located within, or close to, the Slievenaglasha Limestone Formation. For example, the GSI mineral survey of the upper Viséan platform limestones of northwest Clare records the composition of 20 veins which contain minerals other than calcite (O'Raghallaigh *et al*. 1997), and of those 13 of the 14 veins containing galena, 7 of the 10 containing chalcopyrite and all 6 containing sphalerite/smithsonite are within the Slievenaglasha Limestone Formation (Fig. 8). 19th Century mining activity produced trial adits and shafts for a number of sites in the Burren, but with no quantifiable records of output (Cole 1922). Activity at Sheshodonnell mine, for example, was short-lived (1862-1863), involving production of galena from a calcite vein up to 45cm thick, but with the sulphide-bearing zone decreasing over a distance of 100m. The vein contained galena, smithsonite and fluorite, with the main constituent being botryoidal smithsonite, which is typically an alteration product of sphalerite. Moguohy mine, 1km to the north of Sheshodonnell, is located along what appears to be the same lead-bearing calcite vein (Fig. 12). This vein contains fluorite and rare chalcopyrite but with no record of sphalerite/smithsonite, suggesting that the content of the sulphide-bearing veins is very heterogeneous. About 2.5km to the north within the newly discovered Poll Gonzo Cave (Bunce 2010; Boycott *et al*. 2011) and along what appears to be the same structure (Fig. 12), a number of siliceous veins are very well exposed, but with no apparent concentrations of either galena or sphalerite/smithsonite. Minor amounts of fluorite occur within several veins across the Burren, with the vein-hosted deposits at Kilweeran and Doolin exploited commercially. Doolin Fluorspar Mine produced up to 31 tonnes of fluorite in the 1940s from Burren Limestone Formation and Kilweeran involved workings in opencast pits within the 1960s from calcarenite horizons in the same formation (Pracht *et al*. 2003). The Doolin fluorite deposit is spatially associated with the Doolin phosphate deposit, one of the overlying Clare Shale Formation sedimentary phosphate deposits, which comprise granules of fluoroapatite and collophane (Fig. 8; Pracht *et al*. 2003).

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Timing of veins - field evidence

Several previous studies have suggested that N-S vein systems contained within the Carboniferous sequences of the west of Ireland, and the Burren and the Shannon Basin in particular, are of late Variscan age (Coller 1984; Dolan 1984; Sanderson 1984; Gillespie *et al*. 2001). This study has identified three main lines of evidence also suggesting that veining is late Variscan, partly overlapping with, but mainly post-dating, folding:

1. The extensional nature of N-S veins and the sinistral component of displacement of those that are oriented east of north is consistent with N-S compression, rather than bulk E-W extension. This stress configuration is consistent with both Variscan and Alpine compression, but recent work shows that Alpine structures in Ireland are dominated by conjugate NE- and NNW- strike-slip faults often with m-scale apparent vertical displacements (Fusciardi *et al*. 2004; Cooper *et al*. 2012; Moore and Walsh 2013; Anderson *et al*. 2018).
2. Exposures within cave systems demonstrate the presence of bedding-parallel, and therefore often sub-horizontal, calcite veins developed within the Burren Limestone Formation (Fig. 3C). These veins often possess slickenfibres which are attributed to flexural slip and yet their relationship with the N-S vertical veins varies. In some cases, bed-parallel veins offset N-S veins (Fig. 3C) and in others the bed-parallel veins are transected by the N-S veins or are connected to them. If the bed-parallel veins are related to Variscan folds, the main structures in the area, then N-S veins are at least partly synchronous with folding.
3. Finally, examination of vein systems in the main area of folding suggests timing which is either broadly synchronous with or entirely post-dates Variscan folding. Whilst mapping of major veins suggests they transect individual folds, closer examination at outcrop scale indicates synchroneity of development, with N-S veins at least locally rotating adjacent to monoclinal short limbs and connecting with fold-parallel veins and, in other cases, vein geometries associated with folding showing more consistent orientations when corrected for bed tilt (Gillespie *et al*. 2001).

Taken together, we suggest that the available field evidence supports the contention that vein development at least partly overlaps in time with folding, an issue which we return to when we consider the origin of the system.

Impact on hydrogeology

The importance of N-S structures in controlling the development of associated karst and related cave systems in the Burren has been understood for some time (Drew 1990, 2007). Since Gillespie *et al*. (2001) documented the differences in scaling and, in particular, vertical persistence between veins and joints, more recent studies have suggested that veins, rather than the superficially developed and variably oriented joints, exercise the most important control on cave formation (McSharry 2006; Moore and Walsh 2013). The importance of NNE-oriented veins on the localisation of caves is shown for the series of Cullaun Caves (Fig. 5; Mullan 2003). For example, Cullaun Two Cave is oriented parallel to, and contains, a thick vein and associated hydraulic breccias which have been the locus for dissolution and karstification (Fig. 5C). Even where the veins are mainly quartz filled, such as at Poll Gonzo, the cave system is clearly controlled by the veining, extending both downwards and along strike (Fig. 6B). A profile of Poll Gonzo shows that the cave is also strongly controlled by Ailwee Memder clay wayboards, which do not affect the continuity of the veins but are responsible for a staircase trajectory in passage formation, with veining and layering controlling cave geometry (Fig. 6A). Consideration of the associated hydrogeological processes are beyond the scope of this contribution and is the subject of ongoing research, but the main causes are believed to be the vertical persistence of the veins and the localisation of dissolution on either the calcite infill or the interface between non-calcite veins and the associated limestones (Moore and Walsh 2013).

Vein mineralogy

The vast majority of the veins in the Burren are pure calcite, with only occasional and mainly larger veins in the south containing additional mineral phases. Due to their purity, relatively thick veins (< 1m thick) in the north, such as the Black Head and Bell Harbour veins, were mined in the late 17th Century and also in the 1970s for glass making (Pracht *et al*. 2003). In this section we briefly describe the petrographic character of veins containing other mineral phases. A number of samples of silica veins were collected from Poll Gonzo (Fig. 6). These comprise highly siliceous multiple veins composed of interlocking subhedral quartz crystals ranging from 0.1mm to 1.0mm in size, through to cross-cutting 2-4mm veins of coarser subhedral quartz with crystals up to 2.0mm in size. Significant parts of the veins contain calcite (up to 50%), occurring primarily as either coarse (up to 1.5mm) single calcite crystals, probably infilling remnant porosity, and as fine disseminated irregular anhedral to subhedral crystals, clearly replacing existing quartz or infilling dissolution porosity (Fig. 13). In hand specimen spongiform textures observed in weathered veins arise from the selective dissolution of calcite in the mixed silica/calcite portions of veins during karstification, leaving the residual insoluble, in-situ quartz as a “spongiform” vein.

INSERT FIGURE 13 around here. Allow one full page width

Mineralized spoil samples associated with historic lead mining at Sheshodonnell illustrate the nature of associated mineralisation with irregular intergrowths of cm-scale galena and mm-scale euhedral quartz replacing limestone (Fig. 13C). Within these mineralized limestones, veins up to a few centimetres wide contain coarse purple fluorite. Pale yellow to yellow-green colloform smiths onite coats the fluorite, which is sometimes partially resorbed and in altered limestone smithsonite commonly coats galena and quartz. No sphalerite was observed at Sheshodonnell, but it has been observed elsewhere, within the veins at Slievenaglasha, for example (Fig. 13D). Late very fine-grained brown material, probably iron oxide/hydroxide, has overgrown smithsonite in places and is an important characteristic of veins elsewhere (Fig. 13C-D). An estimated ~20% porosity remains in the veins, and whilst it is not clear if this is primary or due to dissolution of calcite, the association with carbonate alteration of sulphides and probably iron oxide/hydroxide is consistent with a groundwater-related, supergene, origin.

Vein geochemistry

Our consideration of the geochemistry of veins in the Burren concentrates on the sources of the vein-related fluids and of the sulphides, in particular. The fluid source has previously been considered by O’Connor *et al*. (1993) using fluid inclusion data from fluorite in a selection of Burren veins, including the galena-bearing vein at Sheshodonnell. They considered two potential sources: the underlying Carboniferous and associated basement rocks, and the Galway Granite. The potential contribution of the Galway Granite arises from its *possible* southward extension into the northern part of the Burren (to just south of Slieve Elva; Fig. 8; MacDermot *et al*. 2003) where it is proposed to be unconformably overlain by the Carboniferous sequence. Previous work has also suggested the presence of a Caledonian intra-terrane boundary, the Orlock Bridge Fault (Murphy *et al*. 1991), extending east-west from approximately Gort to Doolin below the basal Carboniferous unconformity. This fault defines the boundary between the Northern and the Central and Southern Belts of the Central-Southern Uplands accretionary prism terrane. Since earlier work has suggested that the source of much Irish Zn-Pb mineralization was in the underlying Lower Paleozoic rocks (O'Keefe 1986; Everett et al. 2003), we have performed Pb isotope analysis of galena from Sheshodonnell veins to establish whether the galena has the same signature as the underlying basement and associated Mississippian Zn-Pb deposits.

Fluid inclusions:

The earlier study of fluid inclusions and rare-earth element (REE) chemistry within fluorite by O'Connor *et al*. (1993) analysed N-S veins within both the Galway Granite and the Burren region. All but one of seven sample localities included in that study were from the Burren (Fig. 8), with associated veins always containing calcite, fluorite and sulphides (galena, chalcopyrite) and/or some carbonate derivative (smithsonite ($ZnCO_3$) and, less often, cerussite ($PbCO_3$)). Associated fluorite-bearing hydrothermal fluids show no REE evidence of a granitic 'precursor' and instead display sedimentary signatures reflecting their carbonate host rock. This is consistent with the fact that the fluorite- and sulphide-bearing veins are generally developed to the south of the interpreted contact of the Galway Granite (Fig. 8), within a 10km wide E-W oriented zone approximately straddling the extrapolation of the Orlock Bridge Fault. Their compositions define a dilution trend between relatively high homogenisation temperatures (< 140^0C) and salinities through to lower homogenisation temperatures (c.80^0C) and minimum salinity, consistent with later mixing with meteoric waters at shallow levels in the crust. From Rb-Sr and Sm-Nd isotope analysis, Menuge *et al*. (1997) attributed the Galway Granite vein system (sampled in the Costelloe Murvey Granite) to the precipitation of fluorite and calcite, where hot dilute fluids rising through the granite mixed with cooler more saline, fluorine-rich, fluids of basinal origin migrating downwards through the overlying Mississippian limestone sequence. They suggested that the available geochemical evidence indicated low temperature downward migrating fluids, perhaps deriving fluorite from fluorapatite in the Serpukhovian phosphorites of the overlying Clare Shale Formation.

Pb isotopes:

Several researchers have documented systematic shifts in Pb isotope ratios and calculated μ values (source $^{238}U/^{204}Pb$) for galena occurrences across Ireland (e.g. O'Keefe 1986; LeHuray *et al*. 1987; Everett *et al*. 2003). Lead isotope ratios in galena reflect those of the source region, with model ages approaching the age of mineralisation. Whereas galena from Lower Paleozoic mesothermal Au and volcanogenic massive sulfide deposits of the north of Ireland (e.g. Cavanacaw, Charlestown) are characterised by a Pb source region with a μ value of ~9.2 and low $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios, similar mineral deposits from southeast Ireland (e.g. Avoca) are characterized by a μ value of ~9.9 and higher ratios. This reflects clear differences in the basement from which Pb was sourced - Laurentian crust in northwest Ireland and Gondwanan-affinity crust in the southeast. Interestingly, Lower Paleozoic hosted basement veins from the Down-Longford Terrane and Carboniferous-hosted Zn-Pb deposits form linear arrays between these two μ curves (Fig. 14). These trends reflect the incorporation of lead from both sources (see O'Keefe 1986). Contours of mean Pb isotope ratios in

Ireland follow a strictly Caledonian (NE-SW) trend across the north and west Ireland, reflecting variations in basement terranes (Fig. 14B). Lead isotope ratios from the Burren are comparable to Lower Paleozoic basement veins and Carboniferous Zn-Pb occurrences from the surrounding area. Lead in the Burren veins is isotopically distinct from fluorite-bearing veins of the Galway Granite, and is most comparable to crustal sources directly along strike to the northeast at Ballinalack. The $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ values measured are consistent with metals from a predominantly Gondwanan source for Pb (µ of ~9.9), with additional Laurentian Pb most likely derived from the overlying Down-Longford accretionary prism.

INSERT FIGURE 14 around here. Allow one full page width

Geochronology:

This study and previous work have performed $^{207}Pb/^{204}Pb$ and ^{40}Ar-^{39}Ar geochronological analysis of N-S veins within the Galway Granite and Burren area. O'Connor *et al*. (1993) suggested a Triassic age for some N-S fluorite-quartz-calcite veins in the Galway Granite on the basis of vein-related alteration of a late Carboniferous dolerite dyke. ^{40}Ar-^{39}Ar dating of a clinopyroxene provided an age of 231 +/- 4 Ma which was attributed to wall rock alteration of not only the dyke but also the host rock Costelloe Murvey granite, a highly evolved, high heat production Caledonian Granite (O'Connor *et al*. 1993). Menuge *et al*. (1997) reinterpreted this age as a mineralisation date for the vein system arising from low temperature (<<100^0C) downward-migrating fluorine-rich fluids. Our Pb isotope analysis of two galena samples from the Sheshodonnell deposit yielded very useful constraints on the source of Pb, but can also be used to calculate model ages according to the two-stage global model of Stacey and Kramers (1975). The derived model ages are 226-213 Ma (Upper Triassic; Norian age), with calculated µ values of 9.58-9.52. While this might provide support for a possible mineralisation event at that time, model ages are subject to very significant errors, and in Ireland are often 20-100 Myr too young when calculated using the Stacey and Kramers (1975) model. For further evidence of this, analysed galena from the Lisheen and Silvermines Zn-Pb deposits yields mean model ages of ~317 Ma (n=84; personal communication Stephen Hollis and colleagues) and ~229 Ma (n=15; recalculated from Boast *et al*. 1981; O'Keefe 1986; Mills *et al*. 1987; LeHuray *et al*. 1987). These are considerably younger than recent Re-Os dating of pyrite from both of these deposits (Lisheen 346.6 ± 3 Ma; Silvermines 334 ± 6 Ma; see Hnatyshin *et al*. 2015) and known stratigraphic constraints (e.g. Andrew 1986). Similarly, the Navan deposit (Ashton *et al*. 2015) yields model ages ranging from 465 to 196 Ma (mean 311 Ma, n=62; data from Boast *et al*. 1981; Mills *et al*. 1987; LeHuray *et al.* 1987). Whilst it is clear that no significance can be attached to our model ages, we suggest that future work investigates the extent to which Caroniferous and later Variscan mineralisation may be discriminated in geochronological terms. In our later discussion, we try to reconcile the field study evidence supporting a late Variscan age (c.290Ma. early Permian) with the mid-Triassic dates derived from geochronology.

O'Connor *et al*. (1993) tentatively suggested that both the Galway Granite and the Burren veins might be related, but acknowledged that available constraints did not support anything other than a post-Viséan age for the latter. Nevertheless, the Triassic ages derived from their work is associated with approximately N-S oriented veins which are fluorite/calcite/quartz-bearing. The main differences are, however, that veins in the Burren are overwhelmingly calcite-dominated, with fluorite as a very minor constituent and sulphides a distinctive but accessory mineral of only some of the larger veins. Of course, this difference could simply reflect the underlying Carboniferous limestone dominated fluid source of the Burren region, and the granitic source of the Galway Granite veins. An entirely Triassic age for the calcite-quartz-fluorite veins of the Burren is not, however, consistent with previous structural studies, all of which suggest a late Variscan age (Coller 1984; Dolan 1984; Sanderson 1984; Gillespie *et al*. 2001), and with the field evidence supporting a late Variscan hydraulic fracturing origin arising from the upward flow of overpressured fluids, partly overlapping in time with Variscan folding. One of the defining features of the fluorite- and sulphide-bearing veins in the Burren is, however, the widespread alteration of sulphide phases to botryoidal smithsonite and blade-like cerussite, an event which could be linked to the Triassic mineralisation event. For example, the Sheshodonnell vein is recorded as containing perhaps as much as four tonnes of smithsonite, an alteration product of primary sphalerite.

Middle to late Triassic deformation elsewhere in Ireland and the UK is generally attributed to the early stages of North Atlantic stretching, with associated rift basins varying from N-S through to ENE-WSW oriented. O'Connor *et al*. (1993) and Menuge *et al*. (1997) implicated this regional extension in the formation of the N-S veins of both the Galway Granite and the Burren. Whilst most Permo-Triassic basins surround onshore Ireland, some faults and basins were developed in the north and east of Ireland (e.g. Larne and Rathlin Basins, Tow Valley and Kingscourt Faults). The N-S oriented Slyne Basin and the northern part of the Porcupine Basin are c.100km to the west of the Burren and are the closest Permo-Triassic basins to the study area. Although the Burren vein system is compatible with N-S compression, rather than E-W extension, in view of the presence of strike-slip displacements and the absence of associated normal faulting, it is possible that the ingress of saline fluids during the Triassic may have utilised the pre-existing vein system. The downward sinking of fluids could have been localised along the larger and most vertically persistent veins, a model which would be compatible with the field observations and available dating. The importance of downward-directed fluid flow is supported by the wide-scale alteration of Pb- and Zn- sulphides, to form smithsonite and to a lesser extent cerrusite, alteration which is consistent with the ingress of relatively cool fluids. Such alteration would not, however, require Triassic rift-related fluid flow and could simply reflect groundwater flow and associated supergene alteration of pre-existing Variscan veins, an origin which is our preferred interpretation at this stage.

Discussion

Analysis of the geometry and structure of N to NNE oriented calcite vein systems in the Burren region highlights a variety of characteristics which are useful indicators of their origin, source fluids and timing. Our consideration of these structures has benefited from the otherwise relatively simple structure of the Burren, a feature which we have attributed to the post-rift nature of the exposed sequence and the consequent paucity of rift-related normal faults which at deeper structural levels towards the base of the Carboniferous serve to strongly localise later Variscan inversion and related folding. The decrease in structural complexity from the east towards the west within the Gort Lowlands has previously been attributed to the presence of the NNE-striking Fergus Shear Zone (Fig. 1), a structure for which we cannot find strong evidence. A strike-swing from NE to E-W orientations towards the west does occur, but this is typical of the Caledonian-Carboniferous structure of the entire west of Ireland. This strike swing is accompanied by a gentle westward structural dip on the eastern limb of an approximately N-S oriented large scale syncline. Further south this syncline has an amplitude of c.100km between the Silurian-Devonian rocks of the Dingle Peninsula in the west and the Kilamalluck-Cahir inlier in the east. The origin and timing of this large-scale (approximately N-S oriented) gentle fold, together with other similar folds across Ireland, is presently unknown. The combined effects of these regional structural changes is that the absence of normal faults and associated strong localisation of Variscan inversion reflects the post-rift nature of associated sediments in central and west Clare, a change which is more temporal than spatial, and does not support the sub-division of previously defined zones of Variscan deformation (Gill 1962).

The effect of relatively simple structure in the Burren is the widespread exposure of associated sequences and the transecting vein system. N-S veins are ubiquitous within the Carboniferous rocks of the Irish Midlands, but their geometry is not easily mapped. In the Burren, however, the vertical persistence of vein clusters on different scales is evident and their hydraulic origin is clear, with the development of vuggy through to fibrous calcite vein infills and breccias. The presence of vertical N-S extension veins through to NNE-striking regional veins, sometimes showing a component of sinistral strike-slip movement, supports a fluid-driven origin associated with N-S compression.The absence of any evidence of normal faults thus rules out crustal extension with high differential stresses as the principal tectonic driver. Cross-cutting relationships between fold-related bed-parallel slip and N-S veins support their contemporaneous development, with the generation of southward-verging synclines above pre-existing, and underlying, northward dipping Mississippian normal faults and the valving of overpressured fluids from associated basins. Overpressuring is a natural consequence of disequilibrium compaction, pressure solution and a variety of other processes within subsiding extensional basins (Swarbrick *et al*. 2002), with pressure compartmentalisation controlled by regionally extensive shaley units/sequences and fault sealing (Walsh *et al*. 2018). Estimated Carboniferous burial depths of 3km, assuming post Serpukhovian-Bashkirian sequence thicknesses equivalent to those in the UK and Ireland, are capable of generating overpressures particularly in a basin characterised by extensive shale seals. Uplift and exhumation during the later stages of orogenesis provides a means of increasing overpressures to host rock fracture gradients with the development of extensional and strike-slip vein networks which valve overpressures (e.g. Corcoran and Dore 2002). Similar N-S extensional veins and NNE-NNW strike-slip veins associated with folding are seen in other parts of the Variscides (e.g. Muchez *et al*. 1995) and at broadly similar burial depths (Helsen and Köningshof 1994). Within a system dominated by locally derived carbonate rich fluids, the presence of quartz veins is attributed to either interbedded cherts or perhaps even the presence of underlying siliciclastic rocks belonging to the Old Red Sandstone, whilst previous geochemical studies indicate that fluorite contained within occasional veins is most likely derived from the Mississipiian basin fill (O'Connor *et al*. 1993).

Sulphides contained within the Burren veins are most easily sourced by scavenging from deeper basement rocks or by remobilisation from Mississippian Zn-Pb deposits. The potential for mineral deposits underlying the Burren region is supported by the presence of the Tynagh, Silvermines and Kilbricken mineral deposits within 40km to the east of the exposed Burren sequences. Early exploration studies at Kilbricken, which is adjacent to Quin in southeastern Clare (Fig. 1), originally identified sulphides in N-S calcite vein systems developed within Viséan stratigraphic units overlying the typical Waulsortian Limestone Formation host rock for Irish Zn-Pb deposits. N-S veins, which are a ubiquitous feature of the area, were used to vector into stratigraphically underlying potential

Waulsortian deposits (John Colthurst pers comm.), an approach which indirectly led to the discovery of Kilbricken. The presence of N-S veins and breccias transecting the Kilbricken deposit therefore makes a strong case for the source of sulphides within the vein system and provides a useful tool for Zn-Pb exploration. Furthermore the galena, sphalerite and chalcopyrite content of occasional N-S veins is consistent with the significant Cu content at Kilbricken, which is marked by elevated Cu content compared to many other Irish Zn-Pb deposits/prospects. Pb isotope ratios indicate a deep, predominantly Gondwanan source, but with a Laurentian contribution from the immediately underlying Down-Longford accretionary prism. Lead at the Burren is isotopically distinct from fluorite-bearing veins in the Galway Granite, and is most comparable to crustal sources directly along strike at Ballinalack and to a lesser extent is similar to Kilbricken (Fig. 13). Pb isotope analysis of a fluorite-bearing vein in the Galway granite (Costelloe Murvey Granite) has yielded strongly radiogenic $^{206}Pb/^{204}Pb$ (18.42), $^{207}Pb/^{204}Pb$ (15.61), $^{208}Pb/^{204}Pb$ (38.25) isotope ratios and very high μ (9.67), all uncharacteristically high for this part of Ireland. These values are isotopically distinct to samples from the Burren veins and from further north in Connemara/South Mayo, and are associated with high heat production for this intrusion of the Galway granite (from the breakdown of U and Th minerals; see Farrell *et al.* 2015).

Available geochronological and Pb isotope constraints of sulphide mineralisation within the Burren veins are indistinguishable from those of spatially related Mississippian Zn-Pb deposits. On geological grounds a Variscan timing attributed to hydraulic fracturing of overpressured basinal sediments during N-S compression is our preferred model for the formation of the vein system. Previously published Ar-Ar dating of alteration associated with a N-S vein within the Galway granite (O'Connor *et al*. 1993; Menuge *et al*. 1997) has indicated a Mid-Triassic date attributed to the downward migration of cool saline brines during the onset of mid-Atlantic rifting, an event marked by inception of the N-S oriented Slyne and Porcupine Basins about 100km to the west. Since normal faults did not, however, develop in the Burren region, we suggest that alteration of the Burren vein system, with associated replacement of sulphides by cerussite and smithsonite, may in fact be due to more recent groundwater flow (Cenozoic or younger), associated with karst development within the Burren limestones. This is well illustrated by the cave systems within the Burren, which are often localised along dense clusters of vertically persistent calcite veins (Cullaun 2; Fig. 5). The importance of veins to fluid flow in the Burren is very clear, and we suggest that future studies should investigate further the nature and timing of associated flow events using a range of new and emerging geochemical and geochronological techniques.

Conclusions

(1) Variscan-related deformation in the Burren region is relatively subdued, with gentle southward dips in the north giving way to southward verging folds attributed to the inversion of underlying northward dipping normal faults.

(2) Variscan NNE to NNW oriented extension calcite veins with subordinate strike-slip displacements are a ubiquitous feature of the entire Carboniferous sequence and are attributed to N-S Variscan compression and the hydraulic valving of overpressured fluids in Carboniferous basins.

(3) Changes in structure either side of the Gort Lowlands principally arise from temporal differences between post-rift sequences of the Burren and the normal faulted syn-rift

sequences fringing the Silurian inlier of SE Galway, rather than to the presence of an intervening shear zone.

(4) Sulphides within the Burren vein system, including galena, sphalerite and chalcopyrite, are interpreted to be sourced from underlying basement rocks and/or Mississippian mineral deposits, in an area which is along strike from the Tynagh and Ballinalack Zn-Pb deposits.

(5) Sulphide-bearing calcite veins in Viséan sequences can potentially aid vectoring to underlying Waulsortian Limestone-hosted Zn-Pb mineralisation.

(6) Isotope studies support a basinal origin for vein-related fluids, with petrographic studies indicating a later phase of alteration which is linked to recent groundwater flow and, perhaps, to the downwards ingress of fluids during Mid-Triassic rifting.

(7) Veins and vein clusters are often the locus for groundwater flow, because they are much more vertically persistent than conventional joints.

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Appendix 1:

Pb isotope analysis - methods:
Lead isotope analysis was carried out on two calcite-fluorite-galena-smithosonite veins analysed from Sheshodonnell East Mine, the Burren. Galena was extracted using a handheld dentist drill. Approximately 5mg of galena was dissolved by adding 2.5ml of 6M HCl and 250µl of 70 % HNO_3. The samples were dried a hotplate at ~120°C, and re-dissolved in 19ml of deionised water and 1ml of 70% HNO_3. Subsequently, an aliquot of 10µl was taken, centrifuged, diluted with 2.5ml of 3% HNO_3, and spiked with 25µl of thallium solution of known $^{203}Tl/^{205}Tl$ ratio to correct for mass bias fractionation. Sample solutions were analysed using a Thermo-Scientific Neptune multi-collector inductively coupled plasma mass spectrometer at the National Centre for Isotope Geochemistry, University College Dublin (UCD). The two year mean values of standard NIST NBS 981 (n=25) for this method at UCD is $^{206}Pb/^{204}Pb = 16.9348$, $^{207}Pb/^{204}Pb = 15.4895$ and $^{208}Pb/^{204}Pb = 36.6916$. Data was corrected to the known Pb isotopic ratios for NIST NBS 981 as reported by Yuan *et al*. (2016). Mean standard error (%) of NBS 981 was $^{206}Pb/^{204}Pb = 0.0034\%$, $^{207}Pb/^{204}Pb = 0.0049\%$ and $^{208}Pb/^{204}Pb = 0.0073\%$.

The two samples of galena from The Burren yielded $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of 18.2004-18.2630, 15.5611-15.5778, and 38.0349-38.0994, consistent with samples analysed from the region (see discussion). Calculated model ages are 226-213 Ma (Upper Triassic) according to the two-stage model of Stacey and Kramers (1975). Calculated μ values are 9.58-9.52.

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Figure Captions:

Fig. 1 - Simplified geology of north Clare, including the limestones of the Burren (Mullan 2003, after MacDermot *et al*. 2003). Selected prominent veins are shown in yellow. The locations of Cullaun 2 cave (1), MacDermot's vein/fault (2), Poll Gonzo cave (3) and Sheshodonnell mine (4) are shown in red. The location of aerial photograph in Fig. 4A is shown as red box. The NNE-trending Fergus Shear Zone (FSZ; green dashed lines) from Coller (1984) has been interpreted to separate Zones 2a and 2b of the Variscan deformation map of Ireland developed by Gill (1962); these zones are sometimes referred to respectively as the Central Ireland Zone (Cooper *et al.* 1986) and the Clare Block (Coller 1984).

Fig. 2 - (A) Lithostratigraphic column for north Clare (modified after Gallagher *et al*. 2006, Pracht and Somerville 2015). (B) View southwards over the east side of Black Head in north Clare highlighting the ubiquitous nature of the N-S veins transecting the Burren sequence. Location of close up in Fig. 2C highlighted by red box. (C) Close-up of hillside showing the persistence of veins across the 50cm thick shale at the boundary of the Maumcaha and (overlying) Aillwee members of the Burren Limestone Formation.

Fig. 3 - Veins on the lower slopes of Capanawalla (A) and on the shore of Galway Bay close to Gleninagh Castle (B-C). (a) North-south veins occurring in clusters and transecting bedding (view towards north). (b) Outcrop photo of calcite veins on the shoreline adjacent to Gleninagh Castle (view towards north). (c) Calcite vein offset by bedding parallel slip in Cullaun 2 cave (slickenfibres are developed along this slip surface).

Fig. 4 - Aerial photographs, sourced from Bing, of the Burren at different scales highlighting the presence of veins. (A) Area adjacent to the Poll Gonzo vein system, highlighting other major regional veins (from Bell Harbour (x2) and Turlough vein systems), (B) Larger-scale view of vein system on west side of Turlough hill (location shown in A). Significant veins are vegetated arising from preferential erosion of bedrock, and also groundwater and surface water related karstification.

Fig. 5 - (A) Cave map for Cullaun 2 Cave (Mullan 2003) with selected cave profiles at different positions along the cave system (scale of profiles is x40 that of the map scale). (B) N-S calcite vein (15cm thick) in Cullaun 2. (C) Vein-associated hydraulic breccia within Cullaun 2. The location of this vein is shown with black arrow on map (A).

Fig. 6 - (A) Profile of Poll Gonzo showing the location of drops and horizontal wayboards, with the latter usually developed above clay layers (Bunce 2010). This profile is parallel to a relatively planar cluster of NNE-trending veins, the vertical nature of which is illustrated by the very elongate cave passageways produced by karstification along vein systems. (B) Photograph showing sub-vertical NNE-trending silica and calcite veins, which are partly karstified and iron-stained arising from groundwater flow. The veins crosscut a c.25cm clay wayboard layer elsewhere in the cave system.

Fig. 7 - (A) Quartz vein with carbonate clasts and vuggy infills. (B) Quartz vein with multiple infills. (C) Sub-horizontal slickensides on the margin of quartz vein indicating a component of strike-slip movement.

Fig. 8 - Geological map showing the location of mapped siliceous veins (yellow) and vein-hosted mineral deposits (orange) from the work of Conor MacDermot (GSI); the types of sulphide and

presence of fluorite is recorded for the latter. Siliceous veins generally comprise a subordinate and patchy component of quartz infill within individual veins which are otherwise dominated by calcite: in that sense the red lines only mark the presence of quartz within the broader calcite filled veins of the Burren system. The approximate position of the southern boundary of the Galway Granite (GG) and the Orlock Bridge Fault (OBF) derived from MacDermot *et al*. (2003) are also shown as dashed black lines (see text for details). Map units and symbols are same as those provided in Fig. 1.

Fig. 9 - Clusters of veins containing multiple quartz-bearing, NNE-trending, calcite veins. (A) Main cluster of veins on Turlough Hill (view looking N). (B) Smaller vein from Aillwee Hill (view looking N).

Fig. 10 - Outcrop expression of NNE-trending quartz and quartz-calcite veins which, in contrast to exclusively calcite veins, provide positive relief and resistant ridges which extend discontinuously across the central Burren region. (A) Quartz-calcite vein from Aillwee Hill displaying a rough, almost rubbly, surface arising from the patchy dissolution of limestone clasts and calcite within a hydraulic breccia (1m ruler for scale; looking SE). (B) Ridge associated with a quartz vein, Fahee South (looking N).

Fig. 11 - Geological map and aerial photograph of Fahee South, showing the locations of silica veins originally mapped by Conor MacDermot (GSI online digital archive – GOLDMINE; secure.dcenr.gov.ie/goldmine/index.html). (A) Field sheet and map showing stratigraphic units and veins (highlighted in yellow). (B) Aerial photograph (from Bing) highlighting the very pervasive nature of N-S calcite trending veins compared to those which are quartz-bearing (yellow); closer inspection shows the presence of many structures, interpreted to be veins, parallel to the mapped structures.

Fig. 12 - Aerial photograph showing the Poll Gonzo vein system (yellow line), together with the locations of Poll Gonzo Cave, Poll a Bhallain (a large doline) and the sites of two old Pb mines. Background map image sourced from Bing.

Fig. 13 - (A) Photomicrograph (under cross-polarised light) of quartz with subordinate amounts of calcite transected by coarser quartz vein (central part of image) from Poll Gonzo. (B) Photomicrograph (under cross-polarised light) of vein with quartz-calcite intergrowths from Poll Gonzo, a texture which upon dissolution provides a spongiform texture in hand specimen. (C) Sawn hand-specimen from Sheshodonnell exhibiting limestone replaced by quartz and galena, with vein filled by fluorite overgrown by smithsonite. (D) Outcrop photograph of quartz, fluorite- and sulphide-bearing vein, which includes pyrite, galena and sphalerite: this vein is strongly altered by recent groundwater flow, with the formation of smithsonite and limonite.

Fig. 14 – (A)_^{206}Pb/^{204}Pb - ^{207}Pb/^{204}Pb plot for galena samples from across Ireland. Red and black symbols reflect galena from Lower Paleozoic-hosted mineral deposits across Ireland from the north and south of the Iapetus suture respectively (excluding basement veins of the Longford-Down Terrane). Strictly Laurentian-derived galena can be characterised by a source μ value of ~9.2, whereas those from southeast Ireland (e.g. Avoca, Glendalough) are characterised by a μ value of ~9.9. Samples from Lower Paleozoic basement veins of the Longford-Down Terrane and the Burren (this study) form linear trends between these curves as do other Carboniferous-hosted Zn-Pb deposits such as Navan, Lisheen and Silvermines. (B) Contoured average μ values for galena occurrences from northwest Ireland, with significant Zn-Pb and Au deposits labelled. Contoured using inverse distance weighting in ArcGIS (binned by geometric intervals). Data sources: Everett *et al*. (2003), Kinnaird *et al*. (2002),

LeHuray *et al*. (1987), O'Keefe (1986), Standish *et al*. (2014), and also personal communication Stephen Hollis and colleagues.

Fig. 15 - Schematic diagram illustrating the geometry of Variscan monoclines and vein systems relative to pre-existing underlying normal fault systems. The Mississippian syn-rift (green) and post-rift (blue into orange-tan) sequences show differing amounts of deformation, with only south-facing monoclines developed within higher stratigraphic units of the post-rift sequence. Lower Paleozoic basement (grey) underlies Careboniferous syn-rift and post-rift sequences. Diagram is for illustrative purposes only and is not a 3-dimensional model of the Burren region.

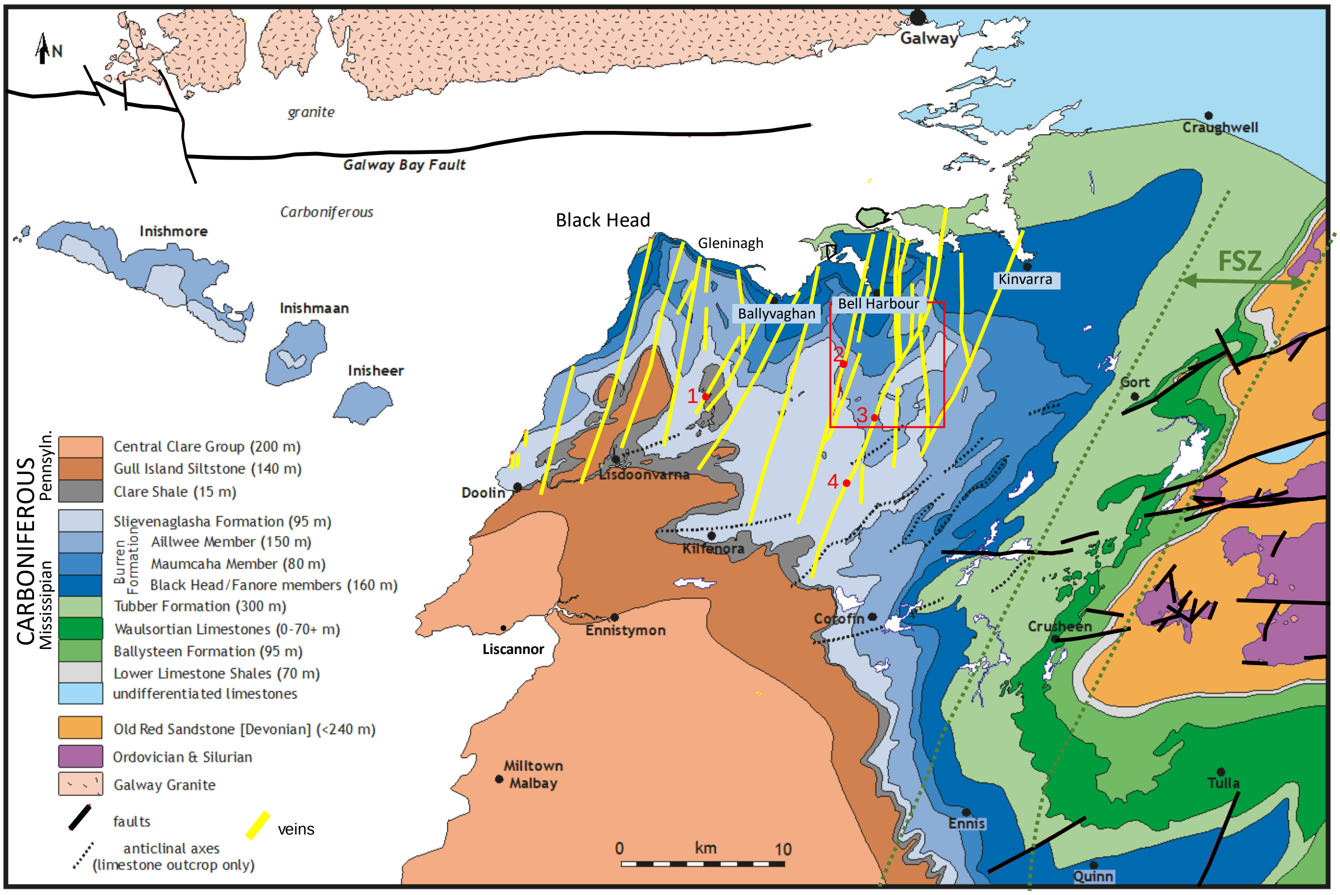

N
Galway
granite
Galway Bay Fault
Craughwell
Carboniferous
Inishmore
Inishmaan
Inisheer
Black Head
Gleninagh
Ballyvaghan
Bell Harbour
Kinvarra
FSZ
Gort
1
2
3
4
Lisdoonvarna
Doolin
Kilfenora
Corofin
Crusheen
Ennistymon
Liscannor
Milltown Malbay
Ennis
Tulla
Quinn
0
km
10
CARBONIFEROUS
Pennsyln.
Mississipian
Burren Formation
Central Clare Group (200 m)
Gull Island Siltstone (140 m)
Clare Shale (15 m)
Slievenaglasha Formation (95 m)
Aillwee Member (150 m)
Maumcaha Member (80 m)
Black Head/Fanore members (160 m)
Tubber Formation (300 m)
Waulsortian Limestones (0-70+ m)
Ballysteen Formation (95 m)
Lower Limestone Shales (70 m)
undifferentiated limestones
Old Red Sandstone [Devonian] (<240 m)
Ordovician & Silurian
Galway Granite
faults
veins
anticlinal axes
(limestone outcrop only)

Figure 1:

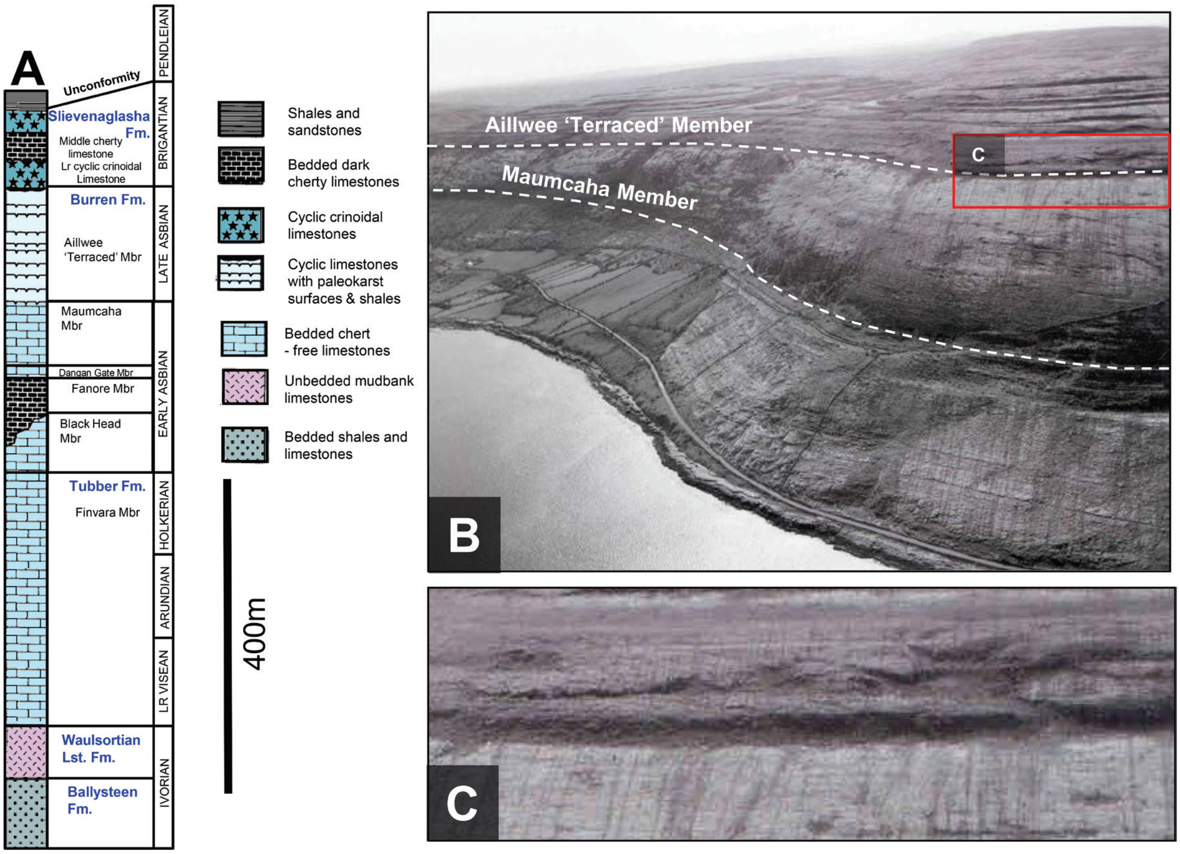

A
Unconformity
Slievenaglasha Fm.
Middle cherty limestone
Lr cyclic crinoidal Limestone
Burren Fm.
Aillwee 'Terraced' Mbr
Maumcaha Mbr
Dangan Gate Mbr
Fanore Mbr
Black Head Mbr
Tubber Fm.
Finvara Mbr
Waulsortian Lst. Fm.
Ballysteen Fm.
PENDLEIAN
BRIGANTIAN
LATE ASBIAN
EARLY ASBIAN
HOLKERIAN
ARUNDIAN
LR VISEAN
IVORIAN
Shales and sandstones
Bedded dark cherty limestones
Cyclic crinoidal limestones
Cyclic limestones with paleokarst surfaces & shales
Bedded chert - free limestones
Unbedded mudbank limestones
Bedded shales and limestones
400m
Aillwee 'Terraced' Member
Maumcaha Member
C
B
C

Figure 2:

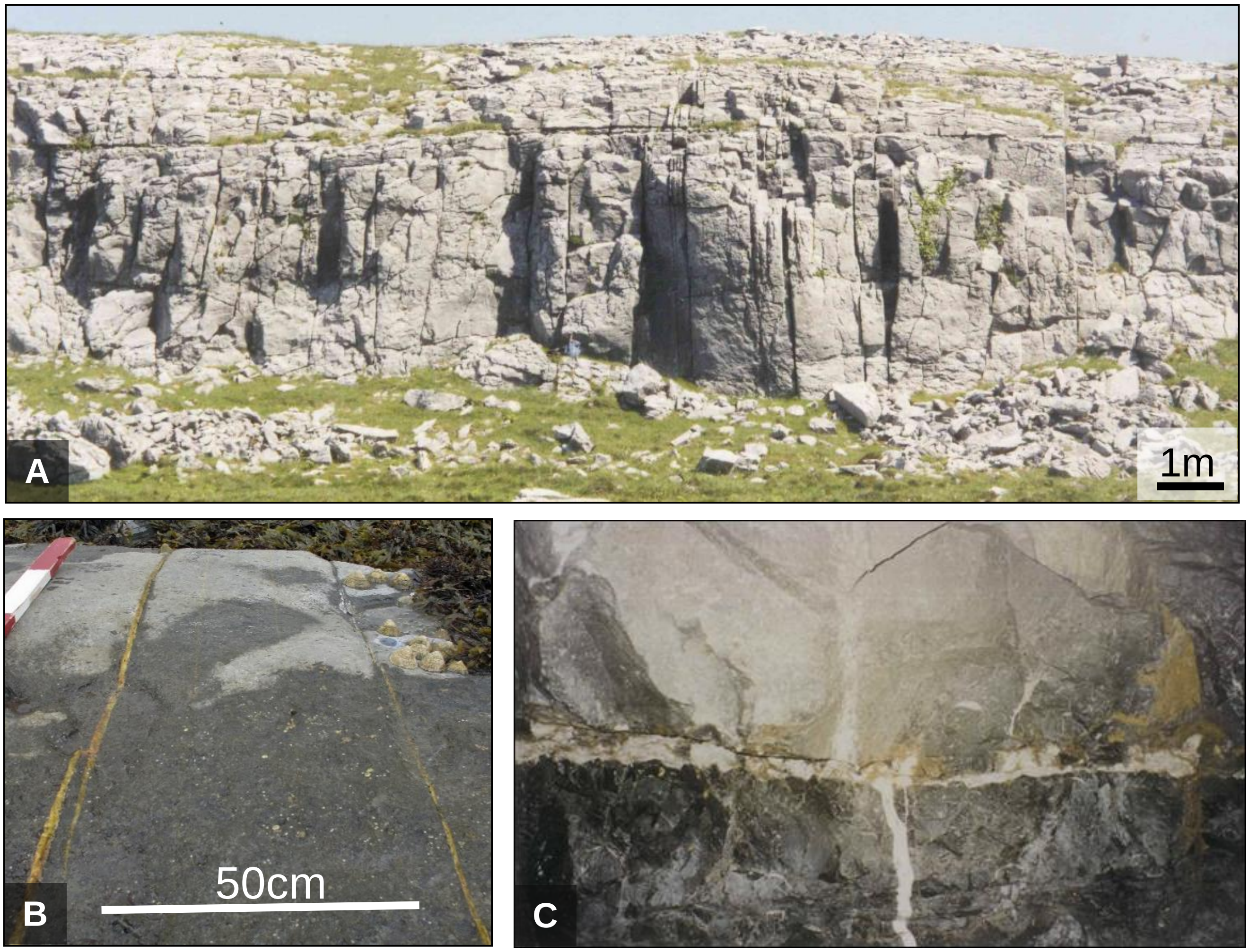


Figure 3:

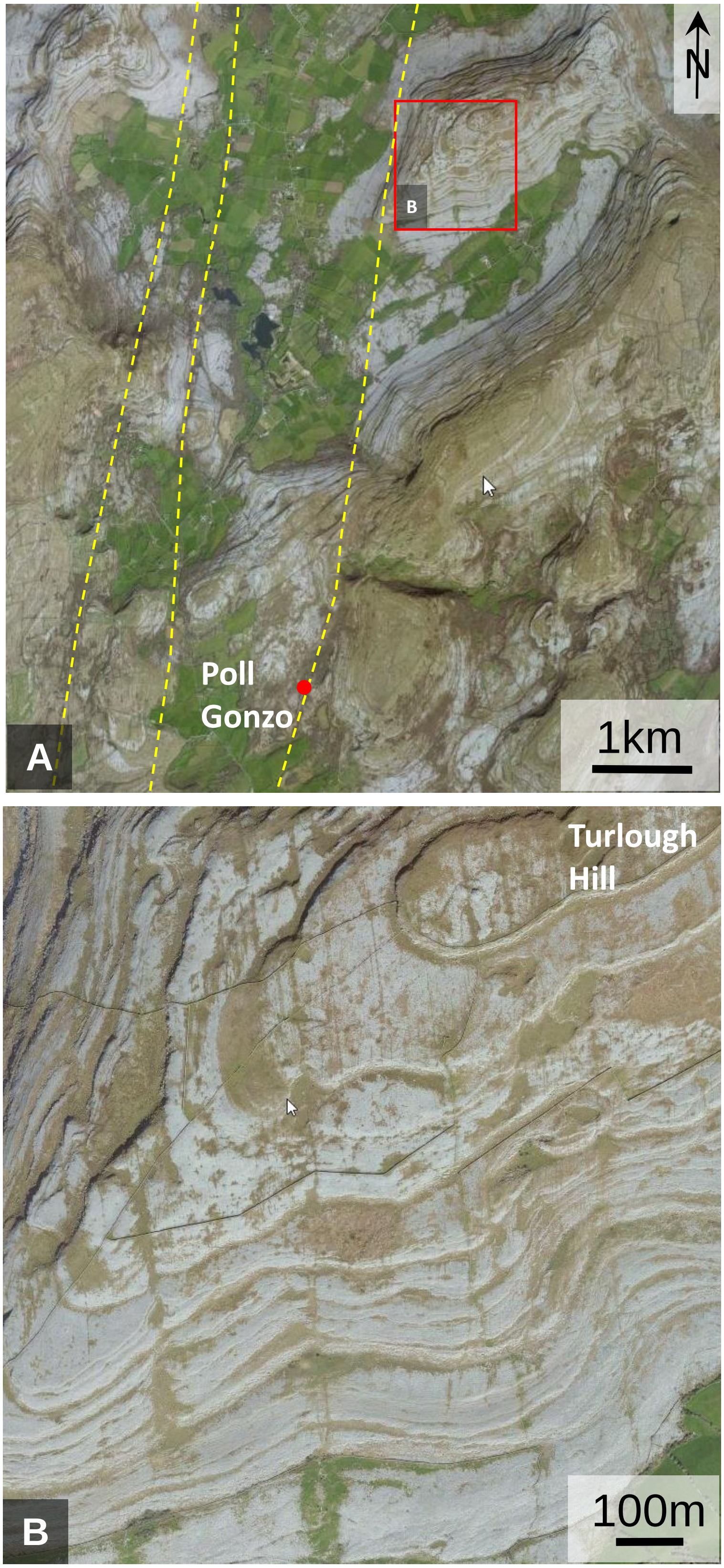


Figure 4:

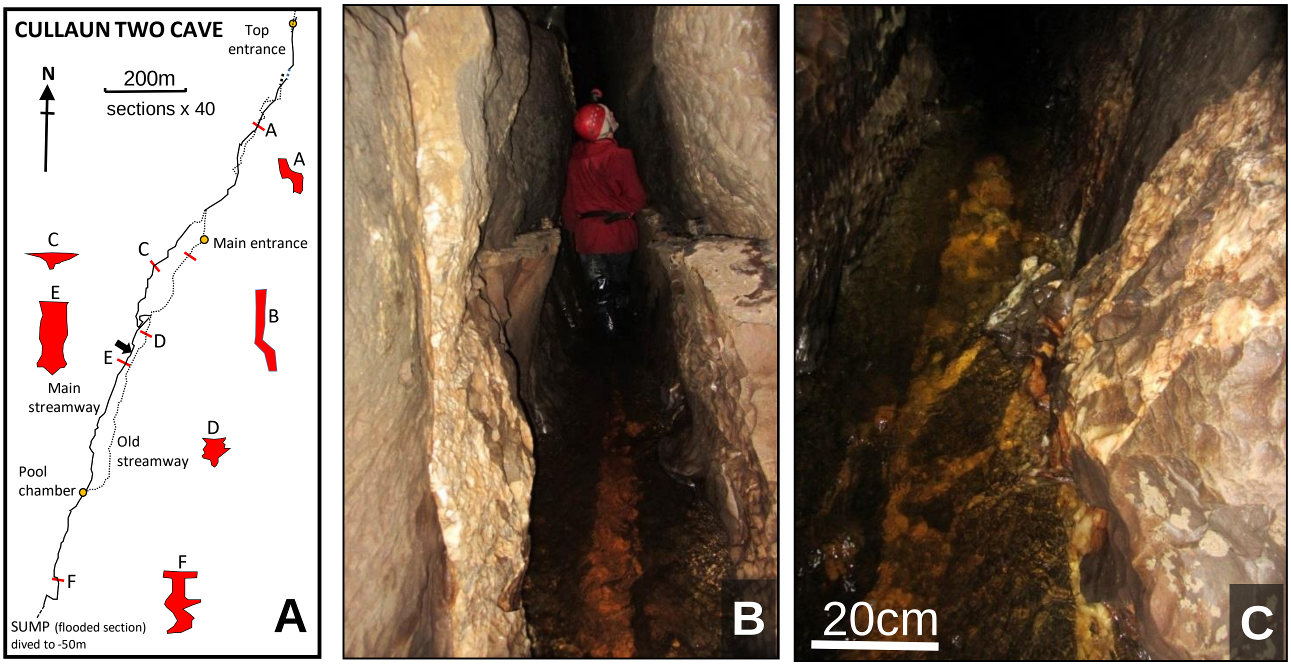

CULLAUN TWO CAVE
Top entrance
N
200m
sections x 40
A
A
C
C
Main entrance
E
B
D
E
Main streamway
Old streamway
D
Pool chamber
F
F
SUMP (flooded section)
dived to -50m
A
B
20cm
C

Figure 5:

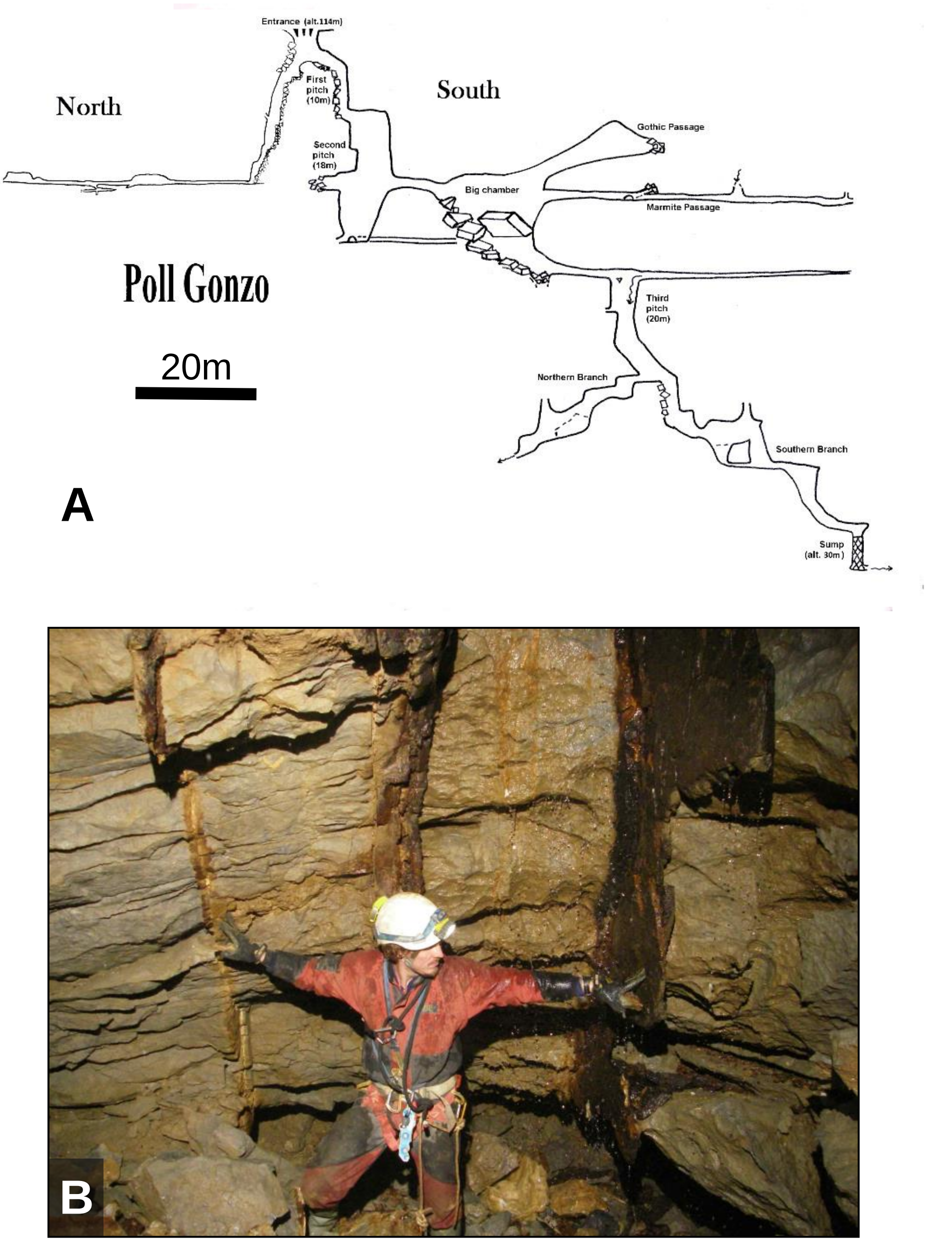

Entrance (alt.114m)
North
South
First pitch (10m)
Second pitch (18m)
Gothic Passage
Big chamber
Marmite Passage
Poll Gonzo
20m
Third pitch (20m)
Northern Branch
Southern Branch
Sump (alt. 30m)
A
B

Figure 6:

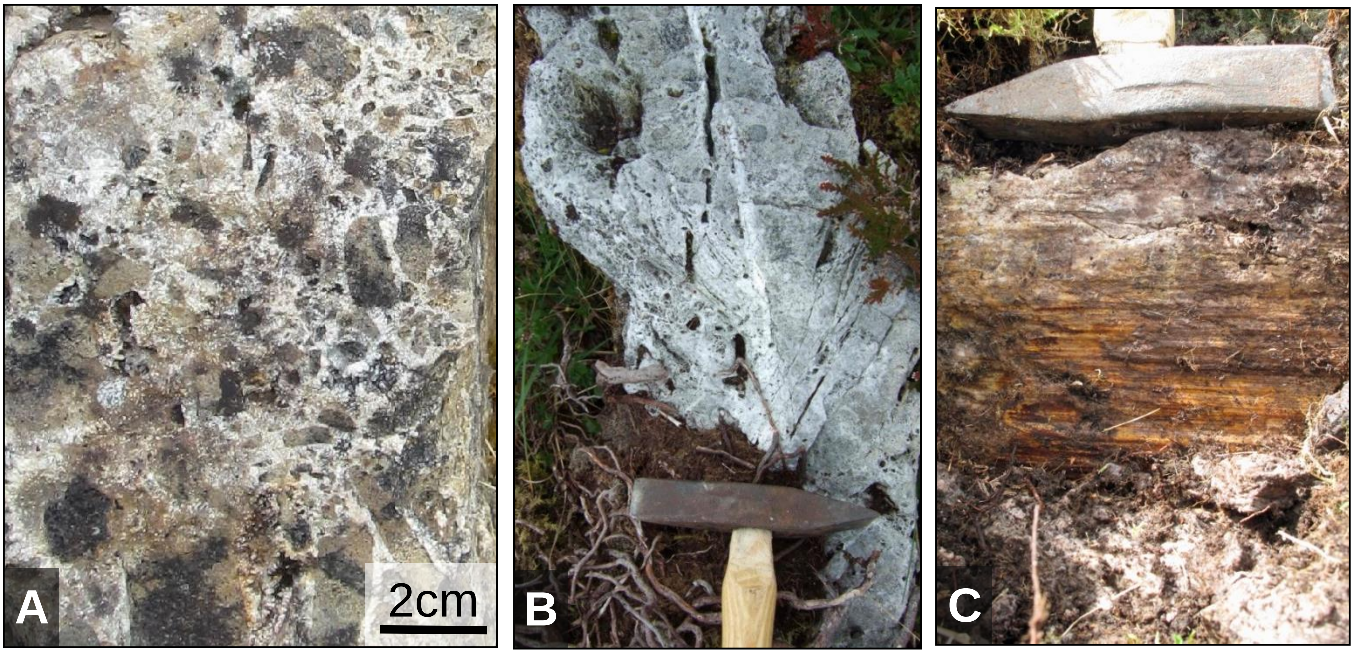


Figure 7:

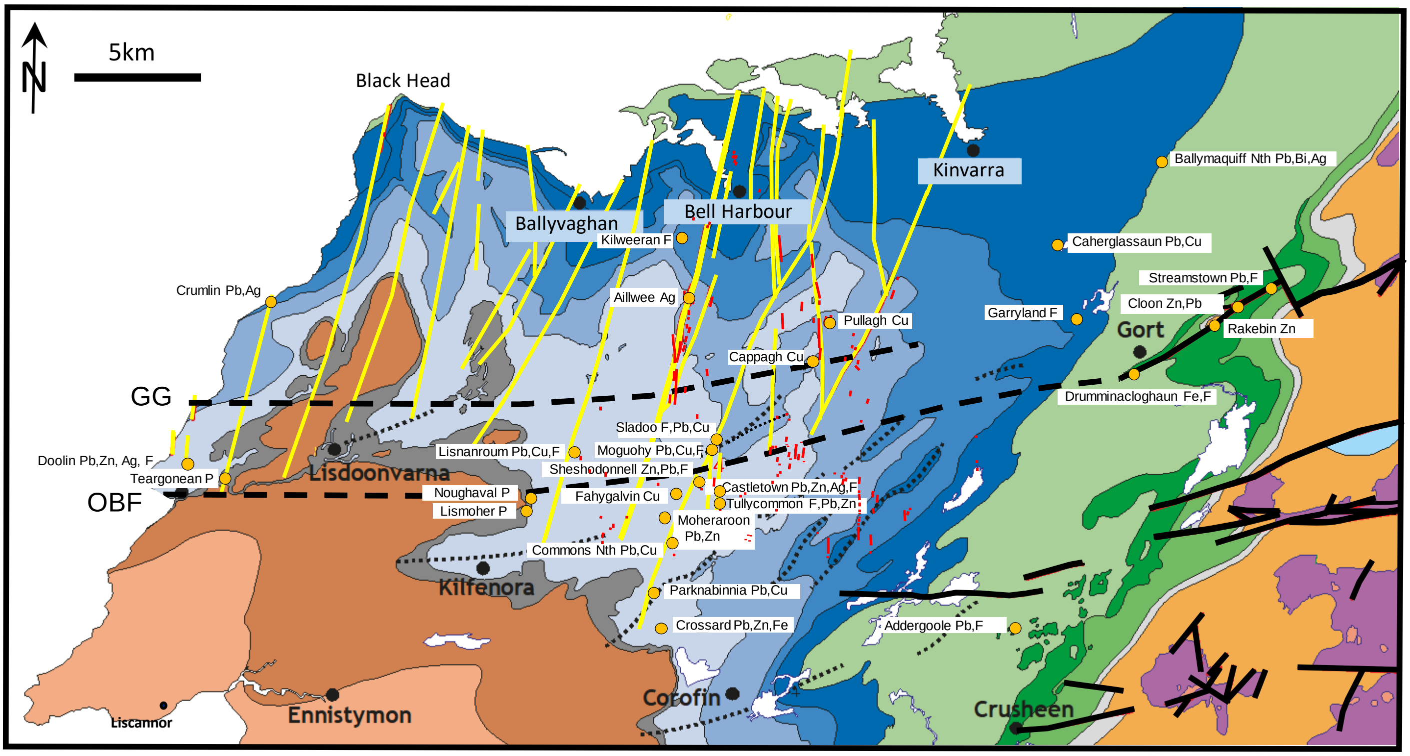

N
5km
Black Head
Ballyvaghan
Bell Harbour
Kinvarra
Ballymaquiff Nth Pb,Bi,Ag
Kilweeran F
Caherglassaun Pb,Cu
Crumlin Pb,Ag
Aillwee Ag
Streamstown Pb,F
Cloon Zn,Pb
Garryland F
Pullagh Cu
Rakebin Zn
Gort
Cappagh Cu
GG
Drumminacloghaun Fe,F
Sladoo F,Pb,Cu
Lisnanroum Pb,Cu,F
Moguohy Pb,Cu,F
Doolin Pb,Zn, Ag, F
Sheshodonnell Zn,Pb,F
Teargonean P
Lisdoonvarna
Castletown Pb,Zn,Ag,F
OBF
Noughaval P
Fahygalvin Cu
Tullycommon F,Pb,Zn
Lismoher P
Moheraroon Pb,Zn
Commons Nth Pb,Cu
Kilfenora
Parknabinnia Pb,Cu
Crossard Pb,Zn,Fe
Addergoole Pb,F
Corofin
Crusheen
Ennistymon
Liscannor

Figure 8:

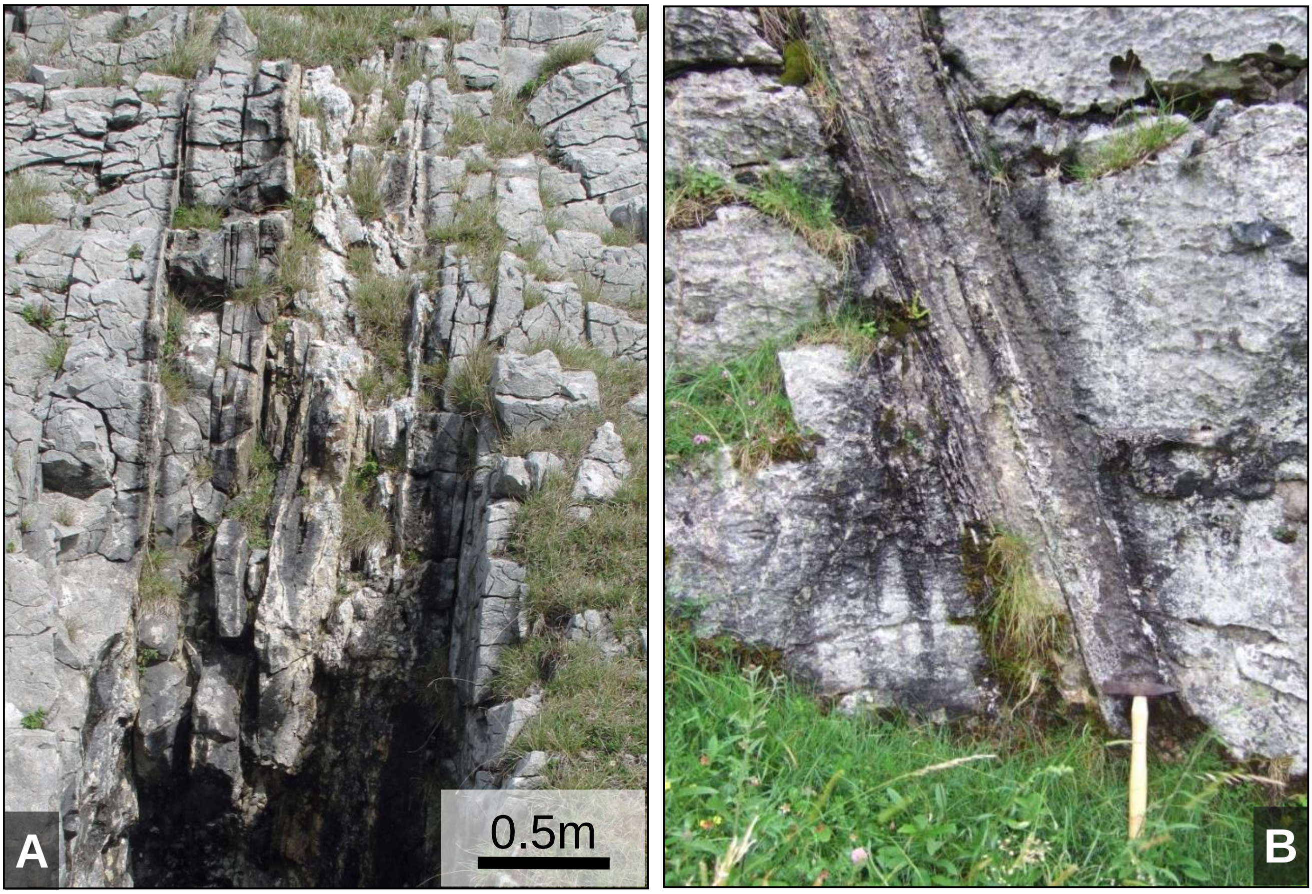


Figure 9:

Figure 10:

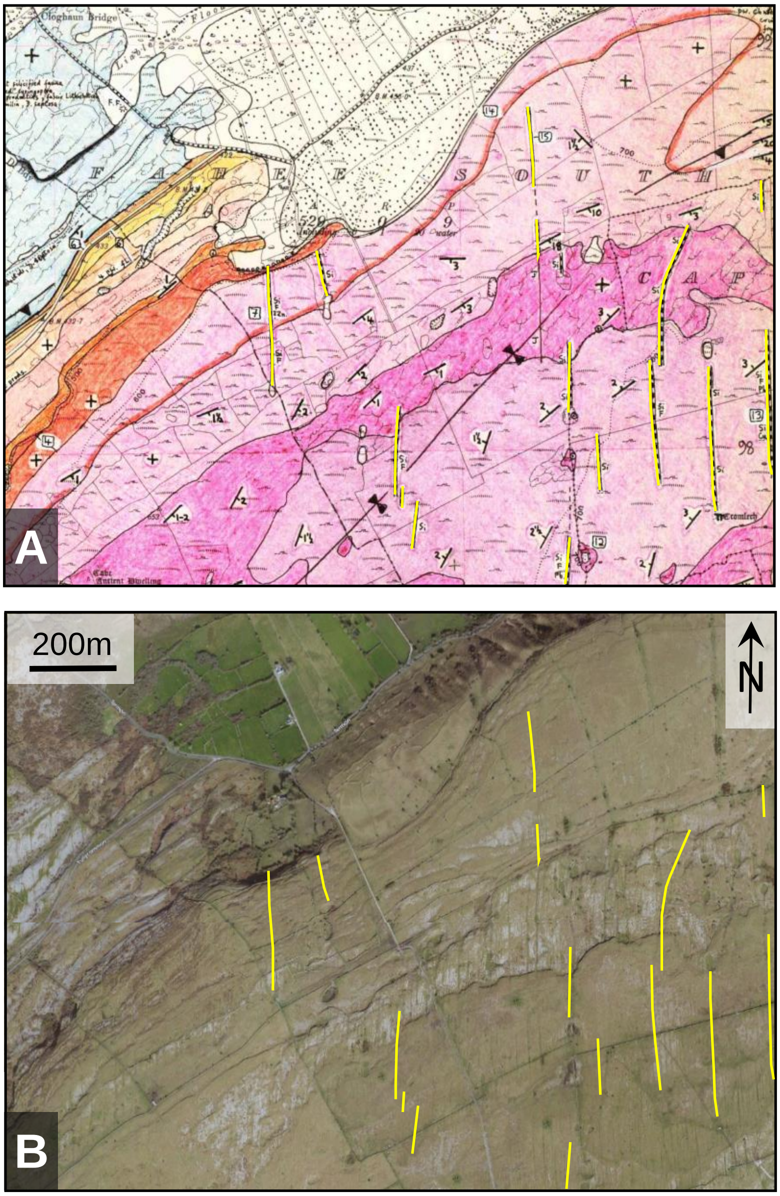


Figure 11:

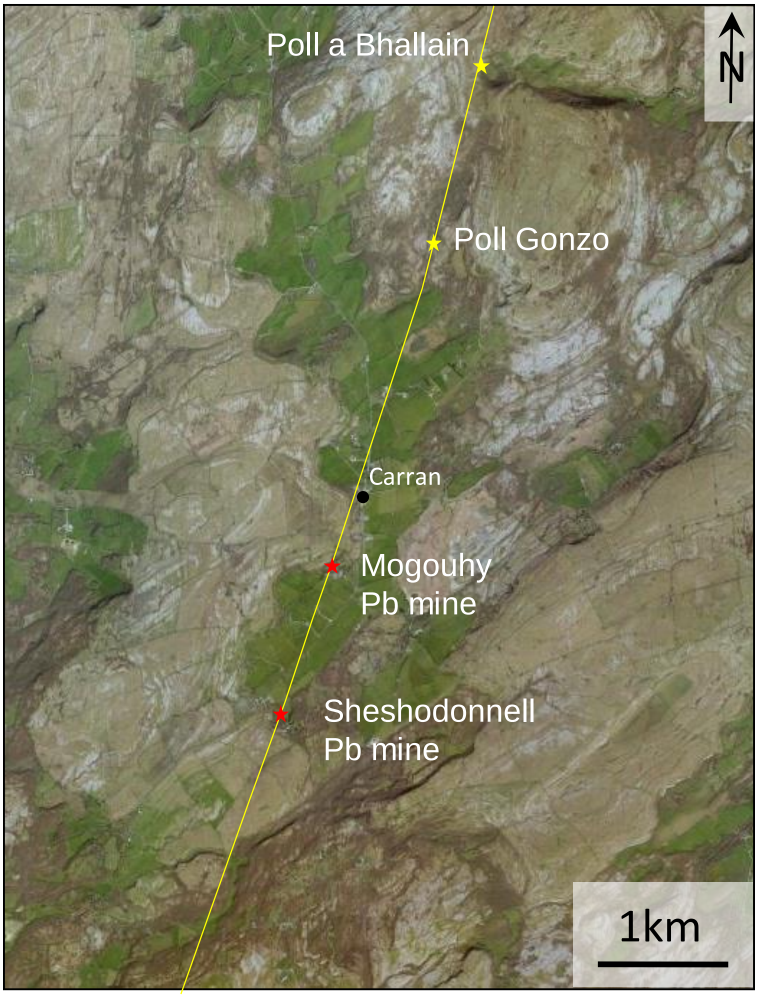
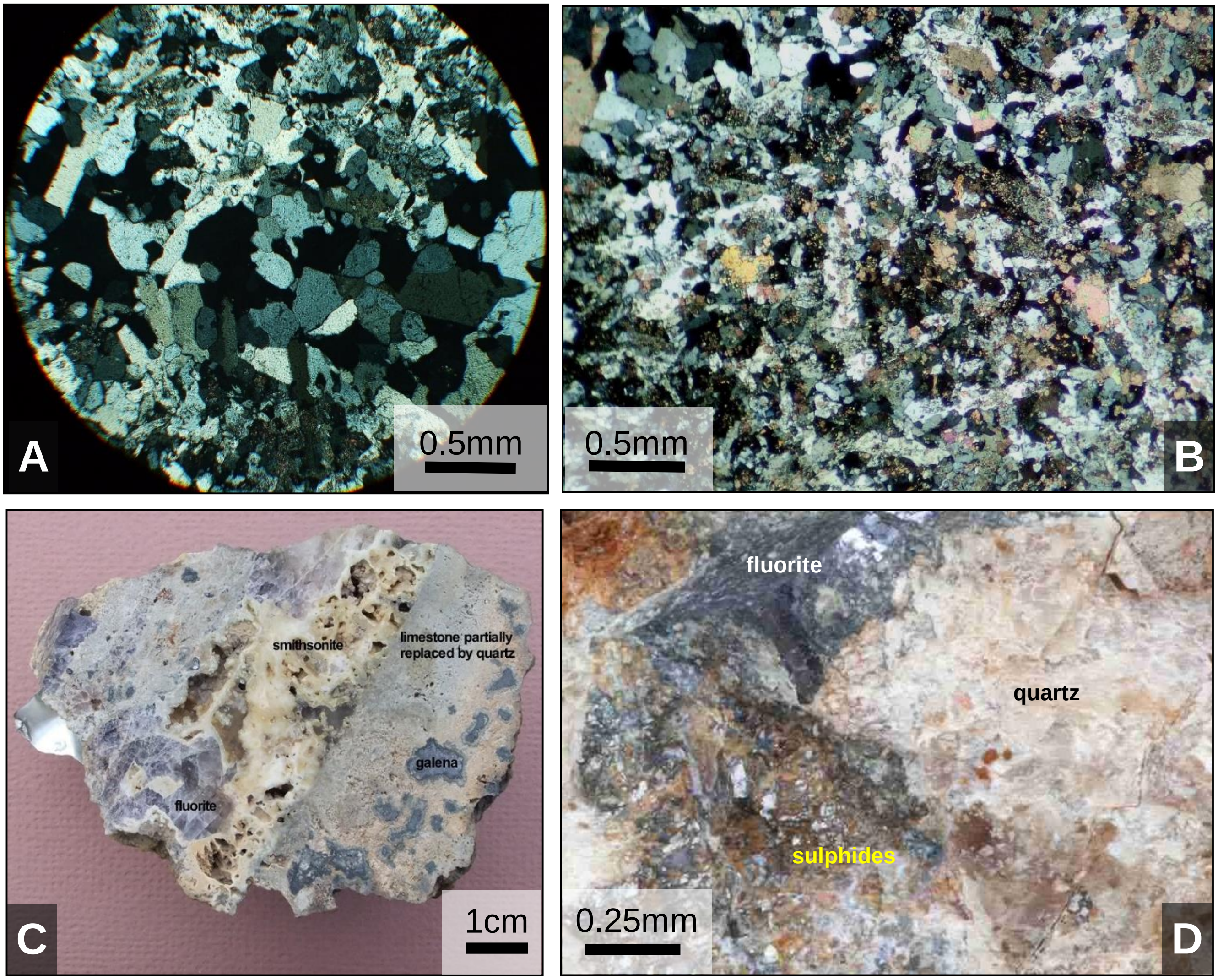

Poll a Bhallain
N
Poll Gonzo
Carran
Mogouhy
Pb mine
Sheshodonnell
Pb mine
1km

Figure 12:


0.5mm
A
0.5mm
B
smithsonite
limestone partially replaced by quartz
galena
fluorite
1cm
C
fluorite
quartz
sulphides
0.25mm
D

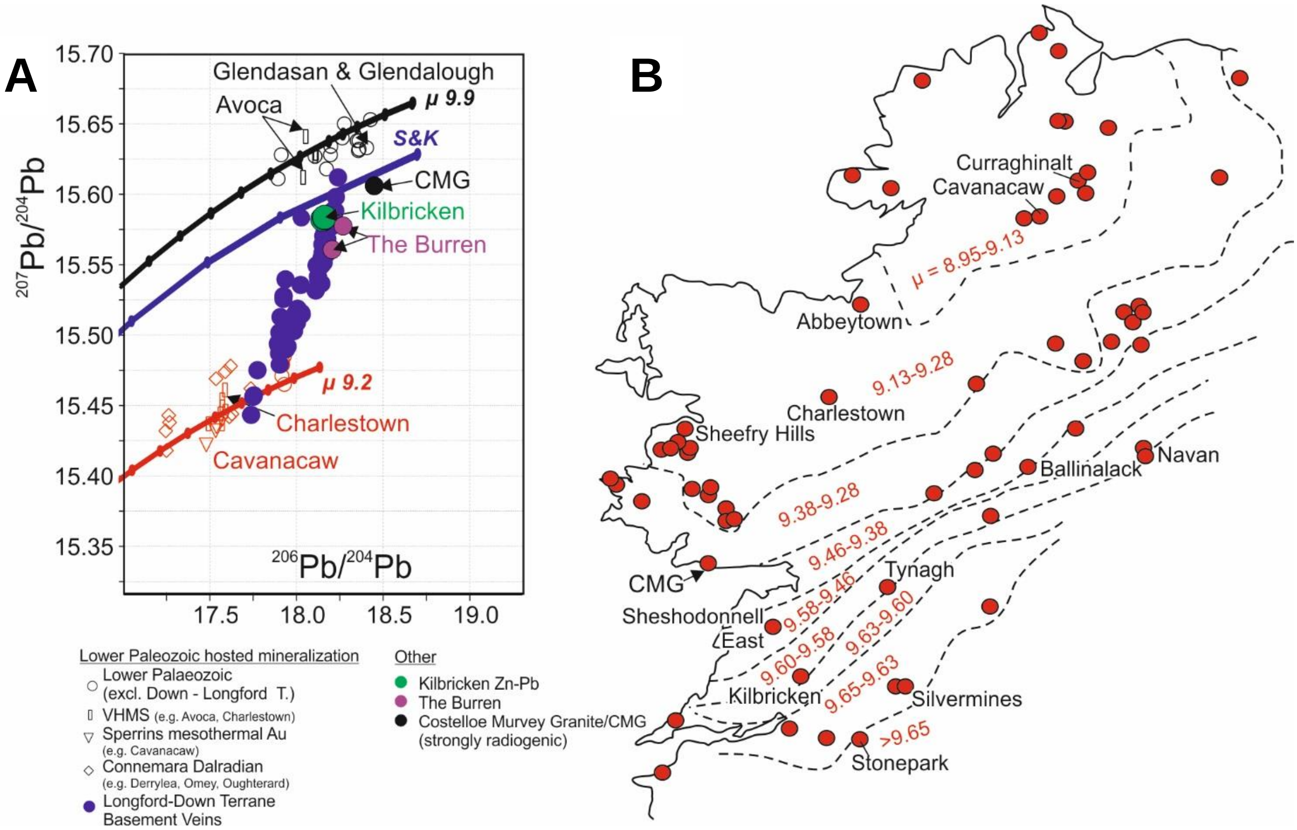

A
B
15.70
15.65
15.60
15.55
15.50
15.45
15.40
15.35
$^{207}Pb/^{204}Pb$
$^{206}Pb/^{204}Pb$
17.5
18.0
18.5
19.0
Glendasan & Glendalough
Avoca
μ 9.9
S&K
CMG
Kilbricken
The Burren
μ 9.2
Charlestown
Cavanacaw
Lower Paleozoic hosted mineralization
○ Lower Palaeozoic (excl. Down - Longford T.)
▯ VHMS (e.g. Avoca, Charlestown)
▽ Sperrins mesothermal Au (e.g. Cavanacaw)
◇ Connemara Dalradian (e.g. Derrylea, Omey, Oughterard)
● Longford-Down Terrane Basement Veins
Other
● Kilbricken Zn-Pb
● The Burren
● Costelloe Murvey Granite/CMG (strongly radiogenic)
Curraghinalt
Cavanacaw
μ = 8.95-9.13
Abbeytown
9.13-9.28
Charlestown
Sheefry Hills
Navan
Ballinalack
9.38-9.28
9.46-9.38
CMG
Tynagh
Sheshodonnell East
9.58-9.46
9.60-9.58
9.63-9.60
Kilbricken
9.65-9.63
Silvermines
>9.65
Stonepark

Figure 14:

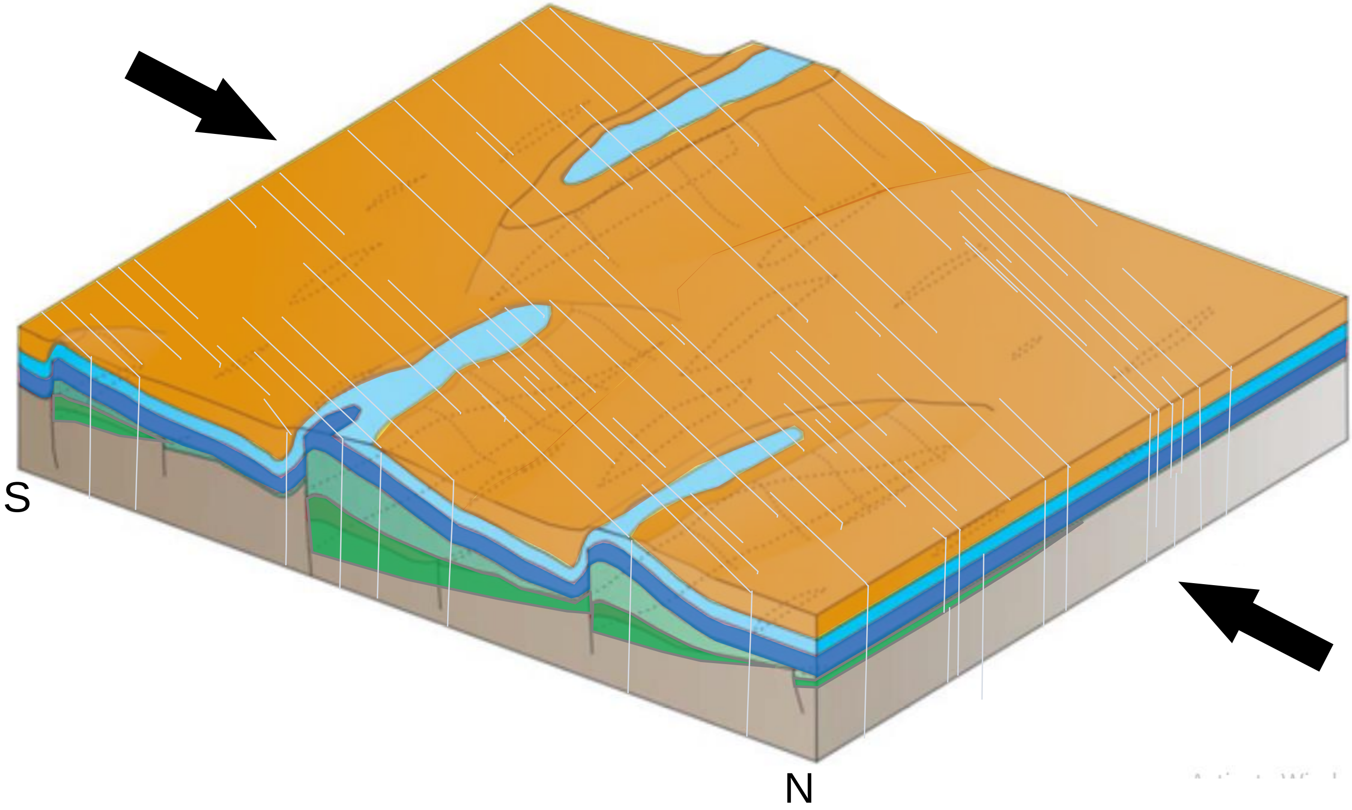


Figure 15