Regional remagnetization of Irish Carboniferous carbonates
dates Variscan orogenesis, not Zn-Pb mineralization

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\textbf{ABSTRACT}

Paleomagnetic methods have been used in economic geology to date mineralization in sediment-hosted ore deposits and thereby help to develop ore deposit models and understand the geodynamic settings in which mineralization can occur. However, paleomagnetic ages are sometimes inconsistent with other geochronological techniques and with geological observations. Here we test the veracity of paleomagnetic ages for sediment-hosted ores through a study of the Irish Midlands ore field. We find that unaltered rocks distal to mineralization that are of equivalent age to the ore host sequence have comparable characteristic remanent magnetic directions to those previously derived from the ores. This indicates that remagnetization of the rocks was probably independent of the ore-forming process. Comparison with the apparent polar wander path for Europe suggests an age of ca. 310 Ma for this event, consistent with the
timing of the Variscan orogeny. Fold test results support this, indicating the signal was acquired after tilting and/or folding of the host rocks. Petrology and magnetic data suggest that nanometric magnetite particles are the remanence carrier. Based on independent geochronological and geological constraints, we conclude that mineralization formed in Ireland in the early Carboniferous coincident with basin development and that paleomagnetic dates were reset during the later orogenic overprint.

Caution is therefore warranted in the interpretation of paleomagnetic dates for ore systems, and geodynamic models for mineral systems based on these may be erroneous.

INTRODUCTION

Sedimentary rock–hosted hydrothermal ore deposits are a major source of lead, zinc, and copper. Their origins are believed to be diverse: formation synchronously with their host rocks from fluids that may have vented at the seafloor (sedimentary exhalative, Sedex, deposits); formation during burial and diagenesis; or synorogenic (Wilkinson, 2014). In many cases, due to the lack of minerals amenable to dating by radiogenic isotopic methods, ore genesis and geodynamic settings of mineralization remain controversial. This is because the timing of mineralization with respect to host-rock deposition can only be inferred from often ambiguous textural relationships between ore minerals and sedimentary structures. This uncertainty affects three important issues: (1) mineral exploration models are based on an assumed age relationship between ore and host rock; (2) viable sulfide precipitation mechanisms are constrained by the physicochemical environment of ore formation; and (3) the geodynamic setting of well-mineralized basins and the fluid-flow systems that formed them are interpreted based on the assumed age of mineralization. For example, Leach et al. (2001) argued for a link
between carbonate-hosted Zn-Pb Mississippi Valley–type (MVT) deposits and supercontinent assembly cycles involving topographically driven fluid flow ahead of the advancing orogen. However, the temporal correlation between deposit genesis and major collisional orogens is largely dependent on paleomagnetic ages for ore formation. If these ages reflect an orogenic overprint, then this association would be expected and the inferred models would be invalidated.

The paleomagnetic dating method involves the isolation of a characteristic remanent magnetic (ChRM) orientation acquired during mineralization and comparison of this with the apparent polar wander (APW) path for the terrane in question within the relevant period of Earth history. Two basic assumptions apply: (1) that the measured magnetic orientation was acquired during the ore-forming event; and (2) that the orientation of the Earth’s magnetic field (APW path) is sufficiently well known for the time period in question.

Here we specifically test the first assumption based on a study of the Irish Midlands Zn-Pb ore field. The region provides an excellent opportunity to address the veracity of paleomagnetic dating because the system has been extensively studied, yet controversy remains regarding the timing of mineralization. Geological constraints and recent Re-Os dating suggest that the ores are early Carboniferous (Hnatyshin et al., 2015), whereas published paleomagnetic dates range from early Carboniferous to early Permian (Symons et al., 2007; Pannalal et al., 2008a, 2008b); the latter have been used to argue for a synorogenic or postorogenic origin for the Irish deposits.

**GEOLOGICAL SETTING AND SAMPLING**
The ore-hosting carbonate rocks are located in the central Ireland Midlands Basin, which began to develop in the Mississippian during a period of dextral transtensional strain across the Laurussian continental margin. This was related to oblique convergence between Laurussia and Gondwana that affected much of northern Europe (e.g., McKerrow et al., 2000). The progressive Variscan collision ultimately led to the amalgamation of Pangea in the late Carboniferous–early Permian (ca. 300 Ma; Stampfli et al., 2013).

A diachronous northward marine transgression across the margin established a shallow ramp environment in which a shale-limestone sequence was deposited. At some stage, hydrothermal solutions flooded through the sequence and precipitated tens of millions of tons of zinc and lead in the form of sulfides (Andrew, 1993; Hitzman and Beaty, 1996; Wilkinson and Hitzman, 2015). The Navan deposit represents the largest accumulation of ore minerals, but economically exploitable ores also formed at Tynagh, Silvermines, Galmoy, and Lisheen (Fig. 1). At least 20 more subeconomic prospects have been identified, making the district one of the most intensely Zn mineralized terrains on Earth.

The most contentious issue with respect to deposit genesis is the timing (and burial depth) of mineralization. Based on geological and isotopic arguments it is thought that the deposits either (1) formed during deposition and early diagenesis, within ~15 m.y. of host rock deposition and within a few hundred meters of the paleoseafloor (e.g., Wilkinson and Hitzman, 2015; Wilkinson et al., 2005); or (2) formed during deeper burial, after lithification was complete (e.g., Peace and Wallace, 2000). Paleomagnetic studies have yielded remagnetizations of mostly late Carboniferous or Permian age,
interpreted in terms of very late epigenetic mineralization (Symons et al., 2007; Pannalal et al., 2008a, 2008b).

In order to assess if there is a link between remagnetization and mineralization we carried out a regional paleomagnetic study of host rock–equivalent age samples from 14 sites in the Irish Midlands over a total area of ~25,000 km², all distal to mineralization (Fig. 1). Samples were mostly taken from the Waulsortian Limestone Formation; at least five individually oriented samples were collected at each site.

**LABORATORY METHODS**

To determine their ChRM, samples were demagnetized using both thermal and alternating-field (AF) techniques at the University of Oxford (UK). Between five and nine samples from each site were subjected to AF demagnetization using a 2G SQUID (superconducting quantum interference device) magnetometer with in-line AF demagnetization coils. The sample natural remanent magnetizations (NRM)s were demagnetized in steps of 5 mT through to 100 mT.

To help identify the magnetic mineral carriers and their grain size, standard hysteresis measurements were made using the Princeton Measurements alternating gradient magnetometer at Imperial College London (UK). Thermomagnetic curves were measured in helium (He) using the Princeton Measurements vibrating sample magnetometer, also at Imperial College London. Scanning electron microscopy (SEM) analysis was carried out using a Cameca SX-500 microprobe located at the Natural History Museum, London, in order to determine sample mineralogy and identify potential magnetic carriers.

**RESULTS**
The majority of the specimens behaved similarly during AF demagnetization (Fig. 2). Approximately 25% appeared to contain well-defined viscous remanent magnetizations acquired in Earth’s current magnetic field; these were normally removed by AFs of 5–10 mT. Subsequent demagnetization steps revealed the presence of a ChRM, generally directed shallowly downward or upward to the south (Fig. 2). Not all samples were fully AF demagnetized at the peak applied AF of 100 mT; however, directions leading to the origin were clearly defined. The ChRM was successfully isolated in nine of the sites. The other five sites yielded no consistent directions (sites BQ, FQ, and GB; Table 1), were too weak to measure (ES), or contained strongly overlapping components such that the ChRM could not be confidently isolated from overprints (RT). Site mean directions in both in situ and tilt-corrected coordinates (Figs. 2D and 2E) show that tilt correction causes an increase in the dispersion of the site mean directions, suggesting that the characteristic magnetization was acquired after tilting and/or folding of the rocks (Fig. 2F), although the increase in dispersion is not statistically significant (McFadden and Jones, 1981).

Thermomagnetic analysis found evidence for iron oxides (magnetite) and sulfides (principally pyrite that transformed irreversibly into magnetite and pyrrhotite on heating). These findings are supported by SEM, which identified fine-grained iron and iron-manganese oxides and pyrite (see the GSA Data Repository1). Iron oxide grains are typically 5–50 µm in diameter and mostly associated with texturally late dolomite. Pyrite grains are mostly ~5–10 µm in size, occasionally occurring as framboidal clusters but more often as disseminated grains in late intergranular porosity suggestive of a diagenetic origin. With the exception of ES, the
samples that did not yield coherent directions contained relatively abundant pyrite and no Fe oxide or dolomite. This, combined with a lack of pyrrhotite Curie temperatures on thermomagnetic warming, suggests that magnetite, developed during dolomitization, is the principal carrier of the ChRM.

Room-temperature magnetic hysteresis loops were generally wasp-waisted, which is indicative of either a two-phase magnetic assemblage or the presence of thermally activated, single-domain behavior, i.e., superparamagnetism (SP). Assuming magnetite as a dominant carrier, the critical SP threshold size is ~30 nm (Muxworthy and Williams, 2008), indicating that nanometric particles, below SEM resolution, are the principal source of the ChRM.

DISCUSSION AND CONCLUSIONS

The mean pole position (332°E; 37°S) derived in our study of unmineralized rocks (Fig. 3) plots close to the 310 ± 15 Ma mean pole of the APW path for Europe of Torsvik et al. (2012). This is consistent with the post-tilting and/or post-folding character of the remanence and indicates that all the Mississippian rocks (ca. 345 Ma) where we could isolate the ChRM have been remagnetized. There is a clear temporal association between the remagnetization and Variscan events, as documented by ⁴⁰Ar/⁴⁰Ar ages of 314 Ma, 300 Ma (synorogenic), and 297 Ma (postorogenic) intrusions in southwestern Ireland (Quinn et al., 2005). The remagnetization direction is, at 95% confidence (Watson, 1983), the same as that found in mineralized and unmineralized zones of the Navan deposit (Symons et al., 2002) and at Lisheen (Pannalal et al., 2008a). Mean directions failed fold and conglomerate tests, indicating a secondary post-tilting chemical magnetization.
The ChRM recorded from the deposits has been interpreted as synmineralization even though it is imprinted on both ore samples and adjacent unmineralized host rocks (e.g., Symons et al., 2002). Furthermore, the principal carrier, magnetite, is not known in the ore assemblage; it occurs only in paragenetically early, distal iron oxide facies, such as at Tynagh (e.g., Schultz, 1966). This is not surprising, given the mildly acidic hydrothermal conditions, suggested by extensive host-rock dissolution and muscovite-illite formation (e.g., Wilkinson et al., 2011), that are inconsistent with magnetite stability (Cooke et al., 2000). We therefore argue that the same ChRM recorded in the vast majority of samples is an overprint on all rocks throughout the Irish Midlands, regardless of their exposure to hydrothermal ore fluids.

This remagnetization event also appears to have affected older rocks (Fig. 3); magnetization of intermediate stability was identified in studies of the Silurian of Dingle (Mac Niocaill, 2000) and of north Galway–south Mayo (Smethurst and Briden, 1988; Smethurst et al., 1994). A pervasive remagnetization with a mean estimated age of 307 ± 6 Ma was also found in Devonian–Carboniferous rocks in southern Ireland (Pastor-Galán et al., 2015). These also overlap those we have recorded, implying a pervasive remagnetization in the late Carboniferous.

Given its synfolding to postfolding timing and age estimate, we attribute this large-scale regional remagnetization to burial and/or fluid flow associated with the Variscan orogeny, coincident with the development of the pan-European Cantabrian orocline (Pastor-Galán et al., 2015). Our findings do not exclude the possibility that mineralization could have been associated with such an event, but an explanation for the localization of the ore deposits within such a context is lacking. Furthermore, none of the
published studies has demonstrated that the remagnetization and mineralization are coeval. Rather, the catalogue of geological and geochemical evidence that supports an early Carboniferous age for mineralization (e.g., Wilkinson and Hitzman, 2015) and the recent derivation of early Chadian (346.6 ± 3.0 Ma) and Asbian (334.0 ± 6.1 Ma) Re-Os dates on ore-stage pyrite (Hnatyshin et al., 2015) lead us to confidently rule out a Variscan age for the ores.

Our results inform the wider controversial debate on the utility of paleomagnetism for dating ore deposits. Globally, such dates have been used to argue for a link between major episodes of Zn-Pb mineralization and the development of collisional orogens during supercontinent assembly cycles (Leach et al., 2001). However, resetting of magnetic signatures by orogenesis, either via fluid-related chemical reactions or burial, has been known for a long time (e.g., McCabe and Elmore, 1989; Katz et al., 1998). Consequently, we question the inferred link between supercontinent assembly and Zn-Pb deposits (also see Kesler and Carrigan, 2002; Kesler et al., 2004) and suggest that at least some of the MVT deposits reviewed by Leach et al. (2001) formed during basin extension and were remagnetized later. For example, the large age discrepancies between geochronological and paleomagnetic ages observed in eastern Tennessee (USA), Upper Silesia (Poland), and Pine Point (Canada) can, in all cases, be explained by a post-mineralization remagnetization. In the case of Pine Point, the Devonian age constraint provided by Rb-Sr dating of sphalerite (Nakai et al., 1993) is consistent with sulfur isotope data that cannot be explained by younger ages (Wilkinson, 2014). The Laramide paleomagnetic age of 71 ± 13 Ma at Pine Point (Symons et al., 1993), as well as other
Laramide ages in the Western Canada Sedimentary Basin (Leach et al., 2001), can be accounted for by orogenic fluid flow (Gillen et al., 1999; Kesler et al., 2004).

Our results from Ireland show that paleomagnetic dates here record orogenic events, rationalizing their contradiction with many other lines of evidence regarding the timing of mineralization in the province. Therefore, we suggest that paleomagnetic ages should only be used to constrain large-scale models for fluid flow and geodynamic models for mineralization where an explicit link can be made between the mechanism of ore formation and remagnetization.

ACKNOWLEDGMENTS

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REFERENCES CITED


Leach, D.L., Bradley, D., Lewchuk, M.T., Symons, D.T.A., de Marsily, G., and Brannon, J., 2001, Mississippi Valley-type lead-zinc deposits through geological time:


FIGURE CAPTIONS

Figure 1. Geological map of Ireland showing the Galmoy, Lisheen, and Navan mines (white circles), sample localities (black circles; codes are given in Table 1), and pre-Carboniferous sample sites from previous work (white stars).

Figure 3. Paleomagnetic pole for this study (blue) with 95% error ellipse. Data for Navan (Symons et al., 2002), Lisheen, and Galmoy (Pannalal et al., 2008a, 2008b) and for overprints in older rocks (Smethurst and Briden, 1988; Smethurst et al., 1994; Mac Niocaill, 2000) are shown with beige and orange error ellipses, respectively. The apparent polar wander path from Torsvik et al. (2012) is plotted in blue; reference poles are in green. Ages are in Ma.

\textsuperscript{1}GSA Data Repository item 2017xxx, SEM microscopy and rock magnetism, is available online at http://www.geosociety.org/datarepository/2017/ or on request from editing@geosociety.org.
### TABLE 1. SUMMARY OF SAMPLE LOCATIONS AND SITE MEAN DIRECTIONS

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<thead>
<tr>
<th>Locality</th>
<th>Code</th>
<th>Age</th>
<th>Site</th>
<th>Strike/dip</th>
<th>N/Nr</th>
<th>R</th>
<th>Dec (°)</th>
<th>Inc (°)</th>
<th>K</th>
<th>as</th>
<th>VGP lat</th>
<th>VGP long</th>
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<td>4.83</td>
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<td>19.2</td>
<td>23.7</td>
<td>16.0</td>
<td>–48.3</td>
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<tr>
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<td>191.4</td>
<td>–7.4</td>
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<td>338.1</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cloughjordan North</td>
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<td>Courceyan</td>
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<td></td>
<td></td>
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<tr>
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<td>330/56</td>
<td>0/8</td>
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<td></td>
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<td>SR</td>
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<td>3/5</td>
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<td>16.6</td>
<td>–24.6</td>
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<td>6/7</td>
<td>5.93</td>
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<td></td>
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<tr>
<td>Mean</td>
<td></td>
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<td></td>
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<td>8</td>
<td>8.63</td>
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<td>21.9</td>
<td>11.3</td>
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</table>

Note: Dec—declination; Inc—inclination; N/Nr—Number of samples from which a stable direction could be determined/total number of samples; VGP—virtual geomagnetic pole.
Oligocene (Lough Neagh clays)
Paleocene basalts
Permo-Triassic
Upper Carboniferous
Lower and Middle Carboniferous
Waulsortian “Reef” mudbank
Devonian
Lower Paleozoic
Dalradian
Pre-Dalradian
Granite/intermed/basic intrusives
a) BH4x  

b) NB2Y  

c) KE6X  

In-situ  

Tilt-corrected  

(1 column width, 2 col. format)
This study

Irish Zn-Pb deposits

Overprint in older rocks

Reference Poles
1. Scanning Electron Microscopy
Scanning electron microscope backscattered electron images (acquired using the Cameca SX-500 at the Natural History Museum, London) illustrating textural relationships between carbonate host rock phases and trace oxides/sulfides.

Figure S1. Pervasively dolomitized limestone from Kells East (sample KE-4). Small Fe oxide grains are associated with grain boundaries and are intergrown with dolomite. EDS spectra confirm the phase identifications.
Figure S2. Dolomite band in partially dolomitized limestone from Tory Hill (sample TH-6). Very small Fe oxide grains are associated with grain boundaries between dolomite crystals and along the contact with surrounding calcite. Relics of calcite within the dolomite indicate that the dolomite has replaced it during its formation. EDS spectra confirm the phase identifications. Spectrum 3 contains peaks for Ca, Mg, K, Al and Si due to beam overlap with neighbouring phases (calcite, dolomite and trace clays).
Figure S3. A. Small sub- to euhedral pyrite grains associated with intergranular porosity in limestone from Newmarket Bypass (sample NB-4). B. Minor dolomite is present, infilling voids between calcite crystals. EDS spectra confirm the phase identifications.
Figure S4. Composite Fe (Mn, Ni, As) oxide grain in dissolution porosity with trace clays in limestone, Swords Roundabout (sample SR-2). Heterogeneous backscatter intensity and EDS spectra indicate a complex oxide intergrowth.
Figure S5. A. Large barite grain within intergranular porosity in limestone from Trim Quarry (sample TQ-1). B. Euhedral disseminated pyrite infilling pores and replacing the host rock in the same sample.
Figure S6. A. Chrome spinel (possibly chromian magnetite, including Mn, Ni) associated with dolomite after ?crinoid ossicle within limestone from Cloughjordan North (sample CN-5). B. Subhedral Fe oxide (after pyrite?) in dissolution pore in the same sample.
Figure S7. A. Anhedral patches of Fe-Zn oxide and probable clay associated with dolomite vein cutting limestone from Ballykane Hill (sample BH-8). B. Hexagonal form of Fe oxide within limestone in the same sample.
Figure S8. A. Euhedral pyrite intergrown with dolomite that has replaced calcite in partially dolomitized limestone from Knockshangarry Quarry (sample KQ-3). B. Veinlet and patchy dolomitization of limestone in the same sample; fine pyrite is associated with dolomite.
Figure S9. A. Euhebral Fe(-Mn) oxide situated on grain boundaries between dolomite crystals in strongly dolomitized limestone from Barrow River (sample BR-3). B. Pervasive dolomitization of limestone in the same sample.
2. Rock magnetic analysis

During most of the thermomagnetic analysis, most samples displayed the same behavior (Type A, Fig. S10a), that is on heating in helium a new strongly magnetic phase starts to form at around 400°C, which has a Curie temperature close to that of stoichiometric magnetite (−560 – 580 °C, Table S1). On cooling, a single magnetic phase with Curie temperature similar to that of magnetite is generated (Table S1, Fig. S10a): the curves are not reversible. This behavior is most likely due to the oxidation of pyrite to magnetite during heating, and has been reported previously for limestones (e.g., Gong et al., 2008). This indicates that the thermal demagnetization results higher than ~400°C are not stable. In some cases, the cooling curve displays a distinct secondary Curie temperature in the region 300 – 320 °C (Type B, Fig. S10b, Table S1), which is likely due to the formation of pyrrhotite from pyrite: heating was in a He atmosphere and there was possibly insufficient oxygen for complete oxidation of pyrite and formation of magnetite. Some of the samples had magnetisation dominated by a diamagnetic signal, and the Curie temperature could not be determined meaningfully (Type C, Fig. S10c, Table S1).

Figure S10. Thermomagnetic curves for samples: a) TH (Type A); b) GB (Type B); and c) TQ (Type C), displaying behavior types A-C respectively.

The samples’ hysteresis properties are summarised in Table S1. The samples’ hysteresis loops were generally wasp-wasted, which is indicative of either a two-phase magnetic assemblage or the presence of thermally activated single domain (SD) behaviour, i.e., superparamagnetism (SP). For magnetite, the critical SP threshold size is approximately 30 nm, indicating that there is a significant proportion of nanometric material in the samples. Due to the weakness of the samples’ magnetic signal, the hysteresis loops were rather noisy.
Table S1. Summary of the rock magnetic measurements on the samples. Standard hysteresis parameters are given: saturation magnetization, $M_S$, saturation remanence $M_{RS}$, coercive force, $B_C$, and coercivity of remanence, $B_{CR}$.

<table>
<thead>
<tr>
<th>locality</th>
<th>$B_C$ (mT)</th>
<th>$B_{CR}$ (mT)</th>
<th>$M_{RS}/M_S$</th>
<th>warming $T_C$ (°C)</th>
<th>cooling $T_C$ (°C)</th>
<th>class</th>
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<td>BR</td>
<td>5.8</td>
<td>43</td>
<td>0.22</td>
<td>562</td>
<td>559</td>
<td>A</td>
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1 Sample too weak to measure accurately.
2 Poorly defined

Reference