A missing link in the mid-late Permian record of north-eastern Pangea: A sedimentological evaluation of the Permian Belfast Harbour Evaporite Formation of County Antrim, Northern Ireland

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Abstract
Ancient salt deposits preserve a record of highly specific environmental, climatic and biological conditions, including past surface water chemistry and water depths, local air temperatures, atmospheric composition and halophilic microorganisms. This paper presents the first sedimentological study of the mid-Late Permian Belfast Harbour Evaporite Formation of Northern Ireland. This formation is dominated by bedded halite, contains some siliciclastic mudstone and bedded anhydrite, and is cross-cut by intrusive igneous rocks. The bedded halite lithology contains bottom-growth chevron and cornet crystals, efflorescent crusts and dissolution pipes, which are evidence of a saline surface brine that underwent periods of evapoconcentration, desiccation and flooding. The mudstone lithology contains dewatering structures, intraclasts and mudcracks, which indicate flooding and desiccation in dry mudflats. Bedded anhydrite was deposited as beds of gypsum cumulate crystals in saline surface waters. The Belfast Harbour Evaporite Formation was formed by saline lakes with associated mudflats, based on sedimentary characteristics and supported by mineralogical, geochemical and stratigraphic context. Diagenetic features reflect dissolution and cementation at the surface and shallow subsurface in the depositional environment and limited late-stage alterations. Syndepositional dissolution pipes in bedded halite were formed by flooding events. Early halite cement is present in dissolution pipes and mudstones. Gypsum/anhydrite repeatedly dehydrated and rehydrated to form an interlocking crystal mosaic. Later features include fluid migration and the intrusion of mafic rocks. The Belfast Harbour Evaporite Formation was deposited by an ephemeral saline lake and dry mudflat system in an arid climate. This study, when compared to age-equivalent continental deposits elsewhere, suggests that arid settings with saline lakes existed across much of Pangea during the Permo-Triassic. The Belfast Harbour Evaporite Formation stratigraphically underlies the extremely low pH saline lakes of the Mercia Mudstone Group, implying that it aids in understanding the formation of Pangean acid brine lakes.
INTRODUCTION

Evaporites, such as halite and gypsum, are found in the global depositional record from the Precambrian through modern time. Evaporite rocks are key to determining transitions in some depositional environments (e.g. marine to continental), changes in water chemistry over time (e.g. neutral to acid brines), and/or shifts in climate (e.g. aridification; see Goldstein, 2001 and references within). Detailed sedimentological work, complemented with geochemical analyses, can reveal depositional environment and palaeoclimate, which can then be used to answer such large-scale questions as how do acid saline lake systems form and how do saline environments respond to climate change?

The Permian Belfast Harbour Evaporite Formation (BHEF) is a halite-dominated, ca 178 m thick stratigraphic unit located in the Larne Basin in the subsurface of Northern Ireland (Figure 1). This article is the first comprehensive sedimentological study of this formation with supportive geochemical analyses. The goal of this paper is to characterise the depositional environments and diagenetic history of this evaporite-rich formation. These interpretations will allow

FIGURE 1  Map of Northern Ireland. The Larne Basin is outlined by dashed black line (modified from Andeskie et al., 2018; Naylor et al., 2003). Major cities are illustrated by black squares. Approximate location of the Islandmagee-01 core is noted by the open star. Open circle and black circle mark approximate locations of the ISME Kilroot salt mine and the Carnduff-1 and Carnduff-2 core locations
us to hypothesise how Northern Ireland transformed from a fluvial-dominated and eolian-dominated environment in the Permain to an acid, saline lake system in the Triassic.

This study uses a combination of analyses including core slab observations, thin section petrography, fluid inclusion petrography, mineralogical identifications and elemental analyses of the Islandmagee-1 core from County Antrim, Northern Ireland. Observations of sedimentary textures and sedimentary structures give essential information about depositional processes. Elemental and mineralogical abundances help us understand depositional water chemistry. Collectively, these observations assist in the interpretation of the depositional environment and diagentic history.

2 | BACKGROUND

2.1 | Stratigraphic context

The BHEF is part of the Belfast Group and is stratigraphically bounded by Permo-Triassic siliciclastic and evaporite rocks within the Larne Basin (Figure 2; McCann, 1991; Naylor et al., 2003). The Larne Basin is a NE-SW trending, structurally-controlled basin that developed on top of the Midland Valley terrane (Trewin, 2002). The underlying Permain Enler Group contains reddish pink mudstone, siltstone, sandstone and conglomerate, as well as early Permain mafic volcanic and volcanioclastic units (Penn et al., 1983). The siliciclastic rocks of the Enler Group have been interpreted as alluvial fan deposits (BGS Lexicon; Mitchell, 2004; Naylor et al., 2003).

Overlying the Belfast Group is the ca 626 m thick Permo-Triassic(? Sherwood Sandstone Group, composed of red, yellow and brown sandstones characterised by bimodal grain-size distribution, fining-upward sequences, trough cross-bedding and channel forms (BGS Lexicon; Warrington, 2005). Rare conglomerates are present. The Sherwood Sandstone Group has been interpreted as continental deposits formed in eolian, fluvial and alluvial environments (Buckman et al., 1998; Cowen, 1993). In Northern Ireland, the ca 592 m thick Triassic Mercia Mudstone Group overlies the Sherwood Sandstone Group and is composed of bedded halite, bedded gypsum, displacive halite and red siliciclastic mudstone (Andeskie et al., 2018; Naylor et al., 2003; Warrington, 2005). Based on a core study in the Larne Basin, these rocks were deposited in low pH, shallow perennial saline lakes, saline mudflats, dry mudflats and desert palaeosols (Andeskie et al., 2018).

The exact stratigraphic position of the Permo-Triassic boundary in Northern Ireland is unknown (Mitchell, 2004). The age of the Sherwood Sandstone, studied mainly in England, Wales and Scotland, is estimated to be Permo-Triassic based on the presence of reptile footprints, including Chirotherium and Rhynchosauridae, and other fossils, including conifers, horsetails, brachiopods, bivalves, crustaceans (Euestheria and ostracods), scorpions, fishes (Gyrulepis, Diperonotus and Ceratodus) and amphibious lizards (Mastodonsaurus; Benton et al., 1994; Old et al., 1991; Tresise & Sarjeant, 1997; Warrington et al., 1999; Walker, 1969). The early Permain volcanic rocks of the underlying Enler Group and the vague Permo-Triassic age estimates for the Sherwood Sandstone allow for a general middle-late Permain relative age for the Belfast Group.

The Belfast Group contains three formations: (a) the basal ca 235 m thick Magnesian Limestone Formation, (b) the ca 178 m thick BHEF and (c) the White Brae Mudstone Formation. The Magnesian Limestone Formation is described as a greyish-yellow, sandy, calcareous unit that is over 235 m thick with abundant gastropod and bivalve fossils (Mitchell, 2004; Geological Core Description Report for Exploration Well Islandmagee-1, 2015). The White Brae Mudstone Formation, commonly referred to as the Permain Upper Marls, of the Permain Belfast Group, is dominated by anhydrite and reddish-brown mudstones and siltstones (Mitchell, 2004). Within the White Brae Mudstone Formation, Lueckisporites virkkiae and Perisaccus granulosus miospore assemblages were observed and determined to be Middle Permain (Guadalupian) to Late Permain
This study describes the BHEF in the Islandmagee-1 (IM-1) core from County Antrim, Northern Ireland (Figure 1). The IM-1 core was drilled in 2015 by Islandmagee Energy Limited in the north-western part of the Islandmagee Peninsula of Northern Ireland along the north-eastern shore of Larne Lough at 53°26′45″N, 5°52′02″E to a total depth of 1,753.6 m, encompassing the formation in its entirety. This core was drilled from 15 May to 14 June 2015 to explore for possible energy resources. The remaining core is located at the core repository of the Geological Survey of Northern Ireland (GSNI) in Belfast. The report by Islandmagee Energy Limited provided representative photographs of core in transmitted and reflected light and described general lithology, petrography, grain fabric, structural features, bulk mineralogy and bromide concentrations for unslabbed core within the formation. The bromide concentrations in the drillers report vary from 77 to 186 ppm, with a slight increasing trend up-section. In addition, rock-mechanical testing, general petrographic analysis and dissolution tests were completed by Island Energy Limited. These analyses used and destroyed ca 25% of the recovered core. The geological core report, by Islandmagee Energy Limited, identified mudstone, anhydrite, rock salt and basalt. The remaining core is located at the core repository of the Geological Survey of Northern Ireland (GSNI) in Belfast. The core report by Islandmagee Energy Limited did not include observations of sedimentary features, sedimentary structures, types of halite crystals, detailed mineralogy or detailed elemental concentrations.

3 | METHODS

For this study, methodologies include petrography, mineralogy and elemental data to characterise the BHEF. Observations were used to form interpretations of depositional environments and diagenetic features. The Islandmagee-1 core was slabb ed vertically using a DeWalt D24000S wet tile saw with limited water directed at the blade and away from the sample so halite did not dissolve, overheat or fracture. Colour was described using the Munsell Soil Chart. Sedimentary textures, sedimentary structures (including halite crystal types), any fossils, any reaction to HCl, obvious minerals and diagenetic features in core were documented and used to make a centimetre-scale measured section and stratigraphic column (Figure 3). Representative core slabs were sampled and mailed to West Virginia University.

At West Virginia University, core slabs were re-slabbed with a rock saw for thin and thick section preparation. Slabs of bedded halite units were used to create thick sections. Halite slabs were polished while dry with a 5 inch Black & Decker Random Orbit Sander and manually sanded with grit, ranging from 1,000 to 40 grit size, on a glass plate. Twenty-two thick sections, that are ca 0.5–1 cm thick, were prepared. Five large-format (5.1 cm × 7.5 cm) thin sections were prepared at Spectrum Petrographics, Inc. and were made with minimal water directed at the blade and away from the sample so halite did not dissolve, overheat or fracture. Two of these large-format thin sections are mudstone and three are anhydrite. In addition, halite chips were prepared by slicing core slab fragments with razor blades and hand polishing with sandpaper, ranging from 3,000 to 1,000 grit size, for a thickness of ca 1 mm. These chips were used for fluid inclusion petrography.

Both thin and thick sections were examined using an Olympus SZX10 microscope (20–2000× magnification).
and an Olympus BX53 microscope (6.3–63× magnification) with plane transmitted, reflective, polarized and UV-vis light sources. Observations made with microscopes included colour, sedimentary textures, mineral composition, sedimentary structures, fossils, diagenetic features and notable contacts. Photomicrographs were taken using a digital camera and SPOT5 digital imaging system.

3.2 | Mineralogical analyses

X-ray diffraction (XRD) of bulk rock and detailed clay mineralogy was completed by James Talbot at K-T Geoservices, Inc. Four halite samples were analysed for bulk rock mineralogy. Due to the limited amount of mudstone in the formation, only one sample of mudstone was analysed for bulk rock and clay mineralogy. These samples were not located near an igneous intrusion within the core.

3.3 | Elemental analyses

Instrumental neutron activation analysis was completed at Activation Laboratories. Fifteen samples of bedded halite and three samples of mudstone were tested for arsenic, bromide, calcium and iron concentrations.

4 | RESULTS

The BHEF is composed of three sedimentary lithologies. According to the driller’s report and confirmed by
the measured section (conducted as part of this current study), the IM-1 core consisted of 92.2% bedded halite (although only 66.8% remained for study after sampling for mechanical tests by Islandmagee Energy Limited), anhydrite (2.5%) and mudstone (2%; Figure 3). The formation has been cross-cut by basaltic intrusions, which account for 3.2% of the formation thickness in this measured section.

There are some trends evident in the stratigraphic column, based on the measured section (Figure 3). The BHEF is mainly composed of bedded halite. This halite gradually transitions up-section from grey to pink. There are mudstone units, two near the base and two close to the top of the formation. The two bottom mudstone units are massive, whereas the top two mudstone units contain sedimentary structures. The formation is capped by a unit of bedded anhydrite. Igneous intrusions cross-cut the formation in four places in the core. The lithologies present in the BHEF are described in sedimentological detail below.

4.1 | Bedded Halite

4.1.1 | Sedimentological Observations

Bedded halite is the most abundant lithology present in the BHEF. The colour of this lithology gradationally changes up-section from cloudy-white/grey (GLEY 1 5/N) to pink (5.1YR 2.7/0.5; Figure 4). Beds of halite are ca 0.5–1.5 cm thick and contain a variety of sedimentary textures and sedimentary structures. While cutting core slabs, a limited amount of fine, insoluble, white-grained material accumulated on the saw; this sediment was interpreted as a clay mineral.

The bedded halite is composed of three types of halite crystal textures: (a) chevron bottom-growth crystals, (b) cornet bottom-growth crystals and (c) efflorescent crusts. Chevron and cornet halite crystals nucleate from one surface, typically the sediment—surface water interface and grow upwards into a saline surface water (Figure 5A). Chevron crystals grow into a sub-cubic shape with a corner

**FIGURE 4** Bedded halite from IM-1 core. Pink bedded halite in core slab at a depth of (A) 1,365.5 m; (B) 1,367.55 m and (C) 1,377.5 m. Grey bedded halite in core slab at a depth of (D) 1,472 m; (E) 1,482.1 m and (F) 1,503.1 m
FIGURE 5  Petrography of bedded halite. (A) Bedded halite nucleated on a surface and draped with an efflorescent crust at 1,377.5 m. (B) Primary fluid inclusions at 1,377.5 m. (C) Close-up of primary fluid inclusions at 1,377.5 in Figure 5B. (D) Secondary fluid inclusions at 1,379.3 m. (E) Secondary fluid inclusions at 1,367.6 m. (F) Solid fluid inclusions at 1,377.5 m. (G) Solid inclusions at 1,433.3 m. (H) Fluid inclusion with solids at 1,367.6 m, shown in partial crossed polars. (I) Fluid inclusion with solids at 1,367.6 m, shown in crossed polars. (J) Fluid inclusion with solids in plane light at 1,367.6 m. (K) Fluid inclusion with solids in partial crossed polars at 1,367.6 m. (L) Primary fluid inclusions with circular, orange feature at 1,367.6 m.
oriented up and cornet crystals grow into a cubic shape with a flat crystal face oriented up. Both crystal types are centimetre-scale and contain growth bands varying in transparency from cloudy, fluid inclusion-rich bands to clear, fluid inclusion-poor bands. Cumulative halite crystals were not observed.

There are two kinds of fine-grained laminae in the bedded halite lithofacies. Twenty-four opaque white/pale grey laminae with a microcrystalline texture were observed in the bedded halite (Figure 4A). These microcrystalline laminae are continuous across the core and are interpreted as efflorescent crusts. In contrast, rare, laminated mud drapes are composed of silt-sized grains (Figure 4D,E).

Bottom-growth halite crystals include chevrons and cornets that are rich in primary fluid inclusions. Petrographic observations of thick sections determined that halite was mostly clear with some primary and secondary fluid inclusion assemblages (Figure 5B through E). Most primary fluid inclusions were ca 5–10 μm in size, sub-cubic in shape with rounded corners, and found along growth bands in parallel assemblages. Primary fluid inclusions in the chevrons and cornets are all-liquid and/or contain solid daughter inclusions (Figure 5B,C).

Solids in primary fluid inclusions have a variety of colours and shapes. Some solids are 5 μm in diameter red spheres, and have no fluorescent response to UV-vis light. These solids may be algae, beta-carotene, or a mineral such as iron oxide or jarosite (Figure 5L). Other solids in fluid inclusions are <5 μm in size, have a variety of shapes from rectangular to spherical and are highly birefringent (Figure 5H,I,K).

Most solid inclusions in halite have rectangular shapes that range from ca 30 μm long and ca 10 μm wide to ca 1 mm long and ca 0.3 mm wide. These solids are clear and isotropic. Based on optical appearance, these solids are tentatively interpreted as either sylvite (KCl) inclusions in halite or small crystals of halite trapped in host halite (Figure 5F,G). These solid inclusions are abundant throughout the bedded halite units containing chevrons and cornets.

Some secondary fluid inclusion assemblages cross-cut primary fluid inclusion growth bands. At least two types were identified. One type of secondary fluid inclusion assemblage contains small (ca 2 μm), all-liquid inclusions (Figure 5D). The other type is composed of large (ca 2.5 mm), gas-rich, elongated inclusions (Figure 5E). When cut with a razor blade or crushed for geochemical analyses, the large, elongated secondary fluid inclusions make a ‘snapping’ sound and smell like sulphur (Figure 5E). The gas-rich fluid inclusions did not fluoresce in UV-vis light.

Vertically oriented, ca 0.3 cm wide and ca 1–1.5 cm long, cylindrically shaped pipes were also found in the bedded halite with chevrons and cornets. These cylindrical pipes were observed truncating primary fluid inclusion bands. The pipes are filled with clear halite.

4.1.2 | Geochemical observations

Bulk and detailed (clay mineral) mineral identification was completed using XRD analysis on two efflorescent crusts located at depths of 1,490.5 and 1,433.3 m. The same elements in similar abundances were detected in each efflorescent crust sample. In order from most to least abundant, these minerals include 93.6%–94.2% halite (NaCl), 4.3%–4.9% anhydrite (CaSO₄), 0.5%–0.8% gypsum (CaSO₄ ⋅ 2H₂O), 0.1%–0.5% quartz (SiO₂), 0.3%–0.4% calcite (CaCO₃) and 0.2% bassanite (2CaSO₄ ⋅ H₂O; Table 1).

Bulk XRD analysis (Table 1) was completed on two samples of chevron-rich and cornet-rich bedded halite: (a) grey bedded halite at 1,469.8 m and (b) pink bedded halite at 1,379.7 m. The goal of this analysis was to determine if the colours were influenced by variations in mineralogy. However, both halite beds had halite as the dominant mineralogy (99.5%–100%) with trace amounts of quartz (0.2%) and anhydrite (0.2%; Table 1). There were no major differences in mineralogy noted between the grey and pink halites.

Bromide concentrations in bedded halite from 15 depths in the core identified a range of values from 57.7 to 163 ppm (Figure 6). There was a slight, generalised trend of these bromide concentrations increasing up-section.

4.2 | Mudstones

4.2.1 | Sedimentological observations

In the Islandmagee-1 core, four mudstone beds were observed, with a total thickness of ca 4 m. The mudstones contain a variety of colours, sedimentary textures and sedimentary structures. There are two main types of mudstone present: (a) massive and (b) sedimentary structure-rich.

The massive mudstone units occur from 1,490 to 1,492 m and 1,333.5 to 1,332 m depths and range from dark grey (GLEY1 4/N) to brick red (5.4YR 4.2/3.1) in colour. The grains are well-sorted and well-rounded silt. Detailed clay XRD analysis was completed on a sample of red mudstone from 1,333 m and identified 25.5% anhydrite, 17.8% quartz, 15.5% illite and mica, 15.2% plagioclase, 12.8% halite, 4.5% chlorite, 2.6% K-feldspar, 1.9% haematite, 1.7% smectite/chlorite, 1.7% kaolinite and 0.9% calcite.

The sedimentary structure-rich mudstones exist at 1,333.8–1,333.5 m and 1,332.1–1,331.6 m depths in the core. These units range in colour from bluish-grey (0.7Y5/0.1) to red (3.5Y 5.6/0.9) and are composed of clay-sized to silt-sized grains and rare sand-sized intraclasts. These units contain wavy laminae, discontinuous laminae, climbing ripple cross-bedding and mudcracks (Figure 7A through F). Wavy laminae are 2–5 mm thick and are continuous across the core. Discontinuous laminae...
range from 1 to 3 mm thick and vary in length from 2 to 5 cm. Climbing-ripple cross-bedding are 1 cm in height. Both massive and sedimentary structure-rich mudstone units have sharp bottom and top contacts with vertically adjacent lithological units.

There are multiple diagenetic features in the mudstone units, including intergranular halite cement and late-stage halite veins. The halite veins are 1–2 mm in width and are composed of blocky-shaped halite crystals. The massive mudstone units contain circular grey reduction spots that are ca. 0.25–0.5 cm in diameter and are distributed randomly (Figures 7A and 8C).

4.2.2 | Geochemical observations

The concentrations of arsenic, bromide, calcium and iron measured in three (of the four total) mudstone units are shown in Table 2. Arsenic was below detectable limits in the grey mudstone sample from 1,491.8 m depth. However, there are 2.1 and 2.6 ppm arsenic at depths of 1,461.5 m in a grey mudstone and at 1,332 m in a red mudstone, respectively. In contrast, bromide concentrations in mudstones decreased up-section, from 23.1 ppm at 1,491.8 m depth in a grey mudstone, 14.4 ppm at 1,461.5 m depth in a grey mudstone, to undetectable at 1,332 m depth in a red mudstone. Calcium levels increased up-section from 3% at a depth of 1,491.8 m to 8% at both 1,461.5 and 1,332 m. Iron levels varied from 6.0% at 1,491.8 m, 7.8% at 1,461.5 m and 3.5% at 1,332 m depth (Table 2).

4.3 | Anhydrite

Bedded anhydrite exists only at the top of the BHEF in the IM-1 core (1,331.6–1,327.1 m depth; Figure 8). The outside of the core had a white, chalky-textured, bumpy rind at this depth range. Once slabbed, the rock was dark grey when dry.
FIGURE 7  Mudstones from IM-1 core. (A) Siltstone core slab from 1,332 m with varying colour, wavy laminae and reduction spots. (B) Core slab from 1,332 m composed of claystone and siltstone with discontinuous laminae. (C) Red claystone core slab from 1,333 m with reduction spots. (D–F) Thin section photomicrographs from 1,332 m in plane transmitted light. (D) Alternating wavy laminae of claystone and siltstone. (E) Reduction spots in claystone. (F) Claystone with cross-cutting halite veins
FIGURE 8 Photomicrographs of anhydrite thin sections. (A and B) Photomicrographs from 1,329 m depth of interlocking anhydrite crystal mosaic at various magnifications. (C and D) Photomicrographs from 1,330 m depth of interlocking anhydrite crystal mosaic in plane and reflected light, respectively. (E) Photomicrographs of anhydrite from 1,327 m depth. The sample is dominated by interlocking anhydrite crystal mosaic with ovoid shapes composed of black mud and blocky anhydrite crystals denoted by arrow. (F) Close-up of the structure in E.
(0.5YR 3/2) and black when wet (N 1/0) with rare hints of red (2.5YR 3.3/0). In hand sample, the lowermost anhydrite, from 1,329 to 1,330 m depth, has an interlocking crystalline mosaic texture. The uppermost anhydrite, at 1,327 m depth, contains both an interlocking crystal mosaic and a mottled texture of varying shades of grey that has ‘phantom’ circles that are ca 3 mm in diameter.

In order to observe the anhydrite textures further, three large-format thin sections were prepared. Two types of anhydrite textures were identified: (a) an interlocking anhydrite crystal mosaic and (b) blocky anhydrite crystals in black mud. The interlocking crystal mosaic contains anhydrite crystals that vary from 0.2 to 0.4 mm in size (Figure 8A through D). These crystals were observed in the deepest anhydrite units at depths of 1,329 and 1,330 m. In plane light, these crystals are white to grey in colour. In polarized light, these crystals are teal, emerald green, burnt orange and red. There are no sedimentary structures in the interlocking anhydrite crystal mosaic.

The uppermost anhydrite, at 1,327 depth, contains both an interlocking crystal mosaic and blocky anhydrite crystals in black mudstone patches. The interlocking crystal mosaic is very similar to the lowermost anhydrite. The interlocking crystal mosaic (85% of thin section) surrounds the blocky anhydrite crystals in black mud (15% of thin section). The black mud contains 0.5 mm long and 0.1 mm wide needle-shaped anhydrite crystals oriented inward in circular, black patches of mud (Figure 8E,F). The anhydrite needles and mud clasts form circles that are ca 1.5 mm wide and 3 mm long.

### 4.4 Igneous Intrusions

In the Islandmagee-1 core, there are four depths at which igneous intrusions cross-cut bedded halite units. The age of the intrusions is unknown, but are interpreted as younger than the bedded halite based on the stratigraphic relationship. The halite surrounding the igneous intrusions is cloudier in colour and is fractured, in contrast to the mostly clear, unfractured halite further from an intrusion. The igneous intrusions are dark grey to black in colour, have high specific gravity and have a green rind in the contact with the halite (Figure 9). These intrusions are composed of basalt. The basalt had low integrity and crumbled easily. Some intrusions were fragmented (Figure 9). Rare clear halite veins cross-cut basalt intrusions.

### 5 INTERPRETATIONS

#### 5.1 Depositional environments

The BHEF was deposited in a shallow saline lake system with surrounding mudflats. Below are the supporting arguments.

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![Figure 9](image-url) Brecciated basalt intrusion in halite at a depth of 1,443 m. Basalt clasts are green when in contact with host halite. Halite is highly fractured and cloudy.

#### 5.1.1 Shallow saline surface waters

The bedded halite and bedded gypsum of the BHEF contain evidence for ephemeral, shallow, saline surface waters. Halite chevrons and cornets grow in shallow, sodium-chloride-rich surface waters (Arthurton, 1973; Lowenstein & Hardie, 1985). In addition, the presence of bedded anhydrite indicates...
that the surface waters were calcium-rich and sulphate-rich at times.

Efflorescent crusts formed upon desiccation of the saline surface waters (Lowenstein & Hardie, 1985; Smoot & Castens-Seidell, 1994). Efflorescent crusts are finely crystalline, evaporite layers that form from the wicking of shallow saline groundwaters to a subaerially exposed surface, where they immediately precipitate tiny crystals (Lowenstein & Hardie, 1985; Smoot & Castens-Seidell, 1994). In this study, efflorescent crusts in the BHEF are interpreted from the laminae composed of microcrystalline halite and anhydrite/gypsum with traces of calcite, bassanite and quartz. The abundant efflorescent crusts atop beds of chevrons and cornets in the BHEF indicate that the saline lakes were frequently fully desiccated. It is probable that an arid climate drove these processes.

Dissolution pipes form when bedded halite partially dissolves during flooding events, such as rainstorms or sheet floods (Lowenstein & Hardie, 1985). The vertically oriented, ca 0.3 cm wide, cylindrical pipes in chevron and cornet halite are interpreted as dissolution features. Few core depths were observed with dissolution pipes. In contrast to the great number of efflorescent crusts, the low number of distinct dissolution pipes is further evidence that this environment was a desert, with arid conditions more common than rain events.

Collectively, the minerals, crystal types and sedimentary structures of the bedded halite of the BHEF reveals information regarding the depositional environment and processes. The presence of bedded halite and gypsum/anhydrite indicates deposition from saline lakes enriched in sodium, chloride, calcium and sulphate. Chevrons, cornets, efflorescent crusts and dissolution pipes indicate shallow water bodies that underwent periods of desiccation and floods (Benison et al., 2007; Lowenstein & Hardie, 1985; Smoot & Castens-Seidell, 1994).

5.1.2 | Dry mudflats

The mudstones of the BHEF probably formed in dry mudflats surrounding saline lakes. However, the mode of deposition may have been different for the massive mudstones than for the sedimentary structure-rich mudstones. There are four possible depositional mechanisms interpreted for the mudstones: (a) grains were deposited by winds; (b) grains were deposited by flowing surface water; (c) grains formed from chemical precipitation from saline surface water or shallow saline groundwater; or (d) a mixture of these detrital and chemical processes occurred.

The massive mudstones are dominated by well-sorted and well-rounded silt. The mineralogy of anhydrite, quartz, clays, feldspar, halite, haematite and minor calcite suggests that some minerals were either blown or carried into the system as detrital clasts, whereas other minerals may have precipitated from the surface waters or shallow groundwaters (Benison et al., 2007; Sweet et al., 2013). Quartz, plagioclase and potassium feldspar were probably transported into the system (Benison et al., 2007). The relatively high amount of halite in the massive mudstone was probably precipitated as cement by shallow groundwaters. Other minerals, including abundant anhydrite and clay minerals, as well as minor amounts of haematite, may have been deposited as detrital grains, chemical precipitates and/or diagenetic phases (Benison et al., 2007). Anhydrite/gypsum is common in modern saline environments as both physical and chemical sediments, as well as early cements. Clay minerals and haematite are most commonly known as detrital sediment, but, in the case of acid brines, can precipitate directly from lake water and groundwater (Benison et al., 2007). Any of the minerals documented in the mudstones can also be diagenetic products, such as cements (Bowen et al., 2012). The massive mudstones were probably formed by eolian deposition. The high degree of sorting of silt grains and the massive texture are more consistent with eolian processes than aqueous transport and deposition. In addition, traces of quartz in the BHEF halite beds support wind deposition of that quartz into lakes. The rarity of dissolution pipes in bedded halite makes flooding less probable than eolian deposition. Finally, if flooding was the main process that deposited this lithology, massive mudstones would be expected directly overlying halite beds with dissolution pipes, but that is not the case.

The sedimentary structure-rich mudstone is interpreted to have been deposited mainly by flooding events. Sedimentary structures include wavy laminae, discontinuous laminae, climbing ripple cross-bedding and intraclasts. Bedding types were probably formed by deposition in shallow water. In particular, climbing ripple cross-bedding indicates high net deposition in a waning flow, suggesting sheet floods which were probably short-lived (Ashley et al., 1982). Intraclasts probably originated as mud-cracked chips on subaerially exposed surfaces that were transported short distances by floods. It is hypothesised that, after sheet flood deposition, these mudflats would have fully desiccated, based on the presence of dewatering structures and mudcracks. Collectively, these dry mudflats underwent periods of flooding and desiccation.

Regardless of the mode of deposition for the mudstones, shallow saline groundwaters in an arid climate probably promoted early diagenesis. The relatively high amounts of halite distributed through the mudstones suggest the presence of halite cement. Other minerals, including anhydrite, haematite and clay minerals, may have also formed as early diagenetic features. However, the fine grain size of the mudstones precluded robust textural petrographic analysis of diagenetic features for these samples. The combination of siliciclastic grains, reworked chemical sediments and early diagenetic features described for
these mudstones are characteristic of mudflats adjacent to shallow saline lakes in an arid climate (Benison et al., 2007).

5.2 | A case for continental deposition

The depositional environment of the BHEF is interpreted as a continental system, instead of a marine system. There is no diagnostic sedimentological evidence of marine influence, such as marine fossils, or marine/marginal marine sedimentary structures, such as tidal bundles (Shinn, 1983).

Some of the mineralogical evidence obtained from the saline surface water lithofacies is inconclusive for a continental or marine origin, as halite, anhydrite, gypsum, quartz, calcite and bassanite can occur in both lake and marine settings. However, the mineralogical data also identified minimal carbonate minerals, with only trace amounts of calcite detected in one mudstone and two efflorescent crusts. An interpretation of an evaporite marine environment cannot be supported with this paucity of carbonates. Evaporite deposits that form from modern marginal marine and marine waters are associated with abundant carbonate minerals (Butler et al., 1982; Phleger, 1969; Purser, 1985; Shearman, 1978). Even lagoons with both evaporating sea water and abundant eolian siliciclastic input, such as some in Qatar, have a significant amount of carbonate minerals and rocks closely associated with gypsum, halite and siliciclastics (Rivers et al., 2020). Boselli and Hardie (1973) studied Permian and Triassic gypsum-carbonate-siliciclastic units in northern Italy and interpreted them as sabkha and lagoonal deposits, partly due to the dolomitic lithofacies associated with gypsum. In order to evaporate sea water to a point at which it precipitates gypsum and halite, it first must undergo a state at which it is saturated with respect to calcite and dolomite. Therefore, carbonates are expected in a marine or marginal marine evaporative sequence.

Another supportive argument for continental deposition is the stratigraphic context of the BHEF. It is underlain and overlain by rocks that are also considered continental deposits. The Belfast Group overlies alluvial fan deposits of the Enler Group and underlines eolian, fluvial, alluvial, saline lake, mudflat deposits and palaeosols of the Sherwood Sandstone and the Mercia Mudstone Groups (Andeskie et al., 2018; Buckman et al., 1998; Cowen, 1993). This evidence, when paired with detailed sedimentological observations, supports the interpretation that the BHEF was probably deposited in a continental setting.

5.3 | Inconclusive geochemical data

Past studies have claimed that ‘normal marine evaporites’ contain bromide values from ca 67 ppm to as high as 200 ppm (Hardie, 1984; Holser, 1966). Traditionally, halites with bromide over ca 67 ppm were considered marine in origin, as higher bromide value were believed to have formed as sea waters underwent evapoconcentration. In contrast, halites with less than ca 67 ppm bromide were considered continental simply because they had less bromide than sea water or evaporated sea water. However, higher bromide values are not exclusive to evapoconcentrated marine waters and some saline lakes have bromide concentrations higher than that of concentrated sea water. Bowen and Benison (2009) measured bromide values between 0 and 941 ppm in modern shallow, halite-precipitating saline lakes in inland Western Australia (Bowen & Benison, 2009). Kipnis et al. (2020) found a similar wide range of bromide in different saline lake water samples from Western Australia. These lakes have bromide concentrations with a wider range than that interpreted for sea water and evapoconcentrated sea water, challenging the use of bromide in halite as an indicator of marine versus continental origin. Acid or basic saline lake waters and groundwaters, in particular, have enhanced chemical weathering of host rocks, leaching higher concentrations of elements and leading to more complex lake brines. In addition, cycles of flooding and evapoconcentration in shallow saline lakes greatly change salinity and the range of dissolved ions over short time periods (Benison et al., 2007; Bowen & Benison, 2009; Hardie, 1984; Lowenstein & Hardie, 1985; Schubel & Lowenstein, 1997; Smoot & Castens-Seidell, 1994). Due to these depositional processes in some saline lakes, it is not possible to use a certain range of a single element to distinguish between continental versus marine environments. Therefore, the use of bromide concentration as marine indicator is questionable.

The range of bromide in the BHEF (57.7–186 ppm) overlaps the previously construed range of bromide from sea water (67–200 ppm), as well as from modern acid saline lakes in Western Australia (0–941 ppm; Figure 6). Therefore, the bromide concentration in the BHEF is not considered diagnostically evidence of a depositional origin.

There are no clear conclusions about depositional environments or parent brines from the calcium, arsenic and iron values measured in three siliciclastic mudstones. However, there may be suggestions hinting at a continental origin. The presence of high concentrations of arsenic and iron are not commonly found in marine systems but are known from some alkaline and acidic saline lake systems (Bowen & Benison, 2009; Kulp et al., 2004). In both marine and continental waters, calcium is commonly present (Hardie & Eugster, 1971). In the BHEF, calcium levels vary from 3% to 8% in the mudstones, and most of that can be attributed to anhydrite and gypsum, which are much more abundant than calcite. Regardless, the amount of calcium in three mudstones analysed is lower than expected for marine-associated systems. Despite the uncertainty relating composition to depositional environment, the elemental values for bromide, calcium, arsenic and iron help to characterise the BHEF.
5.4 Diagenetic sequence of events

As part of this sedimentological investigation of the BHEF, multiple diagenetic features were observed. The earliest diagenetic event was the partial dissolution of halite as represented by dissolution pipes within the bedded halite. These probably occurred by rainfall within days to months after initial halite deposition. Shortly after the dissolution pipes formed, they were filled with a clear halite cement. The dissolution and infilling of the pipes occur so early in the rock record that they are considered syndepositional and have been witnessed forming in real-time (Casas & Lowenstein, 1989; Lowenstein & Hardie, 1985).

Reduction spots probably formed in mudstones as result of decaying organic matter (Retallack, 2001). Although there is no diagnostic evidence for root features, the patches in the bedded anhydrite filled with mud and gypsum anhydrite crystals may have formed as secondary pores following root decay (Figure 8E and F). The presence of small roots would be consistent with both dry mudflats and desiccated lakes, and, therefore, is a possible explanation for both the reduction spots in the mudstones and the patches of mud and crystals in the bedded anhydrite.

Gypsum dehydrated into anhydrite, rehydrated back to gypsum and dehydrated to anhydrite repeatedly to eventually form an interlocking crystal mosaic. This process of dehydrating and hydrating gypsum is typical of ancient calcium sulphates (Murray, 1964).

The last diagenetic events were the intrusion of magma into the bedded halite and the late-stage halite veins. Basalt intrusions dated as Palaeocene in age are found across the Larne Basin of Northern Ireland as feeders to the Antrim Lava Series (Holford et al., 2009; Naylor et al., 2003); the intrusions cross-cutting the BHEF were probably part of those igneous events. The halite veins are probably a result of partial dissolution and remobilisation of halite from some halite within the BHEF or from a younger halite, such as the overlying Mercia Mudstone Group.

6 DISCUSSION

6.1 Fluid inclusions within the bedded halite

Some fluid inclusions in the BHEF suggest low-level alteration of halite at the micron-scale, mainly by heat due to burial and fluid migration. The primary fluid inclusions are situated along growth bands, are sub-cubic and do not contain vapour bubbles, indicating that they retain unaltered Permian surface water and remain unaltered at the centimetre-scale. However, their rounded corners imply that slight physical stretching of the inclusions has occurred, probably a consequence of the heat and pressure due to burial at their present depth of 1,327–1,504 m. Secondary fluid inclusions formed by diagenetic fluid migration through the bedded halite. Many secondary fluid inclusions contain snapping bubbles that smell of sulphur. These bubbles may be hydrogen sulphide (H₂S) sourced from magma and perhaps related to the Palaeocene igneous activity. However, these fluid inclusions with gas bubbles are not adjacent to the igneous intrusions that cross-cut the core.

There are two main factors that probably affected the subsurface conditions of the halite: (a) heat and lithostatic pressure from burial depth, and (b) contact metamorphism from igneous intrusions. There are four depths in the core where the BHEF has been cross-cut by intrusions. However, the number of igneous intrusions and their geometry in the vicinity of this core are unknown. Therefore, the effect of any physical and chemical alteration of halite from these igneous intrusions is currently unknown and difficult to differentiate from the influence of burial depth.

The halite-rich Triassic Mercia Mudstone Group of County Antrim, Northern Ireland contains well-preserved primary fluid inclusions in shallow bedded halite in the Carnduff-1 and Carnduff-2 cores and in the ISME (Irish Salt Mining and Exploration, Ltd.) Kilroot salt mine, both less than 10 km from the location of the Islandmagee core (Andeskie et al., 2018; Figure 1). Neither Carnduff core nor the salt mine is deep enough to have reached the BHEF. In the Islandmagee core, the Mercia Mudstone Group is ca 625 m above the BHEF and is also cross-cut by Palaeocene igneous intrusions (Andeskie et al., 2018; Holford et al, 2009). The Mercia Mudstone Group fluid inclusions have maintained their integrity, observed in their shape and in the distribution of primary fluid inclusions along growth bands (Andeskie et al., 2018). The integrity of fluid inclusions is evidence that the depth of the BHEF may have influenced its slight alteration more than local heating from intrusions. A detailed study comparing fluid inclusions close to and further away from igneous intrusions would help to distinguish the relative influence of burial depth and intrusive igneous activity on the alteration of halite.

The primary fluid inclusions of the BHEF are well-preserved enough to be evaluated for chemical composition by freezing-melting microthermometric analyses. Although the rounded corners of the fluid inclusions suggest slight stretching, the composition of the inclusion fluid remained constant. Freezing-melting analyses could be used to determine salinity in NaCl equivalents, major ions in solution and extreme pH (Davis et al., 1990; Goldstein & Reynolds, 1994; Jagniecki & Benison, 2010). Future study of inclusion fluid composition in the bedded halite of the BHEF may result in additional geochemical evidence for lake water.
6.2 Comparing the Belfast Harbour Evaporite Group to the Zechstein Group

The Late Permian Zechstein Group from the southern and central North Sea is a widely known evaporite formation. Due to the similarity in age and presence of evaporites, it is important to consider how the Zechstein Group may relate to the Belfast Harbour Evaporite Group. However, these groups are difficult to compare for several reasons. There is limited, if any, detailed, centimetre-scale sedimentological work on high-recovery cores of the Zechstein Group. Much of the Zechstein evaporites have been highly altered, both structurally and metamorphically. In addition, the BHEF is known mainly from the descriptions reported in this current study of one core, so any lateral variations are not yet known. The Zechstein Group contains some highly varied lithologies. Some of the Zechstein Group is composed of organic-rich mudstones, limestones (Halibut Carbonate Formation) and evaporites consisting of anhydrite, halite and polyhalite (Shearwater Formation; Trewin, 2002). The BHEF is composed of organic-poor siliciclastic mudstone, anhydrite and halite. The major differences between the two formations are in the organic and carbonate contents (Glennie & Buller, 1983; Grant et al., 2019; Tucker, 1991). Based on these differences, it is improbable that the two groups were deposited in similar environments.

It seems premature to attempt to correlate and compare the Zechstein Group with other Permian evaporite-bearing stratigraphic units of north-western Europe. Stratigraphically complete sections of evaporite-rich units, especially those containing bedded halite, are rare. Outcrops and most cores have been exposed to dilute waters, either naturally at the surface or by drilling fluids, leading to dissolution of any bedded halite and halite cements and resulting in incomplete sections (Benison et al., 2015). General lack of recognition of the incompleteness of these outcrops and cores has probably led to depositional interpretations based on insufficient data for many Permian and Triassic evaporites. Only cores drilled with brines or hydrophobic oil can extract unaltered halite and other soluble salt minerals. These high-recovery cores, such as the Islandmagee core, are rare. Before a meaningful comparison can be made, more studies of high-recovery, unaltered cores of both the Zechstein Group and Belfast Group are needed.

6.3 Stratigraphic context and a transition to more extreme systems

This current study shows a vertical trend consisting of clean, bedded halite of the BHEF grading upwards, through the red, continental siliciclastics of the Sherwood Sandstone Group, into the overlying red muddy halite and gypsum and red siliciclastics of the Triassic Mercia Mudstone Group. The Mercia Mudstone Group formed in extremely acid (pH < 3) saline ephemeral lake systems in an arid continental setting (Andeskie et al., 2018). Earlier deposition of the BHEF in neutral saline lakes, paired with the previous study of later acid saline lakes of the Mercia Mudstone Group establishes that saline lakes became more acidic, richer in sulphate and iron, and more impacted by eolian sediment over time.

The transition from neutral to acid saline lake deposits is also present at approximately the same time period in North America. An example of this process is in modern day Kansas, where the clean, halite-dominated Permian Hutchinson Salt Member, is overlain by the red continental siliciclastics of the upper Sumner Group, and then by the red siliciclastic-rich and evaporite-rich Permian Nippewalla Group, formed by extremely acid saline lakes and groundwaters (Andeskie & Benison, 2020; Benison & Goldstein, 2001; Benison et al., 1998; Giles et al., 2013). In both Northern Ireland and Kansas, the lower neutral saline lake deposits are separated from the upper acid saline systems by red bed siliciclastics. Here, it is hypothesised that the transition from a relatively neutral saline system to an acid saline system, in the context of an arid climate, may be key to the evolution of these extreme environments of Pangea. A long period of weathering and erosion in a neutral saline lake system can foster the evolution of an acid saline lake system (Benison & Bowen, 2015). An early, warm humid climate may have weathered carbonates and other buffering agents. Then, a drying climate may have increased lake water and groundwater salinity and enhanced water-rock interactions, making evaporites such as the BHEF in Northern Ireland and the Hutchinson Salt in Kansas. Continuation of a widespread arid climate would have promoted eolian deposition and led to the formation of red bed siliciclastics. Acidification of brines may have occurred through oxidation of sulphates, ferrolysis, activity of acidophilic microbes and evapoconcentration, as has been proposed for the modern acid saline lake systems of southern Western Australia (Benison & Bowen, 2015).

Recognition of the same sequence in continental depositional environments in Permo-Triassic time in both the midcontinent of North America and in Northern Ireland suggests that the extreme environments represented by evaporites and siliciclastics may have been widespread and long-lived across Pangea. The new understanding of the BHEF, presented in this current study, provides an important, but previously missing, link to this environmental interpretation. The transition from Pangean neutral saline lakes to acid saline lakes may have implications for continental-scale climate, land-ocean interactions and the biotic crises of the late Permian.
6.4 | Implication for Permian environments and climates of north-eastern Pangea

This study has direct implications for the environments and climates of north-eastern Pangea, including the locations of ancient shorelines. Some studies have interpreted the BHEF to be shallow marine based on the simple presence of evaporites (Mitchell, 2004; Smith, 1986; Ziegler, 1990), directing the placement of interpreted Pangean shorelines on palaeogeographic maps. However, detailed sedimentological studies of these ancient evaporites and siliciclastics suggest that Permian palaeogeographic maps should be reevaluated; interpreted Permian shorelines may truly be continental settings.

It seems quite clear that the mid-late Permian of Northern Ireland experienced an arid climate. The shallow ephemeral lakes in which the bedded halite formed, as well as the evidence of eolian transport and limited, episodic overland water flow in the form of sheet floods, strongly suggest a prolonged dry climate. There is no evidence of channelled flow or perennial surface water. There are no fossils, with the possible exception of uncommon, small root features and preliminary observations of suspect algae in some primary fluid inclusions.

This study of the BHEF yielded important clues about temporal and spatial aspects of Permian environments and climates for the supercontinent Pangea. In this way, these new observations and interpretations from the Islandmagee core serve as a missing link for the long-lived, continental-scale red bed and evaporite system that lasted from the middle Permian until at least the Early Triassic. The influence that this unusual continental system had on continental-ocean exchange and the end Permian mass extinction has yet to be fully considered.

7 | CONCLUSIONS

This study provides the first sedimentological and mineralogical description of the BHEF. Methods utilised in this study include core description, measured section, hand sample, thick section and thin section observations, XRD of bulk rock and detailed clay mineralogy, and instrumental neutron activation analyses. This formation is composed of bedded halite, anhydrite, mudstone and cross-cut by igneous intrusions. Based on the sedimentological and geochemical observations, it is interpreted that the BHEF was formed by a continental saline lake system and surrounding dry mudflats. Since deposition, this formation has undergone multiple diagenetic events over time. Detailed studies on lithologies that are found within the BHEF are of great comparative sedimentological importance for Pangean environments and climates.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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